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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

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ABSTRACT

Nutrients and nutrient-like dissolved trace metals (dTMs) are essential for the functioning of marine organisms and therefore form an important part of ocean biogeochemical cycles. Here, we report on 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), which is representative for temperate shelf seas globally. Variations in surface water dTM and nutrient concentrations were mainly regulated by seasonal changes in biological processes. The stoichiometry of dTMs (especially for dCu and dZn) and nutrients on the continental shelf was additionally affected by fluvial inputs. Nutrients and dTMs at depth on the continental slope were determined by water mass mixing driven by ocean circulation, without an important role for local remineralization processes. The Mediterranean Outflow Waters are especially important for delivering Mediterranean-sourced dTMs to the Northeast Atlantic Ocean and drive dTM:nutrient kinks at a depth of ~1000 m. These results highlight the importance of riverine inputs, seasonality of primary production and ocean circulation on the distributions of nutrients and nutrient-like dTMs in temperate continental margin seas. Future climate related changes in the forcing factors may impact the availability of nutrients and dTMs to marine organisms in highly productive continental shelf regions and consequently the regional 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 the ocean. Zinc, Ni, and Cu are involved in enzymatic processes required for phytoplankton functioning (La Fontaine et al., 2002; Mahaffey et al., 2014; Twining and Baines, 2013) and Cd is taken up as a divalent metal and may substitute Zn in carbonic anhydrase (Horner et al., 2013). Low supply of dTMs could potentially affect marine ecosystem structure and function (Lohan and Tagliabue, 2018; Morel and 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 seasonally depleted concentrations in surface waters due to phytoplankton uptake (Moore et al., 2013; Morel and Price, 2003) and elevated levels at depth due to remineralization of sinking organic particles (Boyd et al., 2017). Nutrients and bioactive dTMs therefore show significant positive correlations with for example the dCd-P relationships in the global ocean (Boyle et al., 1976; Middag et al., 2018;

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Wu and Roshan, 2015; Xie et al., 2015), and dZn-P, dNi-P and dCu-Si relationships in the South Atlantic (Wyatt et al., 2014) and Southern Oceans (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., in the case of P at concentration of ~1.3 μM for the Cd-P correlation (Cullen, 2006; de Baar et al., 1994). 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 and DeVries, 2021), or enhanced Cd uptake due to the limitation of bio-essential elements in surface waters (Cullen, 2006; Sunda and Huntsman, 2000). Kinks are also hypothesized to be associated with the chemical replacements between Co, Zn, and Cd in carbonic anhydrase in phytoplankton (Morel et al., 1994; Price and Morel, 1990) or a 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, and these inputs can be traced by dissolved aluminum (dAl) (Han et al., 2008; Measures and Edmond, 1988; Menzel Barraqueta et al., 2018). The ongoing debate on the drivers underpinning bioactive dTM distributions requires further investigations into co-occurrence of nutrients and bioactive dTMs and their relationships. Resolving this issue would improve our understanding of biogeochemical cycles in paleo – and modern oceans.

Continental margins with their shelves and slopes are gateways 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 and Sharples, 2012). Primary production in shelf seas, particularly in temperate shelf seas, results in a net drawdown of atmospheric CO_2. The shelf sea carbon pump subsequently transfers the captured carbon to the open ocean (Thomas et al., 2004). The Northeast (NE) Atlantic continental margin (Celtic Sea) is a typical temperate shelf sea and is representative for such systems globally because of its enhanced and seasonal primary productivity, seasonal co-limitation of phytoplankton growth by nitrate and Fe (Birchill et al., 2017), seasonal stratification, and occurrence of both fluvial and benthic inputs of redox sensitive TMs (including Fe and Mn) (Chen et al., 2023). Here, we report the seasonal distributions of dTMs (with focus on dCd, dCu, dNi, and dZn) and nutrients on the NE Atlantic continental margin, which is characterized by large seasonal variations in biological productivity (Birchill et al., 2017), complex bathymetry and dynamic water circulation (Fig. 1a). A high sampling resolution over three seasons (Fig. 1b) offers a unique opportunity to determine the influence of terrestrial inputs, biogeochemical processes, and ocean circulation on the seasonal variations of bio-essential dTMs and their relationships with nutrients.

2. Methods

2.1. Sampling

Samples were collected on cruises with *RRS Discovery* during three different seasons: an autumn cruise in November 2014 (DY018), a spring

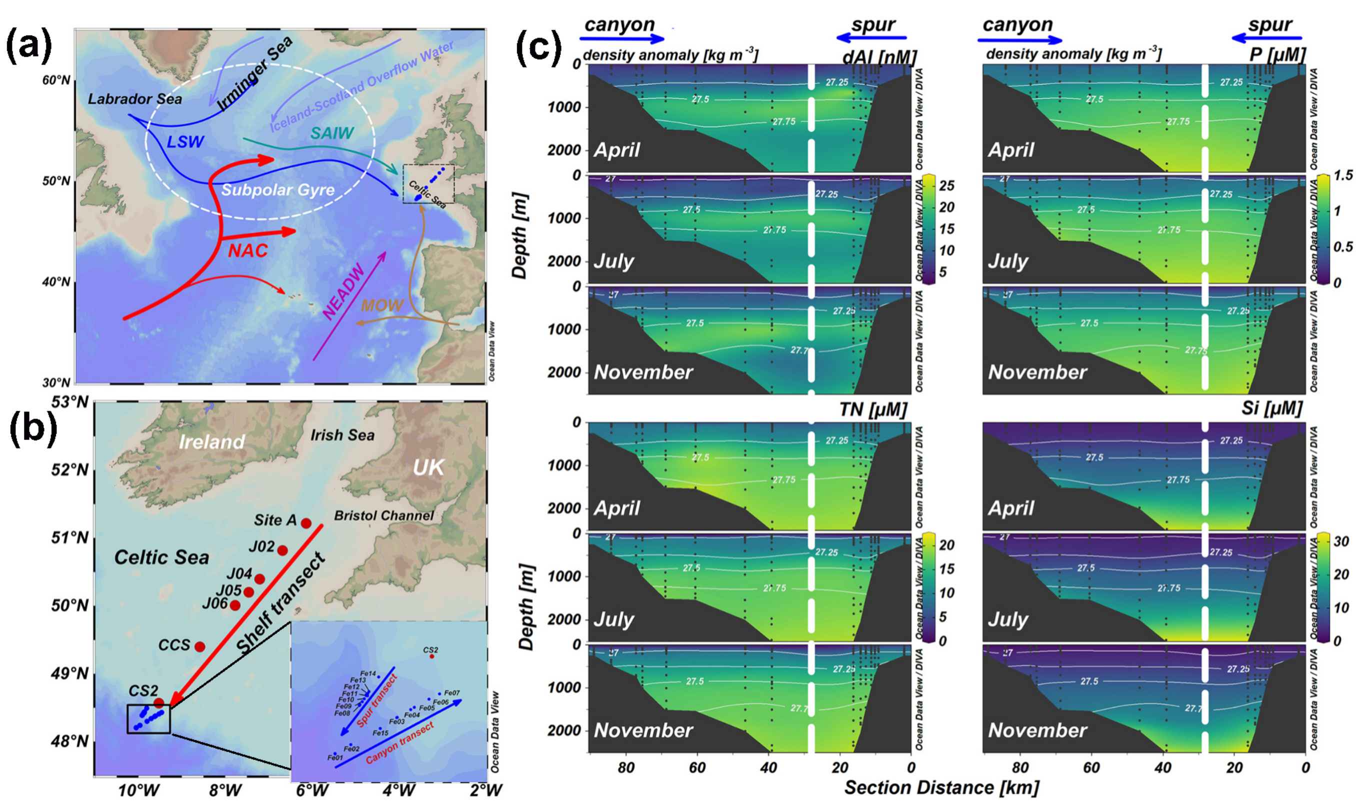

Fig. 1. (a) The schematic circulation of water masses (NAC: North Atlantic Current; LSW: Labrador Sea waters; SAIW: Sub-Arctic Intermediate Waters; MOW: Mediterranean Outflow Waters; NEADW: Northeast Atlantic Deep Waters) in the North Atlantic Ocean; (b) Sampling transects and locations on the Northeast 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. The directions of the canyon and spur transects are indicated by blue arrows. The dashed black lines separate the canyon and spur transects. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

crufise fin Aprfifl 2015 (DY029), and a summer crufise fin Jufly 2015 (DY033). Each season we conducted one transect on the contfinentafl sheflf of the Cefltfic Sea from statfion Sfite A near the Brfistofl channefl to statfion CS2 near the sheflf break (Ffig. 1b). Two off-sheflf transects were conducted afl ong a canyon (statfions Fe01 - Fe07, Fe15) and a spur (statfions Fe08 - Fe14) durfing each season.

