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Chen, X-G

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Ocean circulation and biological processes drive seasonal variations of dissolved Al, Cd, Ni, Cu, and Zn on the Northeast Atlantic continental margin

Xue-Gang Chen[1,2*#], Dagmara Rusiecka[1,3#], Martha Gledhill[1,3], Angela Milne[4], Amber L. Annett[3], Antony J. Birchill[4,5], Maeve C. Lohan[3], Simon Ussher[4], E. Malcolm S. Woodward[6], Eric P. Achterberg[1,3*]

[1] GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany,
[2] Ocean College, Zhejiang University, Zhoushan, China
[3] Ocean and Earth Sciences, National Oceanography Centre, University of Southampton, Southampton, UK
[4] School of Geography, Earth and Environmental Sciences, University of Plymouth, Plymouth, UK
[5] School of Environment, Geography and Geosciences, University of Portsmouth, UK.
[6] Plymouth Marine Laboratory, Plymouth, UK

Corresponding authors:
Xue-Gang Chen, xchen@geomar.de, chenxg83@zju.edu.cn
Eric P. Achterberg, eachterberg@geomar.de
Both authors contribute equal to this paper.

Key Points:

- Biological processes and fluvial inputs drive seasonal variations in surface dissolved trace metals (dTMs) on Celtic Sea.
- Dissolved Al, Cd, Ni, Cu, and Zn concentrations and metal:P ratios at depth are controlled by water

mass mixing.

- Mediterranean Outflow Waters provide a strong imprint on dTM concentrations and metal:P ratios in the Northeast Atlantic Ocean.

Abstract

We report the seasonal distributions of dissolved zinc (dZn), nickel (dNi), copper (dCu), cadmium (dCd), aluminum (dAl), and nutrients on the Northeast Atlantic continental margin (Celtic Sea). Surface dissolved trace metal (dTM) and nutrient variations were mainly regulated by the seasonal cycling of biological processes. The dTM (especially for dCu and dZn) and nutrient stoichiometry on the continental shelf was additionally affected by fluvial input. Nutrients and dTMs at depth on the continental slope were determined by water mass mixing driven by ocean circulation, without invoking local remineralization process. The Mediterranean Outflow Waters are especially important for delivering Mediterranean-sourced dTMs into the Northeast Atlantic Ocean and drive dTM:nutrient kinks at a depth of ~ 1000 m. These results highlight the importance of riverine input, seasonality of primary production and ocean circulation on the distributions of nutrients and nutrient-like dTMs in temperate continental margins, which could further affect local biological carbon pump.

Commented [AB1]: Is there much evidence for Al, Cd, Ni, Cu, and Zn restricting productivity near continental margins?

Commented [CX2R1]: Should remove these words?

Plain Language Summary

Nutrients and nutrient-like dissolved trace metals (dTMs; dZn, dNi, dCd, dCu), as well as their correlations are important for understanding biogeochemical cycles in paleo- and modern oceans. Here we show that dTM and nutrients on the continental shelf of Northeast Atlantic continental margin was determined by the balance between river-derived materials and local biogeochemical processes. Seasonal variations in surface dTMs and nutrients on the continental slope were mainly regulated by biological processes. On the other hand, dTMs and nutrients at depth were controlled by the mixing of water masses with different dTM:nutrient stoichiometry. The most important changes in dTM:nutrient ratios (kinks) at a depth of ~ 1000 m were closely associated with the Mediterranean Outflow Waters. These findings suggest that seasonal variations in dTMs and nutrients on the Northeast Atlantic continental margin were dynamically controlled by external sources (terrestrial materials from rivers), local biogeochemical processes, and ocean circulation. Short-term and long-term temporal variations of these factors may consequently change the availability of nutrients and micronutrients to continental margins, which are important transition zones for the marine carbon cycle.

1. Introduction

Dissolved (< 0.2 μm) bioactive trace metals (dTMs) including zinc (Zn), nickel (Ni), copper (Cu) and perhaps cadmium (Cd), are important micronutrients in marine systems. Zinc, Ni, and Cu are involved in enzymatic processes required from phytoplankton growth (La Fontaine et al., 2002; Mahaffey et al., 2014; Twining & Baines, 2013) and Cd is taken up as a divalent metal (Horner et al., 2013). Low supply of dTMs, therefore, could potentially affect marine ecosystem structure and functioning (Lohan & Tagliabue, 2018; Morel & Price, 2003). Due to their biological uptake, the vertical distributions of dissolved Zn (dZn), Ni (dNi), Cu (dCu), and Cd (dCd) resemble those of nutrients (Nitrate+Nitrite (TN), phosphate (P), and silicic acid (Si)) (Bruland et al., 2014). These dTMs typically exhibit seasonal depleted concentrations in surface waters due to phytoplankton uptake (Moore et al., 2013; Morel & Price, 2003) and elevated levels at depth due to remineralization of sinking organic particles (Boyd et al., 2017). Nutrient and bioactive dTMs, therefore, show significant positive correlations for example the dCd-P relationships in global oceans (Boyle et al., 1976; Middag et al., 2018; Wu & Roshan, 2015; Xie et al., 2015), dZn-P, dNi-P, and dCu-Si correlations in the South Atlantic Ocean (Wyatt et al., 2014) and the Southern Ocean (e.g., Janssen et al., 2020; Saito et al., 2010).