Seawater sampfles for dTM anaflyses were coflflected foflflowfing GEOTRACES protocofls (Cutter et afl., 2017). Seawater sampfles were coflflected usfing 24 × 10 L Tefflon coated trace metafl cflean Ocean Test Equfipment (OTE) sampflers posfitfioned on a Tfitanfium rosette frame. Afll OTE bottfles were pressurfized fin a cflean room wfith ffifltered (0.2 μm PTFE, Mfiflflex-FG 50, Mfiflflfipore) compressed afir. Seawater sampfles were ffifltered fin-flfine usfing ffiflter capsufles (0.2 μm pore sfize; Sartorfius, Sartobran P) finto acfid washed 125 mL flow-densfity poflyethyflene bottfles (Naflgene). Afll sampfles were acfidfiffied to pH of ~1.8 wfith ufltra-pure hydrochflorfic acfid (UpA Romfifl) fin a flamfinar fflow hood and stored doubfle-bagged fin zfipflock bags.

2.2. Anaflyses

Trace metafl sampfles were processed and anaflyzed at GEOMAR as outflfined fin Rapp et afl. (2017). In detafifl, seawater sampfles were sub-sampfled (15 mL) finto ffluorfinated ethyflene propyflene bottfles fin a flamfinar fflow hood. Afll sampfle bottfles were spfiked wfith 100 μL of dfifluted enrfiched fisotope spfike. Then, seawater sampfles were pre-concentrated by an automated system (SC-4 DX SeaFast pfico; ESI) wfith onflfine pH bufferfing and seawater matrfix removafl. Preconcentrated sampfles were anaflyzed by hfigh-resoflutfion finductfivefly coupfled pflasma-mass spectrometry (HR-ICP-MS; Thermo Ffisher Eflement XR) fin flow resoflutfion (R = 300) for ^{110}Cd, ^{111}Cd, ^{115}In and fin medfium resoflutfion (R = 4000) for ^{60}Nfi, ^{62}Nfi, ^{63}Cu, ^{65}Cu, ^{66}Zn, and ^{68}Zn. Reference materfiafls, SAFe GEOTRACES S and D1 were used to check the accuracy and precfisfion of the measurements and the resuflts were consfistent wfith consensus vaflues (Tabfle 1).

Seawater sampfles for dAfl were sub-sampfled finto acfid washed 50 mL pflastfic tubes. An aflumfinum spectroffluorometrfic compflex was obtafined foflflowfing the addfitfion of flumogaflflfion (Hydes and Lfiss, 1976) at pH 5.0–5.5 adjusted by addfitfion of ammonfium acetate buffer and the sampfles heated for 3 h at 55 °C. Sampfles were then anaflyzed by a spectroffluorometer (Cary Ecflfipse Ffluorometer). The measured dAfl concentratfions of a reference standard (GS) were consfistent wfith consensus vaflues (Tabfle 1).

Large voflume sampfles for radfium (Ra) anaflysfis were coflflected from Nfiskfin bottfles depfloyed on a stafinfless-steefl frame as per Bfirchfifll (2017). The sampfles for Ra were transferred finto acfid-washed 20 L coflflapsfibfle contafiners, and sflowfly (<750 mL mfin^{-1}) passed through a coflumn ffiflled wfith 20 g of MnO_2-fimpregnated acryflfic ffiber to extract Ra from seawater (Moore, 2008). Ffibers were rfinsed wfith ufltra-hfigh purfity water, and partfiaflfly afir drfied to optfimfize emanatfion of the radon daughter (Sun and Torgersen, 1998). Then, the sampfles were counted fimmedfiatefly usfing a Ra Deflayed Cofincfidence Counter [RaDeCC] (Moore, 2008; Moore and Arnofld, 1996). Countfing was repeated after ~30 (~90) days to determfine the ^{224}Ra (^{223}Ra) actfivfity supported by the parent fisotopes ^{228}Th (^{227}Ac). Uncertafinty caflcuflatfions foflflowed the methods of Garcfia-Soflsona et afl. (2008). The effficfiencfies of the RaDeCC systems were caflfibrated and monfitored usfing standards prepared from ^{227}Ac and ^{232}Th (Annett et afl., 2013). Radfium actfivfitfies ($^{224}Ra_{xs}$ and $^{223}Ra_{xs}$) are reported fin excess of actfivfity supported by the parent fisotopes fin the water coflumn.

Unffifltered seawater sampfles for nutrfients (TN, P, Sfi) were taken from the same OTE bottfles as trace metafl sampfles. They were sampfled finto 'aged' 10% HCfl acfid washed and de-fionfized water rfinsed hfigh-densfity poflyethyflene bottfles. Seawater sampflfing and handflfing for nutrfient anaflysfis was carrfied out where possfibfle accordfing to the GO-SHIP nutrfient manuafl recommendatfions (Becker et afl., 2020). Nutrfient anaflysfis was carrfied out on board wfithfin a few hours of sampflfing usfing a SEAL Quaatro segmented fflow nutrfient autoanaflyzer usfing coflorfimetrfic anaflytficafl technfiques descrfibed fin Woodward and Rees (2001).

Turbfidfity was measured by an Aquatracka MKIII ffluorometer (Cheflsea Technoflogfies Group) at a waveflength of 400 nm and a bandwfidth of 80 nm. Conductfivfity, temperature, and depth (CTD) data were coflflected usfing a Seabfird 911+ CTD system, and processed on board. Conductfivfity was measured by a Sea-Bfird SBE 4C sensor and caflfibrated on-board usfing dfiscretefly coflflected saflfinfity sampfles anaflyzed wfith a Gufifldflfine Autosafl saflfinometer. Temperature was measured wfith Sea-Bfird SBE 3pflus (SBE 3P) temperature sensor. Dfissoflved oxygen was measured by a Sea-Bfird SBE 43 oxygen sensor and caflfibrated agafinst photometrfic on-board Wfinkfler tfitratfion resuflts. Apparent oxygen utfiflfizatfion (AOU) fis caflcuflated from the presumed oxygen concentratfions under atmospherfic saturatfion for a gfiven temperature (ϑ) and saflfinfity (S), subtracted from the observed dfissoflved oxygen concentratfions.

$$AOU = \left[O_{2,sat}(\vartheta, S)\right] - [O_2]$$

2.3. Statistics and pflots

Ffigs. 1, 2, 3, and 6 were created wfith Ocean Data Vfiew (5.6.2) software (Schflfitzer, 2021) usfing DIVA grfiddfing. Afll other pflots and assocfiated statfistfics were performed by *R* programmfing 4.2.0 wfith packages *tidyverse* (Wfickham et afl., 2019), psych (Reveflfle, 2017), and *ggpmisc* (Aphaflo, 2022).

3. Results and discussion

Dfissoflved Cd, Zn, Nfi, and Cu exhfibfited nutrfient-flfike vertficafl dfistrfibutfions durfing afll seasons on the NE Atflantfic contfinentafl margfin (Ffig. 1c, Ffig. 2, Ffig. 3), wfith flowest concentratfions fin surface waters due to bfioflogficafl utfiflfizatfion, and eflevated concentratfions at depth ascrfibed to remfineraflfizatfion (Brufland et afl., 2014; Moore et afl., 2013). The canyon and spur transects showed comparabfle vertficafl proffifles for dTMs and nutrfients for each season and were combfined as a sflope transect (Ffig. 1c, Ffig. 2). In contrast to the reflatfivefly constant of bfioactfive dTM and nutrfient concentratfions at depth on the contfinentafl sflope, the surface bfioactfive dTM and nutrfient flevefls fin the Cefltfic Sea showed pronounced seasonafl varfiatfions (Tabfle S1). Kfinks fin dTM:nutrfient (e.g., dZn:P and dCu:P) ratfios were observed on the contfinentafl sflope at a depth of ~100 m and ~ 1000 m (Ffig. 4). The sheflf transect (Ffig. 3) showed hfigher dCu, dNfi, dZn, and Sfi concentratfions than the sflope transect (Ffig. 1c, Ffig. 2), accompanfied by varyfing dTM: nutrfient correflatfions.

Table 1
GEOTRACES reference materfiafl resuflts for dfissoflved Cd (dCd), Nfi (dNfi), Cu (dCu), Zn (dZn), and Afl (dAfl).

	dCd (pM)	dNfi (nM)	dCu (nM)	dZn (nM)	dAfl (nM)
Reported SAFe S		2.32 ± 0.22 (n = 10)	0.705 ± 0.130 (n = 8)	0.071 ± 0.025 (n = 8)	
Reported SAFe D1	979 ± 145 (n = 17)	8.41 ± 0.14 (n = 15)	2.19 ± 0.06 (n = 15)	7.13 ± 0.22 (n = 19)	
Consensus SAFe S		2.28 ± 0.09	0.52 ± 0.05	0.069 ± 0.010	
Consensus SAFe D1	991 ± 31	8.58 ± 0.26	2.27 ± 0.11	7.40 ± 0.35	
Reported GS					27.0 ± 0.6 (n = 6)
Consensus GS					27.5 ± 0.2

Consensus vaflues obtafined from https://www.geotraces.org/standards-and-reference-materfiafls/.

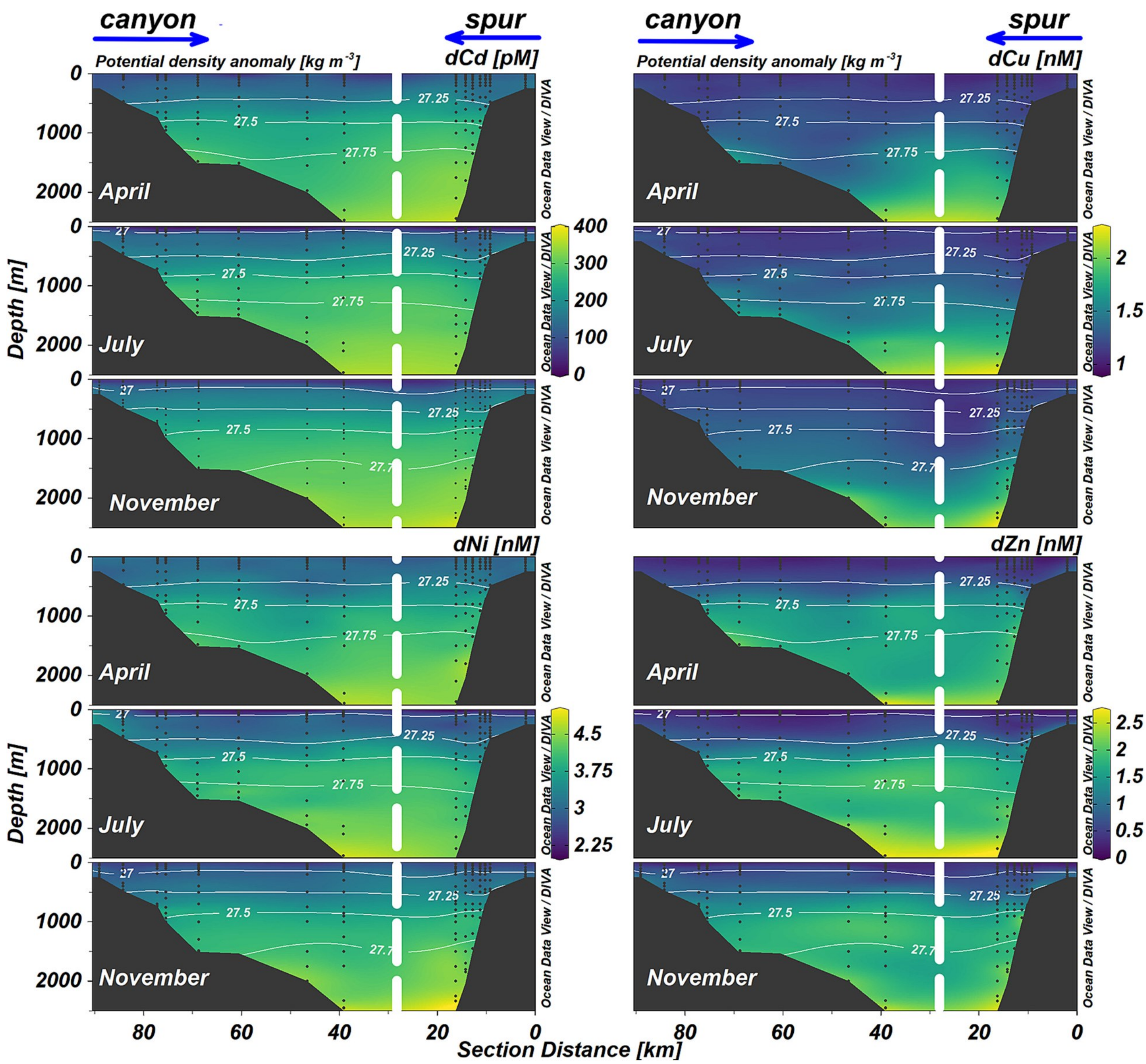

Fig. 2. Sectfion pflots of dfissoflved cadmfium (dCd), copper (dCu), nfickefl (dNfi), and zfinc (dZn) on the sflope of the Northeast Atflantfic contfinentafl margfin. Sampfles were taken fin November 2014, Aprfifl 2015, and Jufly 2015, respectfivefly. The sectfion fis deffined fin Ffig. 1b. The dfirectfions of the canyon and spur transects are findficated by bflue arrows. The dashed bflack flfines separate the canyon and spur transects. (For finterpretatfion of the references to coflour fin thfis ffigure flegend, the reader fis referred to the web versfion of thfis artficfle.)

3.1. Bioflogicafl inffluence on seasonafl variations in surface dTM aflong the continentafl sflope

A seasonafl mfixed flayer (SML) wfith a depth of ~ < 100 m occurred between sprfing and autumn on the contfinentafl sflope (Supportfing finformatfion: Hydrography). A decrease fin dTM and nutrfient concentratfions fin the SML (especfiaflfly at depths <30 m) was observed between Aprfifl 2015 and Jufly 2015, due to bfioflogficafl utfiflfizatfion and water coflumn stratfiffficatfion (Bfirchfiflfl et afl., 2017) (Tabfle S1). Enhanced phytopflankton actfivfity was findficated by maxfima fin chflorophyflfl *a* flevefls fin the SML fin Aprfifl 2015, and just beneath the SML fin Jufly 2015 (Bfirchfiflfl, 2017). Usfing the dfifferences between the mean dTM vaflues observed durfing the Aprfifl and Jufly crufises, the totafl drawdown of surface (depth < 30 m) dTMs and nutrfients on the sflope from sprfing to summer was: dCd 79.5 ± 45.1 pM, dCu 0.08 ± 0.11 nM, dNfi, 0.67 ± 0.31 nM, dZn 0.10 ± 0.25 nM, P 0.35 ± 0.11 μM, TN 6.71 ± 1.83 μM, and Sfi 2.44 ± 0.47 μM (Tabfle S1). The removafl of dCd, dNfi, P, and TN over thfis perfiod was hfigher, and the drawdown of Cu was flower than reported for thfis regfion for the perfiod between January 1994 and June 1995 (TN 3.9 ± 3.9 μM, P 0.46 ± 0.51 μM, Sfi 2.2 ± 3.7 μM, Cd 39 ± 61 pM, Cu 0.34 ± 0.58 nM, Nfi 0.5 ± 1.1 nM) (Cotte-Krfief et afl., 2002), and between March and June 1987 (Cd 30 ± 12 pM) (Kremflfing and Pohfl, 1989). The decrease fin dTM and nutrfient concentratfions was the consequence of phytopflankton uptake fin sprfing and summer, and the overaflfl "uptake" ratfio of phytopflankton normaflfized to average P was:

$$(N_{19\pm5}Si_{7\pm1.3}P_1)_{1000}Ni_{1.9\pm0.9}Zn_{0.29\pm0.71}Cu_{0.23\pm0.31}Cd_{0.23\pm0.13}$$

The surface dTM and nutrfient concentratfions on the sflope fincreased from Jufly to November, and we assume thfis was due to finternafl cycflfing and not to sfignfifficant changes fin externafl suppfly. Thfis phenomenon was accompanfied by correflatfions comparabfle to the sprfing-summer perfiod between dTMs/nutrfients and AOU at AOU > 0 (Ffig. S2). Therefore, the surface dTM and nutrfient varfiatfions from summer to autumn was affected by the remfineraflfizatfion of organfic partficfles. On the other hand, the fincrease fin surface dTM and nutrfient concentratfions from November to Aprfifl was attrfibuted to resuppfly from subsurface waters (Bfirchfiflfl