The linear relationships between bioactive dTMs and nutrients usually show pronounced changes in slopes (kinks), e.g., at a P concentration of ~ 1.3 μM for the Cd-P correlation (de Baar et al., 1994; Cullen, 2006). The origin of such kinks (especially the Cd:P kink) has been debated over the last decades. Some hypotheses point towards deeper regeneration of Cd relative to P (Boyle, 1988; Roshan & DeVries, 2021), or enhanced Cd uptake due to the limitation of bio-essential elements in surface waters (Cullen, 2006; Sunda & Huntsman, 2000). Kinks are also hypothesized to be associated with the chemical replacement between Co, Zn, and Cd in carbonic anhydrase in phytoplankton (Morel et al., 1994; Price & Morel, 1990) or changing bioavailability of Cd through organic complexation (Bruland, 1992). Recent studies demonstrated that the mixing of water masses with different Cd:P ratios could be pivotal for the observed kinks (Baars et al., 2014; Middag et al., 2018; Xie et al., 2015). In addition, external sources of trace metals such as continental inputs and dust deposition can also affect bioactive dTM distributions in the ocean, such inputs can be traced by dissolved aluminum (dAl) (Han et al., 2008; Measures & Edmond, 1988; Menzel

Commented [GM3]: Yes I think you could remove this.

Commented [ML4R3]: I agree it can be removed but as talking about biological process I would just have one sentence stating- Zn, Ni and Cu are involved in enzymatic process required from phytoplankton growth (add a few refs) and Cd is taken up as divalent metal (ref).

Commented [CX5R3]: done

Commented [AB6]: Excess Cu also toxic

Commented [CX7R6]: Yes.

Barraqueta et al., 2018). The ongoing debate over the drivers underpinning bioactive dTM distributions requires further investigation into the co-occurrences of nutrients and dTMs, better informing this debate is crucial for our understanding biogeochemical cycles in paleo – and modern oceans.

Continental margins with their shelves and slopes are junctions between terrestrial systems and open oceans. The disproportionately high primary production and particulate organic carbon export make continental margins important transition zones for the marine carbon cycle (Muller-Karger et al., 2005; Simpson & Sharples, 2012). Here, we report on the seasonal distributions of dTMs and nutrients on the Northeast (NE) Atlantic continental margin (Celtic Sea), which is characterized by large seasonal variations of biological activities (Birchill et al., 2017), complex bathymetry and dynamic water circulation (Fig. 1a). High sampling and seasonal resolution (Fig. 1b) offer a unique opportunity to determine the influence of terrestrial inputs, biogeochemical processes, and ocean circulation on the seasonal variations of bioactive dTMs and their relationships with nutrients.

2. Methods

Samples were collected on board the *RRS Discovery* during three different seasons: an autumn cruise in November 2014 (DY018), a spring cruise in April 2015 (DY029), and a summer cruise in July 2015 (DY033). We conducted one transect on the continental shelf of Celtic Sea, from station Site A near the Bristol channel to station CS2 near the shelf break (Fig. 1b) during each season. Two off-shelf transects were conducted along a canyon (stations Fe01 - Fe07, Fe15) and a spur (stations Fe08 - Fe14) during each season.

Seawater samples for dTM analyses were collected following GEOTRACES protocols (Cutter et al., 2017). Samples were filtered immediately upon collection using a 0.2 µm filter capsule (Acropack). Trace metals were pre-concentrated at GEOMAR using an automated system (SC-4 DX SeaFAST pico; ESI) and analyzed by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Thermo Fisher Element XR) as outlined in Rapp et al. (2017). Dissolved Al concentrations were analyzed by a spectrofluorometer (Cary Eclipse) as per Hydes & Liss (1976). ~~Short-lived radium (Ra) isotopic activities, ^{223}Ra (half-life, $t_{1/2}$ = 11.4 days) and ^{224}Ra (half-life, $t_{1/2}$ = 3.66 days), were counted from large volume~~

~~samples using a Radium Delayed Coincidence Counter (Moore, 2008). Radium isotope activities here are reported in excess of activity supported by their parent isotopes in the water column.~~ Nutrients (P, Si, and TN) were measured on board using techniques described in Woodward & Rees (2001), according to the International GO-SHIP nutrient manual recommendations (Hydes et al., 2010). Further details of sampling and analyses can be found in the supporting information and Rusiecka et al. (2018).

3. Results and discussion

Dissolved Cd, Zn, Ni, and Cu exhibited nutrient-like vertical distributions during all seasons on the NE Atlantic continental margin (Fig. 1c, Fig. 2, Fig. 3), with the lowest concentrations observed in surface waters due to biological utilization, and elevated concentrations at depth ascribed to remineralization (Bruland et al., 2014; Moore et al., 2013). The canyon and spur transects showed comparable vertical profiles for dTMs and nutrients in each season and were combined as a slope transect. In contrast to relatively constant of bioactive dTM and nutrient concentrations at depth on the continental slope, surface bioactive dTM and nutrient levels on Celtic Sea showed pronounced seasonal variations (Table S2). Kinks in dTM:nutrient (e.g., dZn:P and dCu:P) ratios were observed on the continental slope at a depth of ~ 100 m and ~ 1000 m (Fig. S2). The shelf transect (Fig. 3) showed higher dCu, dNi, dZn, and Si concentrations than the slope transect (Fig. 1c, Fig. 2), accompanied by varying dTM: nutrient correlations.