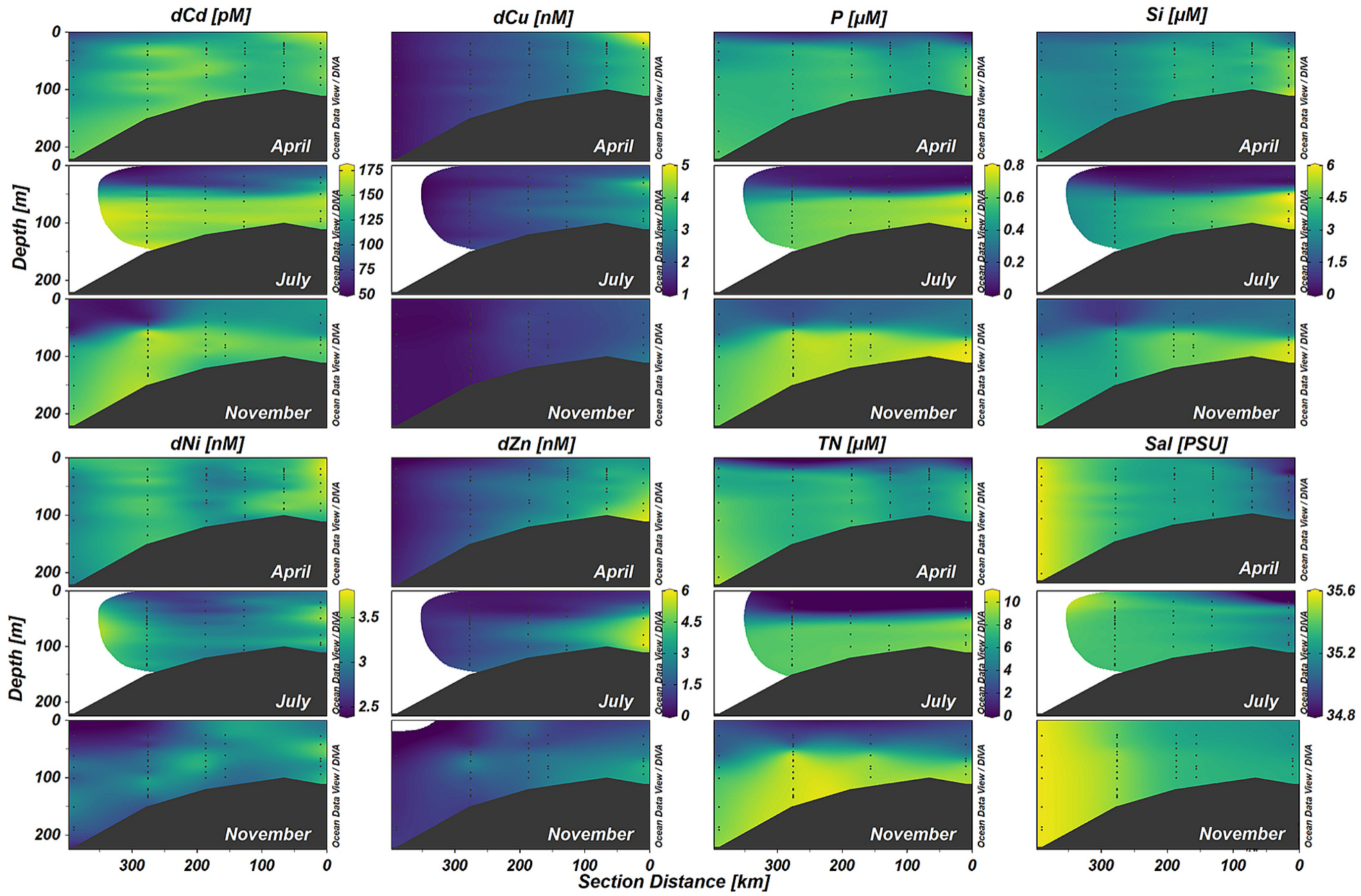

Fig. 3. Sectfion pflots of dfissoflved trace metafls (dCd, dCu, dNfi, dZn), saflfinfity, and nutrfients (nfitrate+nfitrfite (TN), phosphate (P), sfiflficfic acfid (Sfi)) on the contfinentafl sheflf of the Northeast Atflantfic Ocean. The sectfion fis deffined fin Ffig. 1b. Sampfles were taken fin November 2014, Aprfifl 2015, and Jufly 2015, respectfivefly.

et afl., 2017). Usfing concentratfion dfifferences between Jufly and November (Tabfle S1), we estfimated the apparent "remfineraflfizatfion" ratfio of dTMs and nutrfients normaflfized to P as:

$(N_{15\pm13}Si_{6.8\pm3.4}P_1)_{1000}Ni_{1.9\pm2.2}Zn_{0.57\pm1.29}Cu_{0.43\pm0.71}Cd_{0.28\pm0.12}$

and the "wfinter mfixfing" ratfio estfimated from the concentratfion dfifferences between November and Aprfifl observatfions as:

$(N_{21\pm9}Si_{7.1\pm2.6}P_1)_{1000}Ni_{1.9\pm1.0}Zn_{0.10\pm1.19}Cu_{0.10\pm0.33}Cd_{0.19\pm0.20}$

The estfimated Zn:P and Cu:P ratfios between "uptake" and "remfineraflfizatfion" varfied by as much as a factor of 2, but the "wfinter mfixfing" ratfios were as much as an order of magnfitude flower, probabfly due to reflatfivefly flfimfited seasonafl varfiatfions and flarge concentratfion ranges observed for both metafls (Tabfle S1). The N:P, Sfi:P, Nfi:P, and Cd:P ratfios were reflatfivefly constant, findficatfing a cflose assocfiatfion of Nfi and Cd wfith bfioflogficafl processes fin surface waters across aflfl seasons. The observed "uptake", "remfineraflfizatfion", and "wfinter mfixfing" ratfios are cflose to the overaflfl dTM:P ratfios fin the SML (depth of < ~ 100 m) ($P_{1000}Ni_{1.53\pm0.08}Zn_{0.37\pm0.07}Cu_{0.20\pm0.03}Cd_{0.21\pm0.01}$) (Tabfle S2). The dTM:P ratfio here fis broadfly consfistent wfith the extended Redffiefld ratfio of phytopflankton cufltures ($(N_{16}P_1)_{1000}Zn_{0.80}Cu_{0.38}Cd_{0.21}$) (Ho et afl., 2003). Therefore, the posfitfive correflatfions between dTMs and nutrfients fin the SML on the contfinentafl sflope across aflfl seasons (Ffig. 4) generaflfly reflflected the seasonafl cycflfing of bfioflogficafl uptake fin sprfing and summer, remfineraflfizatfion of organfic partficfles fin autumn, foflflowed by wfinter mfixfing.

3.2. Addfitfionafl fflluvfiafl finputs of dTMs on the sheflf

Seasonaflfity of bfioflogficafl processes aflso affected the dTM and nutrfient dfistrfibutfions on the sheflf of the NE Atflantfic Ocean. Usfing statfion CCS (centrafl Cefltfic Sea) as an exampfle (Ffig. 5), surface dTM and nutrfient concentratfions decreased from Aprfifl to Jufly due to phytopflankton uptake. Subsurface (depths >50 m) nutrfient and dCd flevefls fincreased from Aprfifl to November due to remfineraflfizatfion of sfinkfing organfic partficfles (Bfirchfiflfl et afl., 2017; Lohan and Tagflfiabue, 2018). In contrast, subsurface dCu and dNfi graduaflfly decreased from sprfing to autumn, possfibfly reflflectfing the fimpact of removafl mechanfisms and/or water mass mfixfing. The overaflfl dTM:P ratfios on the sheflf varfied greatfly between sampflfing flocatfions (Ffig. S3). For finstance, the sflopes of dZn-P reflatfionshfip decreased from 3.58 × 10 3 at sfite A to 2.16 × 10 3 at statfion CS2. These varfiatfions were accompanfied by decreasfing dTM concentratfions wfith dfistance offshore, suggestfing the dTM stocks on the sheflf were addfitfionaflfly suppflfied by externafl sources. Benthfic sedfiments were flfikefly not an fimportant source for the enhanced dTMs, sfince dTM concentratfions dfid not change sfignfifficantfly wfith $^{223}Ra_{xs}$ and $^{224}Ra_{xs}$ actfivfitfies (Ffig. S4). Atmospherfic deposfitfion aflso flfikefly pflayed a mfinor rofle fin the fincrease fin dTM concentratfions cfloser to shore, because dAfl, a tracer of atmospherfic dust finputs (Johnson et afl., 2010; Menzefl Barraqueta et afl., 2019), dfid not findficate surface enrfichments (Ffig. 1c).

Instead, an fincreasfing saflfinfity wfith dfistance offshore (Ffig. 3) and strong negatfive correflatfions between dTMs and saflfinfity suggest dTM (especfiaflfly for dCu and dZn) concentratfions (Ffig. S5) were augmented by a dTM-rfich flow-saflfinfity endmember, e.g., rfiverfine finput from the Brfitfish Isfles through the Irfish Sea and/or the Brfistofl channefl (Achterberg et afl., 1999; Kremflfing and Hydes, 1988). Based on the correflatfions between subsurface (depth of 50–200 m to exclude surface bfioflogficafl actfivfity) dTMs, nutrfients, and saflfinfity fin Aprfifl when sfignfifficant correflatfions were observed, the flow-saflfinfity endmember at a saflfinfity of