3.1 Biological influence on seasonal variations in surface dTM along the continental slope

A seasonal mixed layer (SML) with a depth of ~ < 100 m from spring to autumn occurs on the continental slope (Supporting information: Hydrography). A reduction in dTM and nutrient levels in the SML (especially at depths < 30 m) was observed between April 2015 and July 2015, due to biological utilization and water column stratification (Birchill et al., 2017) (Table S2). The total drawdown of surface (depth < 30 m) dTMs and nutrients on the slope from April to July 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 0.10 ± 0.25 nM, P 0.35 ± 0.11 μM, TN 6.71 ± 1.83 μM, and Si 2.44 ± 0.47 μM (Table S2). The removal of dCd, dNi, P, and TN over this period was higher, and drawdown of Cu was lower than reported for this region between January 1994 and June 1995 (TN 3.9

Commented [AB8]: Is this true? Identical suggests that at each corresponding sampling depth the concentrations determined remained within the analytical uncertainty of the measurements throughout April, July and November. At least in surface waters there must be some seasonal variation?

Maybe rephrase this, something like ''showed comparable distributions of dTMs and nutrients in each season.''

Commented [CX9R8]: done

Commented [AB10]: I would remove of example and state the ones you are referring to precisely,

Commented [CX11R10]: There are too many to present: dCu and dZn with all nutrients, dCd with TN and Si, dNi and Si.

Commented [AB12]: For Zn also in deeper waters around 2500m?
In the SI might be good include profiles of the dTM:P ratio so the reader can easily see this

Commented [CX13R12]: There are not so many samples at depth > 2500 m. The slopes of linear regression models are the ratios (also summarised at Table S3).

Commented [ML14]: I can't follow this when I look at table S2 (need to add units to the table). How calculated- is this the mean and then std deviation? Di you integrate values within each depth range? As the standard variation is very large- e.g. for Zn and Ni higher than the drawdown- what is the main point here- Not really clear the drawdown- know it is occurring but perhaps you have too wide a region.

Commented [CX15R14]: Yes, these are mean ± sd values. The standard variations are very large, similar to previous studies. The ratios are calculated using mean values.

± 3.9 µM, P 0.46 ± 0.51 µM, Si 2.2 ± 3.7 µM, Cd 39 ± 61 pM, Cu 0.34 ± 0.58 nM, Ni 0.5 ± 1.1 nM) (Cotté-Krief et al., 2002) and March – June 1987 (Cd 30 ± 12 pM) (Kremling & Pohl, 1989). The decrease in dTM and nutrient concentrations was the consequence of phytoplankton uptake in summer, and the overall "uptake" ratio of phytoplankton normalized to P was:

$$(\mathrm{N}_{19}\mathrm{Si}_{7}\mathrm{P}_{1})_{1000}\cancel{\mathrm{Al}_{7.5}}\mathrm{Ni}_{1.9}\mathrm{Zn}_{0.34}\mathrm{Cu}_{0.23}\mathrm{Cd}_{0.23}$$

The surface dTM and nutrient concentrations on the slope increased from July to November assuming no significant annual changes in seawater chemistry at the same month, accompanied by comparable correlations between dTMs/nutrients and AOU at AOU > 0 (Fig. S3). Therefore, the surface dTM and nutrient variations from summer to autumn is additionally affected by the remineralization of sinking organic particles. On the other hand, the increase in surface dTM and nutrient concentrations from November to April was attributed to resupply from subsurface waters (Birchill et al., 2017). Using concentration differences between July and November (Table S2), we estimated the apparent "remineralization" ratio of dTMs and nutrients normalized to P as:

$$(\mathrm{N}_{15}\mathrm{Si}_{6}\mathrm{P}_{1})_{1000}\cancel{\mathrm{Al}_{10.7}}\mathrm{Ni}_{1.9}\mathrm{Zn}_{0.56}\mathrm{Cu}_{0.49}\mathrm{Cd}_{0.28}$$

and the "winter mixing" ratio estimated from the concentration differences between November and April observations as:

$$(\mathrm{N}_{21}\mathrm{Si}_{7.5}\mathrm{P}_{1})_{1000}\cancel{\mathrm{Al}_{5.4}}\mathrm{Ni}_{1.8}\mathrm{Zn}_{0.19}\mathrm{Cu}_{0.06}\mathrm{Cd}_{0.19}$$

The estimated Zn:P and Cu:P ratios between "uptake" and "remineralization" varied by as much as a factor 2, but the "winter mixing" ratios were as much as an order of magnitude lower, probably due to a relatively limited seasonal variations and large concentration ranges observed of both metals (Table S2). The N:P, Si:P, Ni:P, and Cd:P ratios were relatively constant, indicating a close association of Ni and Cd with biological processes in surface waters across all seasons. The observed "uptake", "remineralization", and "winter mixing" ratios are close to the overall dTM:P ratios in the SML (depth of < ~ 100 m) ($\mathrm{P}_{1000}\mathrm{Ni}_{1.53 \pm 0.08}\mathrm{Zn}_{0.37 \pm 0.07}\mathrm{Cu}_{0.20 \pm 0.03}\mathrm{Cd}_{0.21 \pm 0.01}$) (Table S3). The dTM:P ratio here is broadly consistent with the extended Redfield ratio of phytoplankton cultures ($(\mathrm{N}_{16}\mathrm{P}_{1})_{1000}\mathrm{Zn}_{0.80}\mathrm{Cu}_{0.38}\mathrm{Cd}_{0.21}$) (Ho et al., 2003). Therefore, the positive correlations between dTMs and nutrients in the SML on the continental slope across all seasons (Fig. S4) generally reflected the seasonal cycling of biological uptake in summer, remineralization of

Commented [GM16]: This red bit and then next one are referencing literature values. I guess they are not strictly necessary, but also it a shame to remove them. Reviewers generally like to see references to literature values and if you don't have them you get complaints….

Commented [ML17R16]: I agree but these are expressed as % but the data from this paper as concentrations…

Commented [DR18R16]: I agree with Maeve, this is expressed in % whilst our values in actual concetrations

Commented [AB19]: Aluminium, abiotic removal processes too?

Commented [CX20R19]: Should dAl be removed in this section to avoid controversary?

Commented [ML21]: This is great and perhaps all you need- just state drawdown and then this ratio if need to keep paper short

Commented [ML22]: You could get pulled up here as we don't have the Nov after July i.e. Nov 2014 and July 2015- need to put a caveat in here. I think it is reasonable to assume would be similar the next Nov but need to state this

Commented [DR23R22]: Yes, I agree, this needs to be clarified that it's an assumption of the same cycle

Commented [CX24R22]: done

Commented [ML25]: Be careful here as can't use AOU in surface waters as have negative values- remove this from fig. S7 and be specific where you have evidence of remineralisation.

Commented [CX26R25]: Done. I removed AOU < 0 in the figure

Commented [ML27]: Agree with this

Commented [AB28]: Extra aluminium maybe from external dust supply. I think there was a Saharan dust episode that ...

Commented [CX29R28]: dAl removed from this section?

Commented [CX30]: Antony: Maybe you need to consider propagating the uncertainty for these ratios? ...

Commented [CX31R30]: done

organic particles in autumn, followed by winter mixing.

3.2 Additional fluvial inputs of dTMs on the shelf

Seasonal cycling of biological processes also affected the dTM and nutrient distributions on the shelf of the NE Atlantic Ocean. Using station CCS (central Celtic Sea) as an example (Fig. S4), surface dTM and nutrient concentrations decreased from April to July due to phytoplankton uptake. Subsurface (depths > 50 m) nutrient and dCd levels increased from April to November due to remineralization of sinking organic particles (Birchill et al., 2017; Lohan & Tagliabue, 2018). In contrast, subsurface dCu and dNi gradually decreased from spring to autumn, possibly reflecting the impact of external sources and/or water mass mixing. ~~Unlike similar dTM:P ratios at all stations on the slope,~~ The overall dTM:P ratios on the shelf varied greatly between sampling locations (Fig. S5). These variations were accompanied by increasing dTM concentrations with decreasing distance offshore, suggesting the dTM stocks on the shelf were additionally supplied by external sources. Benthic sediments were likely not an important source for the enhanced dTMs, since dTM concentrations did not change significantly with $^{223}Ra_{xs}$ and $^{224}Ra_{xs}$ activities (Fig. S6).

Instead, an increasing salinity with distance offshore (Fig. 3) and strong negative correlations between dTMs and salinity suggest dTM (especially for dCu and dZn) concentrations (Fig. S7) were augmented by a dTM-rich low-salinity endmember, e.g., riverine input from the British Isles through Irish Sea and/or the Bristol channel (Achterberg et al., 1999; Kremling & Hydes, 1988). Based on the correlations between subsurface (depth of 50 – 200 m to exclude surface biological activities) dTMs, nutrients, and salinity in April when significant correlations were observed, the low-salinity endmember at salinity of 33.5 (the typical salinity of the Irish Sea and the Bristol Channel) were calculated as: dCd, 144 ± 59 pM; dCu, 13.0 ± 1.2 nM; dNi, 4.45 ± 1.11 nM; dZn, 22.2 ± 3.2 nM; TN, 9.45 ± 3.85 µM; P, 0.80 ± 0.23 µM; and Si, 12.9 ± 1.8 µM. These values are comparable with the observed dTM concentrations in the low-salinity waters around the British Isles (Kremling & Hydes, 1988). The enrichment of dCu and dZn relative to P in the low-salinity endmember produced gradually decreasing dCu:P and dZn:P ratios with increasing distance stretching from Site A to CS2 (Fig. S9). Fluvial input was not a major source of dCd and dNi, thereby resulting in increasing dCd:P and dNi:P ratios with offshore distance. ~~At station CS2, the dTM:P, TN:P, and Si:P ratios were close to those on the continental slope.~~

Commented [DR32]: Out of curiosity, do you have a suggestion why the ratios of DTMs changed whilst macronutrients remained the same?

Commented [CX33R32]: Nutrients were also changed

Commented [AB34]: I agree with the broader point that any seasonal cycling on the shelf is superimposed on top of a salinity and hence TM concentration gradient. But looking at Fig S8 the uptake and remineralisation picture is less clear than described here?

Yes, there is clear surface drawdown for dCd, looks like dFe and macro nutrients,

dZn, surface draw down yes but remineralistion less clear.

dCu concentrations are relatively homogenous throughout the water column for each month.

For both dNi and dCu concentrations throughout the water column decrease each month. Does the salinity change and maybe indicate a water mass signal? As the Cu and Ni ...

Commented [CX35R34]: Yes. dCd is controlled by local biological processes. dCu and dZn are determined by ...

Commented [AB36]: Salinity increases with distance off shore?

Commented [CX37R36]: Yes. It's a mistake. Salinity increases with offshore distance.

Commented [AB38]: In Fig S12 the correlations for Cu and Zn are convincing but not so for Cd and Ni. Is it possible th ...

Commented [CX39R38]: Yes. I think Cu and Zn are mainly controlled by external sources, while Cd was mainly ...