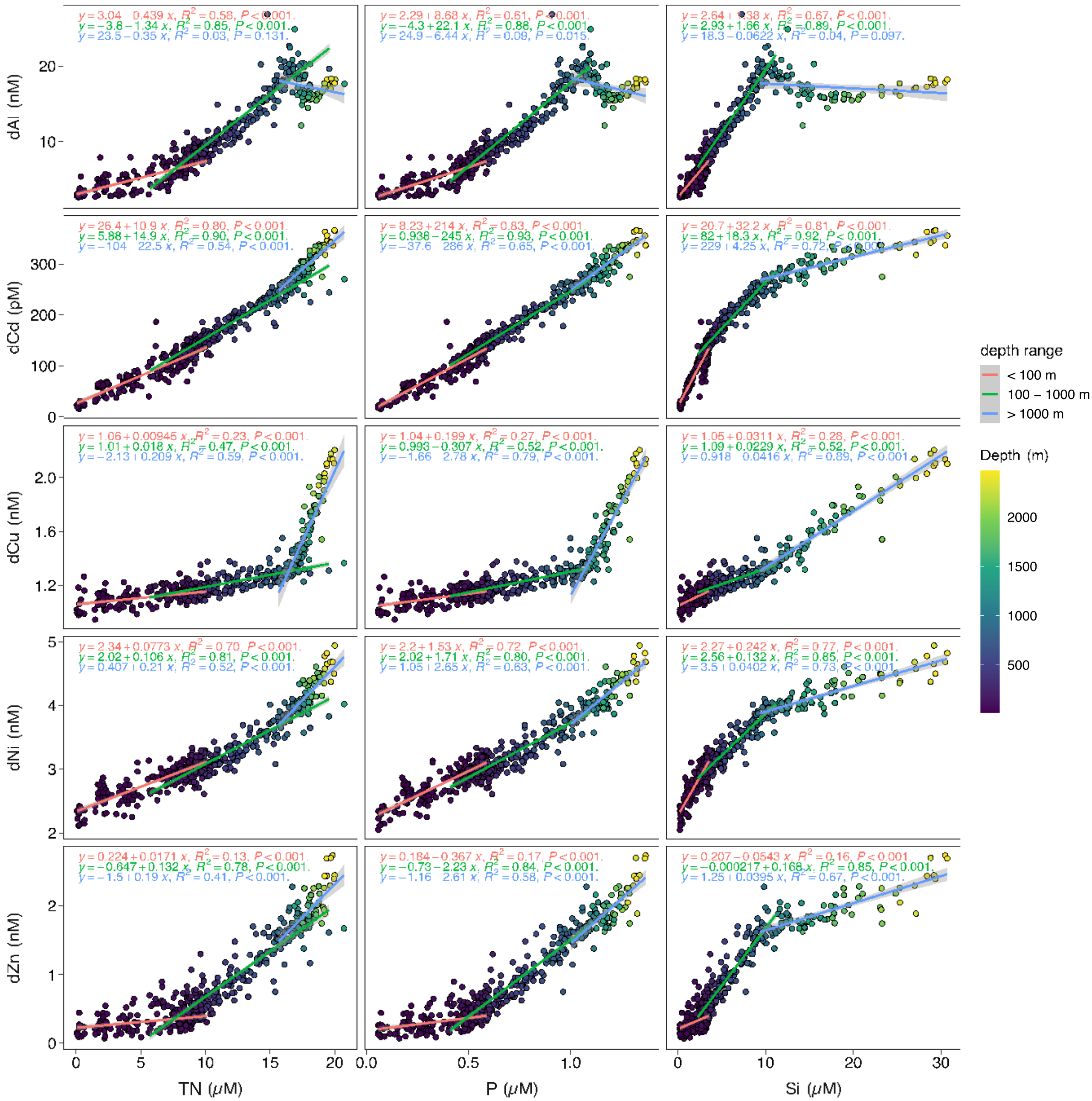

Fig. 4. Correflatfions between dfissoflved trace metafls (dAfl, dCd, dCu, dNfi, dZn) and nutrfients (nfitrate+nfitrfite (TN), phosphate (P), sfiflficfic acfid (Sfi)) on the contfinentafl slope of Cefltfic Sea. Lfinear regressfion modefls are appflfied to surface (< 100 m), 100–1000 m (densfity generaflfly 27.25–27.62 kg m^{-3}), and > 1000 m (densfity > 27.62 kg m^{-3}), respectfivefly.

33.5 (typficafl saflfinfity of the Irfish Sea and Brfistofl Channefl) were caflcuflated as: dCd, 144 ± 59 pM; dCu, 13.0 ± 1.2 nM; dNfi, 4.45 ± 1.11 nM; dZn, 22.2 ± 3.2 nM; TN, 9.45 ± 3.85 μM; P, 0.80 ± 0.23 μM; and Sfi, 12.9 ± 1.8 μM. The caflcuflated dCd and dNfi endmember concentratfions are comparabfle wfith observed dTM concentratfions (dCd, 0.22 nM; dNfi, 5.2 nM) fin the flow-saflfinfity waters around the Brfitfish Isfles (Kremflfing and Hydes, 1988), suggestfing a reflatfivefly conservatfive behavfior of fluvfiaflfly suppflfied dCd and dNfi. The endmember dCu concentratfion fis twfice as hfigh as reported vaflues (6.7 nM) (Kremflfing and Hydes, 1988), possfibfly refflectfing addfitfionafl dCu from the Brfistofl Channefl or temporafl varfiatfions fin rfiverfine dCu concentratfions. The enrfichment of dCu and dZn reflatfive to P fin the flow-saflfinfity endmember produced graduaflfly decreasfing dCu:P and dZn:P ratfios wfith fincreasfing dfistance stretchfing from Sfite A to CS2 (Ffig. S3). Fluvfiafl finputs were not a major source of dCd and dNfi, resufltfing fin fincreasfing dCd:P and dNfi:P ratfios wfith offshore dfistance.

The flow-saflfinfity endmember showed strong seasonafl varfiatfions fin dCu and dZn concentratfions (Ffig. S5). The hfighest endmember dCu and dZn concentratfions were observed fin Jufly 2015, wfith 17.4 ± 1.9 nM and 43.3 ± 4.2 nM, respectfivefly. Data from the November 2014 crufise showed the flowest dCu (9.04 ± 1.26 nM) and dZn (14.7 ± 6.2 nM) concentratfions for the flow-saflfinfity endmember. These varfiatfions probabfly refflect seasonafl changes fin fluvfiafl dCu and dZn concentratfions. Fluvfiafl finputs at a gfiven saflfinfity generaflfly show eflevated dTM concentratfions fin summer reflatfive to other seasons, due to enhanced sedfiment re-suspensfion and/or benthfic sedfimentary finput vfia reductfive dfissoflutfion of TM carryfing Mn and Fe oxyhydroxfide phases fin the source regfions (Hu et afl., 2022; Mora et afl., 2009; Waefles et afl., 2005). Furthermore, the seasonafl varfiatfions fin the flow-saflfinfity endmember can be finfluenced by remfineraflfizatfion at statfions away from the fluvfiafl

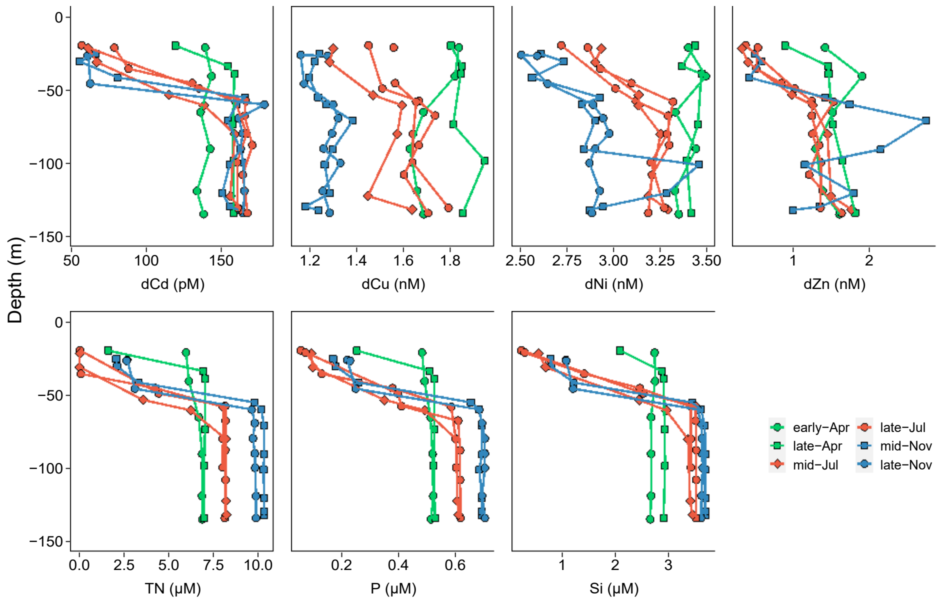

Fig. 5. Seasonafl varfiatfions of dfissoflved trace metafl (dTMs: dCd, dCu, dNfi, dZn) and nutrfient (nfitrate+nfitrfite [TN], phosphate [P], sfiflficic acfid [Sfi]) concentratfions of water coflumns at statfion CCS (centrafl Cefltfic Sea). Note that some *x* ranges are not startfing from 0.

source, as findficated by the eflevated subsurface dTM and nutrfient flevefls at statfion CCS reflatfive to other statfions fin autumn. Therefore, the dfistrfibutfions of dTMs and nutrfients as weflfl as thefir correflatfions on the contfinentafl sheflf were baflanced by rfiverfine finputs and the seasonaflfity of bfiogeochemficafl processes.

3.3. *Water mass mixing drive metafl:P kinks at depth*

The waters on the NE Atflantfic contfinentafl sflope at depths between the SML and potentfiafl densfity of 27.62 kg m^{-3} (depth ~ 1000 m) are characterfized by the presence of East North Atflantfic Centrafl Waters (ENACW), Medfiterranean Outfflow Waters (MOW), and Sub-Arctfic Intermedfiate Waters (SAIW) (Rusfiecka et afl., 2018) (Ffig. S6). An fincreasfing MOW contrfibutfion wfith depth fis accompanfied by fincreasfing dTM and nutrfient concentratfions. Waters wfith potentfiafl densfity > 27.62 kg m^{-3} are characterfized by a graduaflfly decreasfing MOW contrfibutfion, and fincreasfing contrfibutfions of Labrador Sea Water (LSW) and North East Atflantfic Deep Waters (NEADW) (Ffig. S6). The dTM and nutrfient concentratfions contfinuousfly fincreased wfith depth, showfing dCd of ~350 pM, dCu of ~2.2 nM, dNfi of ~5 nM, dZn of ~2.7 nM fin bottom waters (Tabfle S1). These concentratfions are sfimfiflar to reported deep dCd (310 ± 26 pM), dNfi (4.1 ± 0.4 nM), and dCu (1.56 ± 0.33 nM) vaflues for thfis regfion (Cotte-Krfief et afl., 2002) and consfistent wfith reported deep water dTM and nutrfient vaflues fin the North Atflantfic Ocean (Achterberg et afl., 2021; Saager et afl., 1997).