Commented [AB40]: I think for this part you really do need to consider the estuarine behaviour, this assumes a linearit ...

Commented [ML41]: Could this be why you see larger variation in the offshore transects? E.g. large ranges of ...

Commented [CX42R41]: This section refers to the shelf region, while the former section refers to the slope region ...

Commented [DR43]: So on-shelf waters (with fluvial input) were lower in DCd and DNi than the slope surface waters ...

Commented [CX44R43]: No. Just because P is somewhat contributed by fluvial input while Cd and Ni rarely. So the ...

~~The subsurface salinity at station Site A gradually increased from ~ 34.9 in April to ~ 35.3 in November (Fig. 3), suggesting decreasing fluxes of riverine waters or an increasing intrusion of North Atlantic waters. For instance, the water flow of River Severn, the longest river of the British Isles, shows decreasing flows from winter to summer and autumn [website, Open WIMS data].~~ The low-salinity endmember shows the highest dCu and dZn concentrations in July and lowest values in November (Fig. S7), possibly reflecting seasonal variations in the endmember dTM concentrations. This phenomenon can be additionally explained by the enhanced influence of remineralization at stations away from the fluvial source, evidenced by the elevated subsurface dTM and nutrient levels at station CCS relative to other stations in autumn (Fig. S7). Therefore, the distributions of dTMs and nutrients as well as their correlations on the continental shelf were balanced by riverine input and the seasonal cycling of biogeochemical processes.

Commented [AB45]: I think more likely this will be driven by regional ocean-shelf circulation, would be worth reading anything by Sharples or Jo Hopkins relating to the circulation of the Celtic Sea

Commented [CX46R45]: Possibly this sentence could be removed.

3.3 Water mass mixing drive metal:P kinks at depth

The waters on the NE Atlantic continental slope between the SML and potential density of 27.62 kg m^{-3} (depth ~ 1000 m) are characterized by the presence of East North Atlantic Central Waters (ENACW), Mediterranean Outflow Waters (MOW), and Sub-Arctic Intermediate Waters (SAIW) (Rusiecka et al., 2018) (Fig. S8). The increasing MOW contribution with depth is accompanied by increasing dTM and nutrient concentrations. ~~At depths of 950 – 1050 m with the highest MOW contribution (~ 60%), waters showed strongly elevated dAl (20.1 ± 1.5 nM) (Table S4).~~ Water columns with potential density > 27.62 kg m^{-3} are characterized by a gradually decreasing MOW contribution, and increasing contributions of Labrador Sea Water (LSW) and North East Atlantic Deep Waters (NEADW) (Fig. S8). The dTM and nutrient concentrations continuously increased with depth, showing dCd of ~ 350 pM, dCu of ~ 2.2 nM, dNi of ~ 5 nM, dZn of ~ 2.7 nM in bottom waters (Table S2). These concentrations are similar to the reported deep dCd (310 ± 26 pM), dNi (4.1 ± 0.4 nM), and dCu (1.56 ± 0.33 nM) values for this region (Cotté-Krief et al., 2002) and consistent with reported deep water dTM and nutrient levels in the North Atlantic Ocean (Achterberg et al., 2021; Saager et al., 1997).

Commented [ML47]: I would leave this in

Commented [CX48]: Antony: You could summarise this, my suggestion would to hold off on the deleting until you have addressed the comments and then we may be able to edit our way under the word count. It is nice to place the values in context.

No apparent kinks were identified for dCd:P (260 ± 3 µmol mol^{-1}), dNi:P (1.94 ± 0.04 mmol mol^{-1}), and dZn:P (2.26 ± 0.04 mmol mol^{-1}) in waters > 100 m (Table S3). These ratios here are similar to those reported for the North Atlantic Ocean with dCd:P of 278 ± 3 µmol mol^{-1}, dNi:P of 2.01 ± 0.08 mmol mol^{-1}, and dZn:P of 1.77 ± 0.16 mmol mol^{-1} at P of 0.5 – 1.5 µM (GEOTRACES Intermediate Data Product Group, 2021; Middag et al., 2018; Roshan & Wu, 2015). The lack of dCd:P kink also agrees with the linear dCd – P relationship at P < 1.3 µmol kg^{-1} (de Baar et al., 1994; Cullen, 2006; Frew & Hunter, 1992; Middag et al., 2018). In contrast, the dCu:P ratio on the slope of NE Atlantic continental margin increased from 0.31 mmol mol^{-1} at 100 – 1000 m to 2.78 mmol mol^{-1} at depths > 1000 m and the dAl concentrations showed pronounced variations with increasing P levels (Fig. S2). Considering the small variations in surface dCu concentrations (Table S2) and that Al is not a bio-essential element, changes in subsurface dCu:P and dAl:P ratios with water depth should reflect physical (e.g., water mass mixing) rather than biological processes.

We estimated the elemental composition of each water mass using a three-step calculation (Table S4). (1) At potential density < 27.62 kg m^{-3} (depths < ~ 1000 m), endmember MOW concentrations were calculated from the positive linear correlations with dTM concentrations (Fig. S9). (2) Nurtients and dTMs contributed by MOW were removed. At potential density > 27.62 kg m^{-3}, the residual dTMs were contributed by LSW, NEADW, and SAIW, where the endmember SAIW concentrations were calculated from the significant negative linear relationship between corrected SAIW contribution and corrected dTM concentrations (Fig. S10). The endmember NEADW concentrations were evaluated at LSW < 1% (Fig. S11a). (3) Finally, the endmember concentrations of LSW and ENACW were estimated by removing the contributions of MOW, SAIW, and NEADW (Fig. S11b and c).

All dTMs and nutrients showed significant correlations with percentage contributions of LSW and ENACW at the final step, despite uncertainties propagating during each step in the calculations. The predicted dTM concentrations, reconstructed by direct multiplication of water mass fractions with their endmember values, illustrate almost identical values with the observed concentrations with very low residuals (Fig. S12). The calculated endmember concentrations of NEADW agree with deep water (> 4000 m) concentrations in the NE Atlantic Ocean (GEOTRACES Intermediate Data Product Group, 2021; Liu & Tanhua, 2021), where NEADW is a persistent feature (van Aken, 2000a; García-Ibáñez et al., 2015, 2018; Reinthaler et al., 2013). Therefore, our estimations on the apparent endmember concentrations of water masses are robust to show their relative chemical compositions.

Commented [GM49]: Is there a reason you switch from ":" to "-" ?

Commented [CX50R49]: Here dCd-P means the correlation between dCd and P, not their ratio.

Commented [AB51]: Is this shown? What type of variation?

Commented [CX52R51]: Twisted variations, Fig. S2

Commented [DR53]: Please do not put Ni and Al in one sentence here. They are driven by different processes. Whilst DCu was probably actively taken up whilst DAl passively scavenged. DAl also had maxima whilst Dcu did not

Commented [CX54R53]: We are talking about subsurface samples here. They are combined because they both reflect water mass mixing.

Commented [AB55]: Not sure despite is the correct word. You could make a statement about the uncertainty and state a value(s)?

Commented [CX56R55]: It is difficult to state the uncertainty values

Commented [GM57]: If you remove the red bit above, then it may be tricky to make this conclusion?

Commented [CX58R57]: Antony: Could you add any observed end member values to Table S4 from the GEOTRACES IDP?

Commented [CX59R57]: done

The correlations between reconstructed dTMs and nutrients corresponded to the observed results, that no kinks were observed for the correlations between dCd, dNi, dZn, and P, while dCu:P and dAl:P ratios changed sharply at a density of 27.62 kg m^{-3} (depth ~ 1000 m) (Fig. 4). The dTM:AOU and nutrient:AOU ratios changed abruptly at depths of ~ 1000 m and ~ 2000 m across all seasons (Fig. S3), coinciding with the variations of water mass fractions from MOW+SAIW+ENACW at 100 – 1000 m to MOW+NEADW+LSW at > ~ 1000 m. Therefore, the AOU variations at depth mostly reflect physical processes (e.g., water mass mixing) rather than local biological processes. All these observations indicate that subsurface dTMs and nutrients and their ratios on the NE Atlantic continental margin are mainly controlled by water mass mixing driven by ocean circulation with local remineralization making a minor contribution.

3.4 The impact of MOW on the dTM distributions on the NE Atlantic Ocean

The dTM:nutrient and dTM:AOU kinks at ~ 1000 m and ~ 2000 m are closely related to the maximum and diminished occurrence of MOW (Fig. S2, Fig. S3), probably ascribed to the distinctive dTM and nutrient stoichiometry of MOW relative to other water masses (Table S4). For instance, MOW shows much higher dAl:P but lower dCu:P ratios than LSW and NEADW, thus creating kinks of dCu:P and dAl:P ratios at the maximum occurrence of MOW. Therefore, MOW provides an important imprint on the dTM distributions on the NE Atlantic continental slope.

The MOW is formed in the Mediterranean Sea and spreads across the NE Atlantic Ocean at ~ 500 – 1500 m towards the Bay of Biscay and further along the shelf break of Celtic Sea (van Aken, 2000b; Price et al., 1993). ~~The occurrence of MOW in the NE Atlantic Ocean can be observed in elevated dAl concentrations and salinity (Measures et al., 2015; Middag et al., 2022; Rolison et al., 2015) at depths of 900 – 1400 m.~~ The significant correlations between dTMs and salinity (Fig. S13) demonstrate that dTMs in the MOW core were predominantly controlled by the conservative isopycnal mixing between MOW and lower salinity water masses (e.g., SAIW with similar density range to MOW; Johnson & Gruber, 2007) during ocean circulation, rather than removal by scavenging. Specifically, the dAl, dZn, and dNi concentrations of the MOW core decreased with decreasing salinity, suggesting the saline MOW is a net source to deliver Mediterranean-sourced Al, Zn, and Ni into the NE Atlantic Ocean (Middag et al., 2022).

Commented [DR60]: If MOW is Zn and Ni source then why don't we see maxima in DZn and Dni profiles similarly to DAl?

This finding is similar to the long-distance transport of anthropogenic Pb from MOW to the NE Atlantic continental margin (Rusiecka et al., 2018).

Furthermore, the minor seasonal variations of dTMs and nutrients in the MOW core possibly reflect seasonal cycles of water mass circulation along the continental slope. Due to the wind-driven processes (Roque et al., 2019), the influence of SAIW in the NE Atlantic Ocean declines in autumn. Hence, higher MOW signals (e.g., higher salinity) were observed along the continental slope in November with respect to April and July. Accordingly, the MOW core on the slope showed slightly higher dAl and dZn but lower dCd concentrations in November than those in April and July (Fig. S13).

Commented [CX61R60]: Because water mass will evolve during transportation

Commented [DR62]: Do you mean seasonal variations in water mass circulation?