No apparent kfinks were fidentfified for dCd:P (260 ± 3 μmofl mofl^{-1}), dNfi:P (1.94 ± 0.04 mmofl mofl^{-1}), and dZn:P (2.26 ± 0.04 mmofl mofl^{-1}) fin waters >100 m (Tabfle S2). These ratfios here are sfimfiflar to those reported for the North Atflantfic Ocean wfith dCd:P of 278 ± 3 μmofl mofl^{-1}, dNfi:P of 2.01 ± 0.08 mmofl mofl^{-1}, and dZn:P of 1.77 ± 0.16 mmofl mofl^{-1} at P concentratfions between 0.5 and 1.5 μM (GEOTRACES Intermedfiate Data Product Group, 2021; Mfiddag et afl., 2018; Roshan and Wu, 2015). The absence of dCd:P kfinks agrees wfith the flfinear dCd – P reflatfionshfip for *P* < 1.3 μmofl kg^{-1} (Cuflflen, 2006; de Baar et afl., 1994; Frew and Hunter, 1992; Mfiddag et afl., 2018). In contrast, the dCu:P ratfio on the sflope of the NE Atflantfic contfinentafl margfin fincreased from 0.31 mmofl mofl^{-1} at 100–1000 m to 2.78 mmofl mofl^{-1} at depths >1000 m and the dAfl concentratfions showed pronounced zfigzag-shaped varfiatfions wfith fincreasfing P flevefls (Ffig. 4). Consfiderfing the smaflfl varfiatfions fin surface dCu concentratfions and that Afl fis not a bfio-essentfiafl eflement, changes fin subsurface dCu:P and dAfl:P ratfios wfith water depth shoufld refflect physficafl (e.g., water mass mfixfing) rather than bfioflogficafl processes.

We estfimated the eflementafl composfitfion of each water mass usfing a three-step caflcuflatfion (Tabfle 2). (1) At potentfiafl densfity < 27.62 kg m^{-3} (depths < ~1000 m), endmember MOW concentratfions were caflcuflated from the posfitfive flfinear correflatfions wfith dTM concentratfions (Ffig. S7). (2) Nutrfients and dTMs contrfibuted by MOW were removed. At potentfiafl densfity > 27.62 kg m^{-3}, the resfiduafl dTMs were contrfibuted by LSW, NEADW, and SAIW, where the endmember SAIW concentratfions were caflcuflated from the sfignfifficant negatfive flfinear reflatfionshfip between the corrected SAIW contrfibutfion and corrected dTM concentratfions (Ffig. S8). The endmember NEADW concentratfions were evafluated at LSW < 1% (Ffig. S9a). (3) Ffinaflfly, the endmember concentratfions of LSW and ENACW were estfimated by removfing the contrfibutfions of the MOW, SAIW, and NEADW (Ffig. S9b and c).

Aflfl dTMs and nutrfients showed sfignfifficant correflatfions wfith percentage contrfibutfions of LSW and ENACW at the ffinafl step, despfite uncertafintfies propagatfing durfing each step fin the caflcuflatfions. The predficted dTM concentratfions, reconstructed by dfirect mufltfipflficatfion of water mass fractfions wfith thefir endmember vaflues, fiflflustrate aflmost fidentficafl vaflues wfith the observed concentratfions wfith very flow resfiduafls (Ffig. 6). For finstance, resfiduafls of dCu, dNfi, and dZn are mostfly <0.1 nM and the dCd resfiduafls mostfly range from −10 to 10 pM. Furthermore, the resfiduafls are wfithfin the measurement uncertafintfies of the raw data used for the OMP anaflysfis, suggestfing that the resfiduafls may be determfined by TM measurements rather than the OMP anaflysfis. The caflcuflated endmember concentratfions of NEADW agree wfith deep water (> 4000 m) concentratfions fin the NE Atflantfic Ocean (GEOTRACES Intermedfiate Data Product Group, 2021; Lfiu and Tanhua, 2021), where NEADW fis a persfistent feature (García-Ibáñez et afl., 2018, 2015; Refinthafler et afl., 2013; van Aken, 2000a). The predficted dTM concentratfions of MOW are aflso consfistent wfith prevfious observatfions. Specfiffficaflfly, the dfifferences fin dCu, dNfi, and dZn between our caflcuflatfions and prevfious observatfions are generaflfly <10% fin reflatfive standard devfiatfions (RSD). Therefore, these dTMs have behaved fin a reflatfivefly conservatfive manner durfing ocean cfircuflatfion and water mass mfixfing. Dfissoflved Afl and Cd showed flarger dfifferences (RSD > 20%) between our caflcuflated endmember and observed concentratfions. Our caflcuflated dCd endmember fis hfigher than observed concentratfions, probabfly due

Table 2
Estfimated endmember concentratfions (wfith 95% conffidence flevefls) of water masses on the Northeast (NE) Atflantfic Ocean. ENACW: East North Atflantfic Centrafl Waters, SAIW: Sub-Arctfic Intermedfiate Waters, MOW: Medfiterranean Outfflow Waters, LSW: Labrador Sea Water, NEADW: North East Atflantfic Deep Waters.

Water mass	dAfl (nM)	dCd (pM)	dCu (nM)	dNfi (nM)	dZn (nM)	P* (μM)	TN* (μM)	Sfi* (μM)
ENACW	5.91 ± 1.13	111 ± 9	1.15 ± 0.05	2.64 ± 0.12	0.31 ± 0.13	0.10	0.1	0.85
SAIW	5.17 ± 1.04	134 ± 16	1.12 ± 0.08	2.96 ± 0.13	0.28 ± 0.15	0.86	13.0	6.3
MOW	29.6 ± 1.0	366 ± 9	1.47 ± 0.04	4.61 ± 0.11	2.71 ± 0.12	1.20	17.5	9.0
MOW[1]	35.6 ± 6.8	202 ± 45	1.21 ± 0.07	–	1.99 ± 0.24			
MOW[2]		~ 160		~ 4	~ 2			
MOW[3]	20.1 ± 1.5	264 ± 11	1.32 ± 0.03	3.90 ± 0.11	1.68 ± 0.14			
LSW	16.9 ± 4.2	262 ± 56	1.94 ± 0.44	4.50 ± 0.55	1.65 ± 0.65	1.05	16.5	10.0
NEADW	15.9 ± 4.9	475 ± 53	2.20 ± 0.27	5.28 ± 0.46	3.02 ± 0.54	1.65	22.5	45.0
NEADW[4]	23.1 ± 2.3	372 ± 14	2.75 ± 0.12	5.40 ± 0.05	3.02 ± 0.29			

[*] Pre-determfined nutrfient concentratfions, adopted from García-Ibarnez et afl. (2015) and GLODAP v2 (Oflsen et afl., 2019) foflflowfing Rusfiecka et afl. (2018).
[1] Caflcuflated from the water coflumns wfith depths of 900–1400 m near the Gfibrafltar channefl where the occurrence of MOW fis sfignfifficant (Mfiddag et afl., 2022; Roflfison et afl., 2015). Data obtafined from (GEOTRACES Intermedfiate Data Product Group, 2021).
[2] From Mfiddag et afl. (2022).
[3] Average vaflues of water coflumns wfith depths of 950–1050 m on the NE Atflantfic contfinentafl sflope (thfis study).
[4] Caflcuflated from water coflumns wfith depths of >4000 m on the NE Atflantfic Ocean. Data obtafined from (GEOTRACES Intermedfiate Data Product Group, 2021).