Commented [CX63R62]: Yes

Commented [DR64]: How do you know its not ENACW?

Commented [CX65R64]: See Johnson and Gruber, 2007

Commented [AB66]: this is hard to see in the figure S23

Commented [CX67R66]: slightly higher

4. Conclusions

Our findings illustrate the seasonal variations of surface dTMs and nutrients were associated with biological processes on the continental margin of the NE Atlantic Ocean. Surface dTM concentrations on the shelf were also influenced by a low-salinity endmember, likely fluvial materials from the British Isles. Therefore, temperate shelf sea ecosystems can be influenced by local biological processes and external sources, where riverine inputs play an essential role to deliver terrestrial dTMs to the ocean. The dTM concentrations and metal:P ratios at depth in the slope region can be explained by water mass mixing driven by ocean circulation without invoking local remineralization. Specifically, the long-distance transportation of MOW delivers Mediterranean-sourced dTMs (e.g., dAl, dZn, and Ni) into the NE Atlantic Ocean and drives dAl:P and dCu:P kinks at a potential density of ~ 27.62 kg m^{-3} (depth ~ 1000 m) along the NE Atlantic continental slope. Future climate change driven changes in dust inputs into the Mediterranean and water mass characteristics in the subpolar gyre, therefore, will have consequences for nutrient stoichiometry and the biological carbon cycles in the NE Atlantic Ocean.

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NE/K001779/1 (M. L.), NE/K002023/1 (A. A.), and NE/L501840/1 (A. B.)).

Open Research

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

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Figures

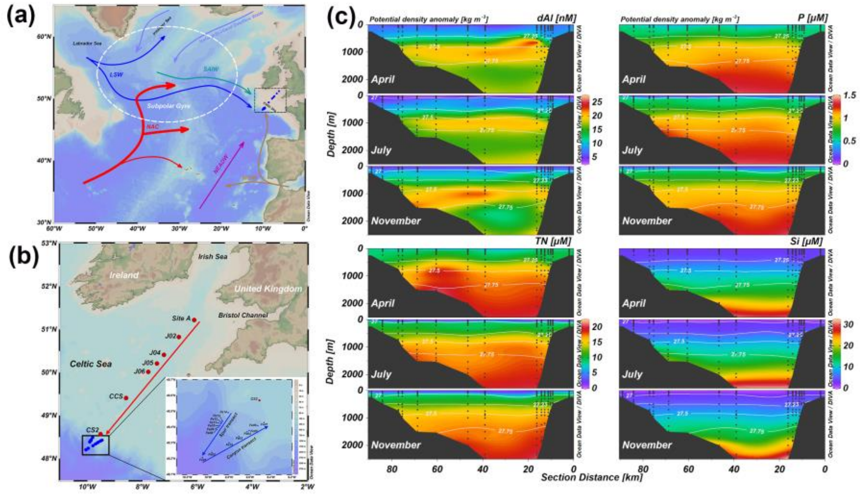

Fig. 1 (a) The schematic circulation of water masses (NAC: North Atlantic Current; LSW: Labrador Sea waters; SAIW: Sub-Arctic Intermediate Waters; MOW: Mediterranean Outflow Waters; NEADW: Northeast Atlantic Deep Waters) in the North Atlantic Ocean; (b) Sampling transects and locations on the Northeast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

Commented [ML68]: Make the black dots larger so can see the sampling resolution

Commented [CX69R68]: Done

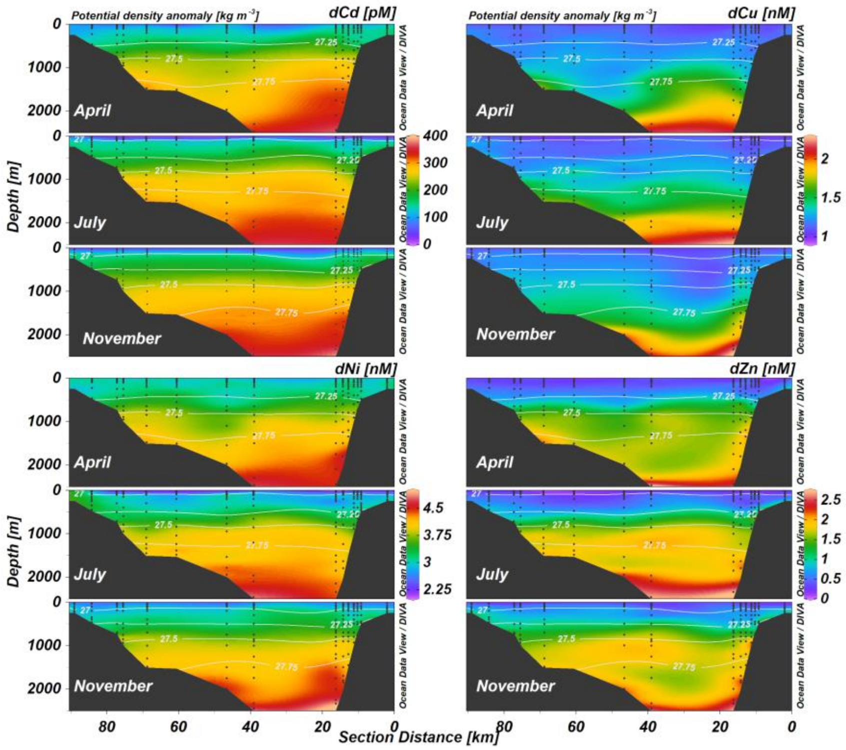

Fig. 2 Section plots of dissolved cadmium (dCd), copper (dCu), nickel (dNi), and zinc (dZn) on the slope of the Northeast Atlantic continental margin. Samples were taken in November 2014, April 2015, and July 2015, respectively. The section is defined in Fig. 1b.