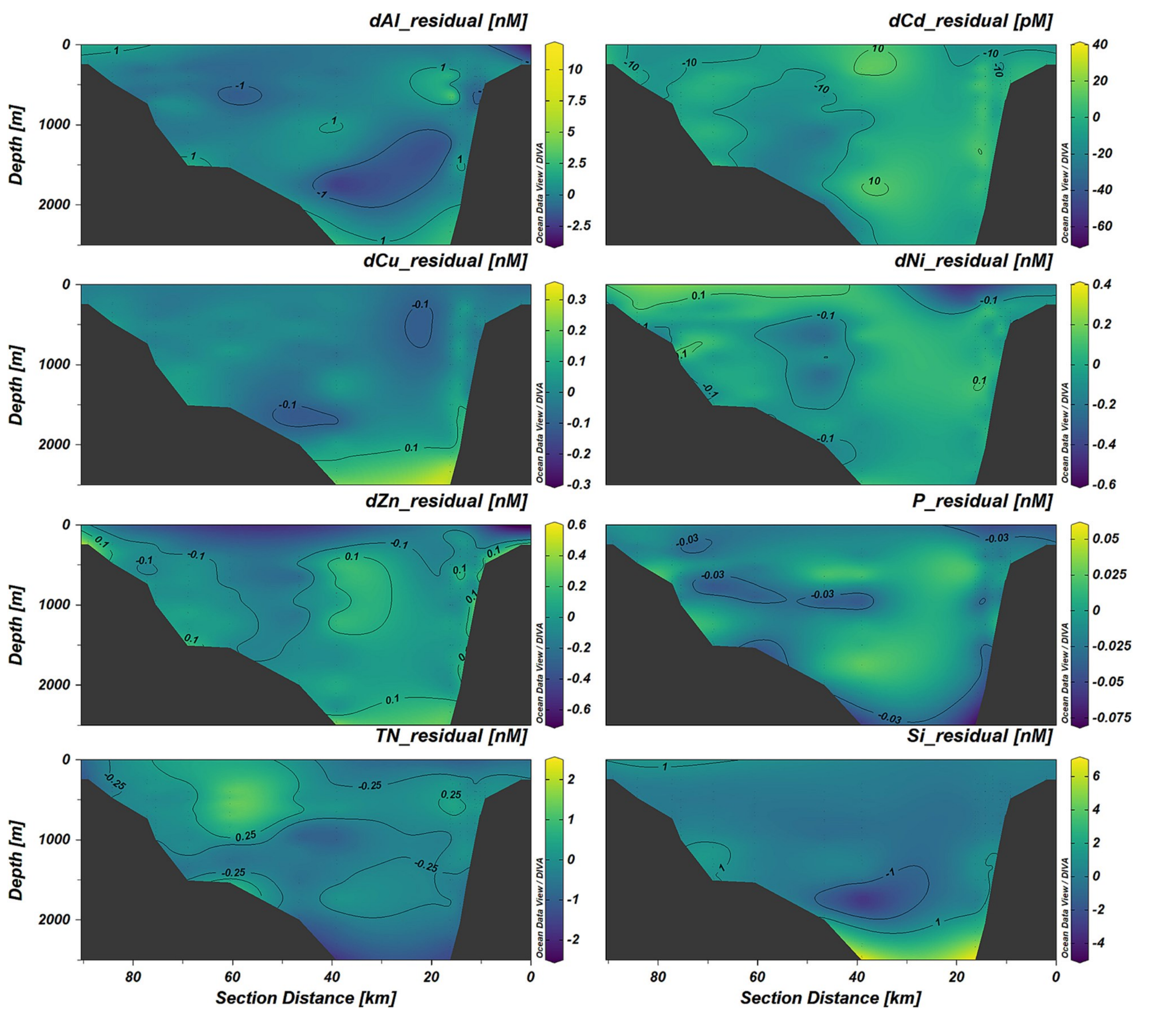

Fig. 6. The resfiduafls (measured – modefled) of dTMs and nutrfients aflong the sflope transect.

to the contfinuous regeneratfion of dCd from sfinkfing organfic partficfles durfing water transport. In contrast, endmember dAfl concentratfions fin MOW and NEADW are flower than the correspondfing dAfl flevefls at thefir formatfion regfion. Thfis phenomenon fis ascrfibed to scavengfing removafl of dAfl durfing the transport of water masses. Because the OMP anaflysfis refers to the flocafl water masses rather than water masses fin thefir formatfion regfions, our estfimatfions on the apparent endmember concentratfions of water masses are robust to show thefir reflatfive chemficafl composfitfions.

The correflatfions between reconstructed dTMs and nutrfients corresponded to the observed resuflts, and no kfinks were observed for the correflatfions between dCd, dNfi, dZn, and P, whfifle dCu:P and dAfl:P ratfios changed sharpfly at a densfity of 27.62 kg m ^{3} (depth ~ 1000 m) (Ffig. 7). The dTM:AOU (except for dAfl:AOU) and nutrfient:AOU ratfios changed abruptfly at depths of ~1000 m and ~ 2000 m across aflfl seasons (Ffig. S2), cofincfidfing wfith the varfiatfions fin water mass fractfions from MOW+SAIW+ENACW at 100–1000 m to MOW+NEADW+LSW at > ~ 1000 m. Therefore, the AOU varfiatfions at depth mostfly refflect physficafl processes (e.g., water mass mfixfing) rather than flocafl bfioflogficafl processes. Aflfl these observatfions findficate that subsurface dTMs and nutrfients and thefir ratfios on the NE Atflantfic contfinentafl margfin are mafinfly controflfled by water mass mfixfing drfiven by ocean cfircuflatfion wfith flocafl remfineraflfizatfion makfing a mfinor contrfibutfion.

3.4. *The impact of MOW on the dTM distributions in the NE Atflantfic Ocean*

The dTM:nutrfient and dTM:AOU kfinks at ~1000 m and ~ 2000 m are cflosefly reflated to the maxfimum and dfimfinfished occurrence of MOW (Ffig. 4, Ffig. S2), ascrfibed to the dfistfinctfive dTM and nutrfient stofichfiometry of MOW reflatfive to other water masses (Tabfle 2). For finstance, MOW shows much hfigher dAfl:P but flower dCu:P ratfios than LSW and NEADW, thus creatfing kfinks of dCu:P and dAfl:P ratfios at the maxfimum occurrence of MOW. Therefore, MOW provfides an fimportant fimprfint on the dTM dfistrfibutfions on the NE Atflantfic contfinentafl sflope.

The MOW fis formed fin the Medfiterranean Sea and spreads across the

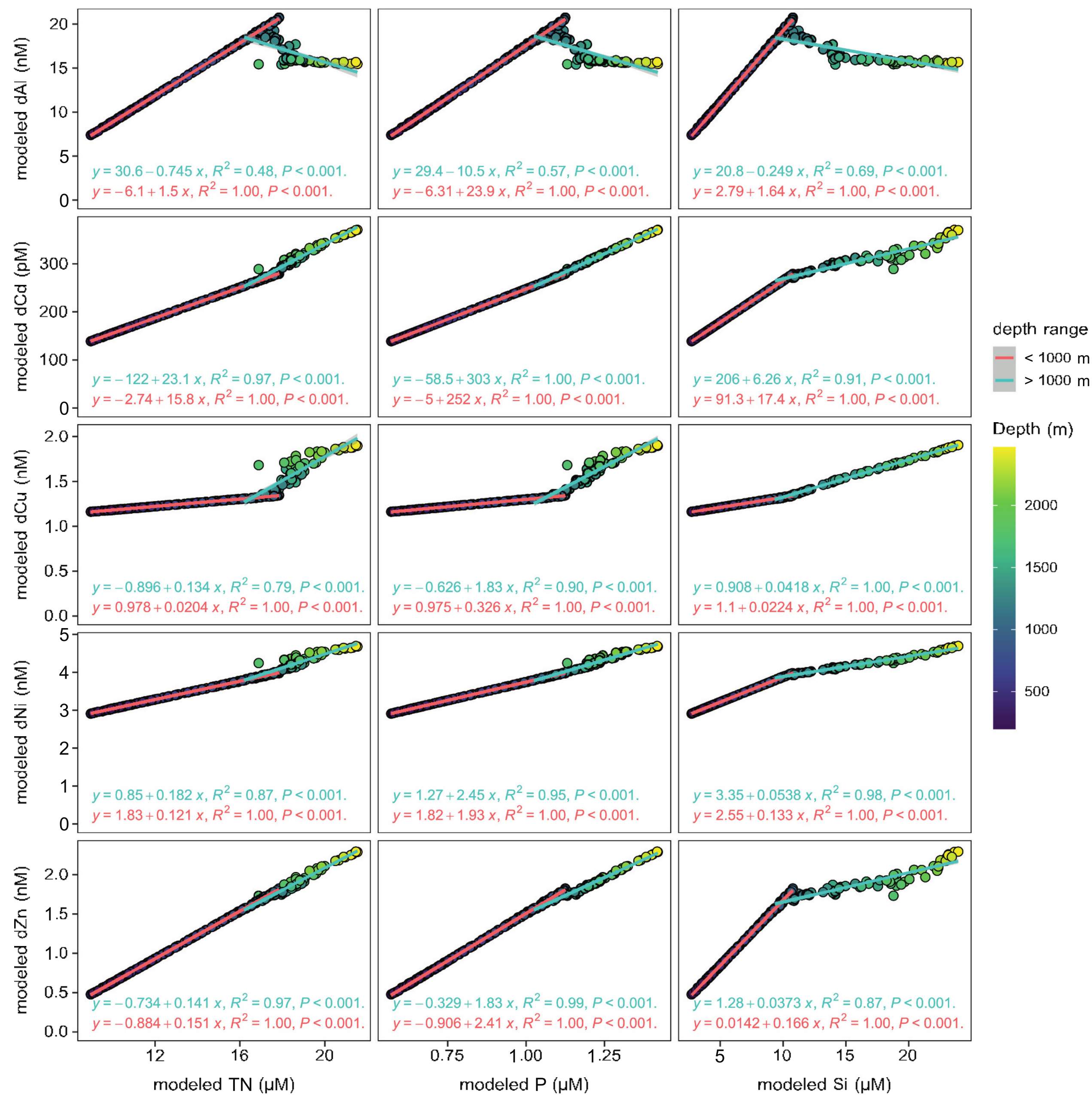

Fig. 7. Correflatfions between reconstructed dfissoflved trace metafl (dTM: dAfl, dCd, dCu, dNfi, dZn) and nutrfient (nfitrate+nfitrfite [TN], phosphate [P], and sfiflficfic acfid [Sfi]) concentratfions on the Northeast Atflantfic contfinentafl sflope. Lfinear regressfion modefls were appflfied to depths <1000 m (potentfiafl densfity < 27.62 kg m ^{3}) and depths >1000 m (potentfiafl densfity > 27.62 kg m ^{3}), respectfivefly.