Commented [CX70]: Antony: Some of the surface density isopyncals are a bit squashed, you might want to remove some of the surface ones

It might be better to plot each transect separately? I know this will double the plots but I think at the moment the apparent features in interpolated section in the middle catches the eye, especially in the dCu and dCd. Either that or reduce the interpolation in ODV so that the middle is left blank?

Commented [CX71R70]: The density isopycnals have been modified. I would like to keep the plots with combined transects because we focus on the water mass mixing here.

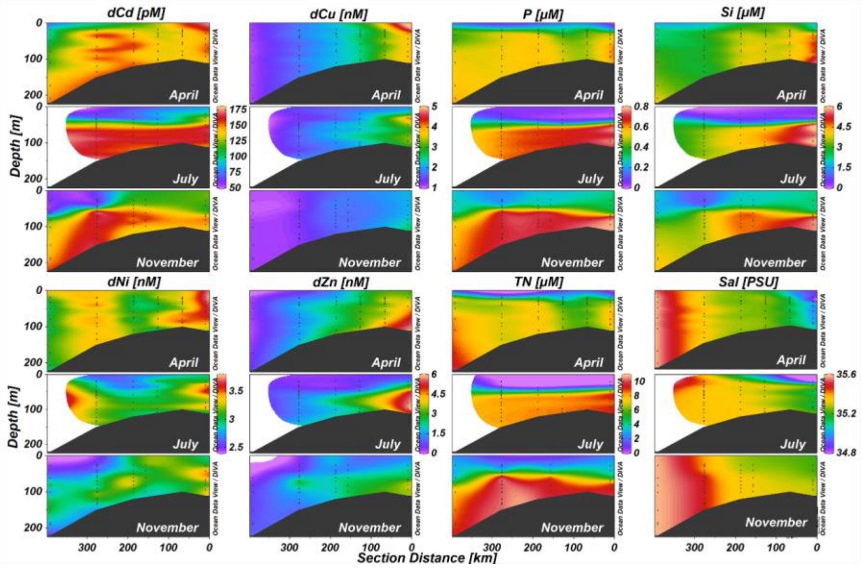

Fig. 3: Section plots of dissolved trace metals (dCd, dCu, dNi, dZn), salinity, and nutrients (nitrate+nitrite (TN), phosphate (P), silicic acid (Si)) on the continental shelf of the Northeast Atlantic Ocean. The section is defined in Fig. 1b. Samples were taken in November 2014, April 2015, and July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

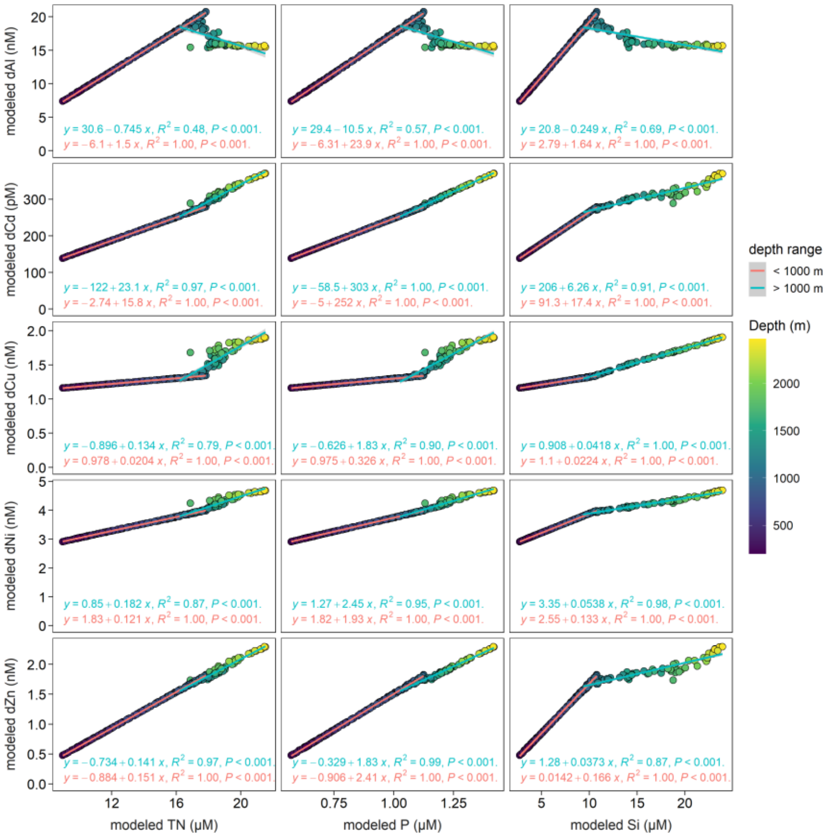

Fig. 4: Correlations between reconstructed dissolved trace metal (dTM: dAl, dCd, dCu, dNi, dZn) and nutrient (nitrate+nitrite (TN), phosphate (P), and silicic acid (Si)) concentrations on the Northeast Atlantic continental slope. Linear regression models were applied to depths < 1000 m (potential density < 27.62 kg m^{-3}) and depths > 1000 m (potential density > 27.62 kg m^{-3}), respectively.

Commented [GM72]: You need to remove the grey background

Commented [XC73R72]: done