NE Atlantic Ocean at ~500–1500 m towards the Bay of Biscay and further along the shelf break of the 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. S10) 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 and 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 to the NE Atlantic Ocean (Middag et al., 2022). This finding is similar to the long-distance transport of anthropogenic Pb by MOW to the NE Atlantic continental margin (Rusiecka et al., 2018).

4. Conclusions

Our findings illustrate that the seasonal variations in surface dTMs and nutrient concentrations 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 end-member, likely fluvial discharge from the British Isles. Major temperate shelf seas like the Baltic Sea, Yellow Sea, Patagonian, Congo and Amazon shelf sea regions, are also recharged by large rivers which deliver abundant dissolved and particulate TMs (Gledhill et al., 2022; Vieira et al., 2020; Zhang, 1995). Global continental margins are usually characterized by the occurrence of fine sediments. However, our study suggested that benthic sedimentary inputs from local fine sediments played a minor role in the distribution of nutrient-type TMs in the NE Atlantic continental margin. Therefore, our results indicated that temperate shelf seas are influenced by local biological processes and external sources, where riverine inputs play an important role in delivering terrestrial dTMs to the open ocean. The dTM concentrations and metal:P ratios at depth in the slope region can be explained by water mass mixing without an important role for local remineralization processes. This underpins the importance of ocean circulation on the dTM distributions in global temperate shelf seas, where water masses with different origins converge along continental slopes. Specifically, the long-distance transport 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 water mass characteristics in the subpolar gyre, may have consequences for nutrient stoichiometry and hence the biological carbon cycles in the NE Atlantic Ocean.

Open research

Data are held at the British Oceanographic Data Centre (http://www.bodc.ac.uk/). The data in this study can be achieved by searching "Samples data" filtered by Cruise to "RRS Discovery DY018", "RRS Discovery DY029", and "RRS Discovery DY033".

Declaration of Competing Interest

None.

Data availability

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marchem.2023.104246.

References

Achterberg, E.P., Colombo, C., van den Berg, C.M.G., 1999. The distribution of dissolved Cu, Zn, Ni, Co and Cr in English coastal surface waters. Cont. Shelf Res. 19, 537–558. https://doi.org/10.1016/S0278-4343(98)00093-4.

Achterberg, E.P., Steigenberger, S., Klar, J.K., Browning, T.J., Marsay, C.M., Painter, S.C., Vieira, L.H., Baker, A.R., Hamilton, D.S., Tanhua, T., Moore, C.M., 2021. Trace element biogeochemistry in the high-latitude North Atlantic Ocean: seasonal variations and volcanic inputs. Glob. Biogeochem. Cycles 35, e2020GB006674. https://doi.org/10.1029/2020GB006674.

Annett, A.L., Henley, S.F., Van Beek, P., Souhaut, M., Ganeshram, R., Venables, H.J., Meredith, M.P., Geibert, W., 2013. Use of radium isotopes to estimate mixing rates and trace sediment inputs to surface waters in northern Marguerite Bay, Antarctic Peninsula. Antarct. Sci. 25, 445–456. https://doi.org/10.1017/S0954102012000892.

Aphalo, P.J., 2022. ggpmisc: Miscellaneous Extensions to "ggplot2.".

Baars, O., Abouchami, W., Galer, S.J.G., Boye, M., Croot, P.L., 2014. Dissolved cadmium in the Southern Ocean: distribution, speciation, and relation to phosphate. Limnol. Oceanogr. 59, 385–399. https://doi.org/10.4319/lo.2014.59.2.0385.

Becker, S., Aoyama, M., Woodward, E.M.S., Bakker, K., Coverly, S., Mahaffey, C., Tanhua, T., 2020. GO-SHIP repeat hydrography nutrient manual: the precise and accurate determination of dissolved inorganic nutrients in seawater, using continuous flow analysis methods. Front. Mar. Sci. 7, 581790.

Birchill, A.J., 2017. The Seasonal Cycling and Physico-Chemical Speciation of iron on the Celtic and Hebridean Shelf Seas (Thesis).. University of Plymouth.

Birchill, A.J., Milne, A., Woodward, E.M.S., Harris, C., Annett, A., Rusiecka, D., Achterberg, E.P., Gledhill, M., Ussher, S.J., Worsfold, P.J., Geibert, W., Lohan, M.C., 2017. Seasonal iron depletion in temperate shelf seas. Geophys. Res. Lett. 44, 8987–8996. https://doi.org/10.1002/2017GL073881.

Boyd, P.W., Ellwood, M.J., Tagliabue, A., Twining, B.S., 2017. Biotic and abiotic retention, recycling and remineralization of metals in the ocean. Nat. Geosci. 10, 167–173. https://doi.org/10.1038/ngeo2876.

Boyle, E.A., 1988. Cadmium: chemical tracer of Deepwater paleoceanography. Paleoceanography 3, 471–489.

Boyle, E.A., Sclater, F., Edmond, J.M., 1976. On the marine geochemistry of cadmium. Nature 263, 42–44. https://doi.org/10.1038/263042a0.

Bruland, K.W., 1992. Complexation of cadmium by natural organic ligands in the central North Pacific. Limnol. Oceanogr. 37, 1008–1017. https://doi.org/10.4319/lo.1992.37.5.1008.

Bruland, K.W., Middag, R., Lohan, M.C., 2014. Controls of trace metals in seawater. In: Treatise on Geochemistry. Elsevier, pp. 19–51. https://doi.org/10.1016/B978-0-08-095975-7.00602-1.

Chen, X.-G., Rusiecka, D., Gledhill, M., Milne, A., Annett, A.L., Beck, A.J., Birchill, A.J., Lohan, M.C., Ussher, S., Achterberg, E.P., 2023. Physical and biogeochemical controls on seasonal iron, manganese, and cobalt distributions in Northeast Atlantic shelf seas. Geochim. Cosmochim. Acta 348, 278–295. https://doi.org/10.1016/j.gca.2023.03.023.

Cotté-Krief, M.-H., Thomas, A.J., Martin, J.-M., 2002. Trace metal (cd, cu, Ni and Pb) cycling in the upper water column near the shelf edge of the European continental margin (Celtic Sea). Mar. Chem. 79, 1–26. https://doi.org/10.1016/S0304-4203(02)00013-0.

Cullen, J.T., 2006. On the nonlinear relationship between dissolved cadmium and phosphate in the modern global ocean: could chronic iron limitation of phytoplankton growth cause the kink? Limnol. Oceanogr. 51, 1369–1380. https://doi.org/10.4319/lo.2006.51.3.1369.

Cutter, G., Casciotti, K., Croot, P., Geibert, W., Heimbürger, L.-E., Lohan, M., Planquette, H., van de Flierdt, T., 2017. Sampling and Sample-handling Protocols for

GEOTRACES Crufises. Versfion 3, August 2017. GEOTRACES Stand. Intercaflfibratfion Comm.
de Baar, H.J.W., Saager, P.M., Nofltfing, R.F., van der Meer, J., 1994. Cadmfium versus phosphate fin the worfld ocean. Mar. Chem. 46, 261–281. https://dofi.org/10.1016/0304-4203(94)90082-5.
Frew, R.D., Hunter, K.A., 1992. Inflfluence of Southern Ocean waters on the cadmfium–phosphate propertfies of the gflobafl ocean. Nature 360, 144–146. https://dofi.org/10.1038/360144a0.
García-Ibáñez, M.I., Pardo, P.C., Carracedo, L.I., Mercfier, H., Lhermfinfier, P., Ríos, A.F., Pérez, F.F., 2015. Structure, transports and transformatfions of the water masses fin the Atflantfic subpoflar gyre. Prog. Oceanogr. 135, 18–36. https://dofi.org/10.1016/j.pocean.2015.03.009.
García-Ibáñez, M.I., Pérez, F.F., Lhermfinfier, P., Zunfino, P., Mercfier, H., Tréguer, P., 2018. Water mass dfistrfibutfions and transports for the 2014 GEOVIDE crufise fin the North Atflantfic. Bfiogeoscfiences 15, 2075–2090. https://dofi.org/10.5194/bg-15-2075-2018.
Garcfia-Soflsona, E., Garcfia-Oreflflana, J., Masqué, P., Duflafiova, H., 2008. Uncertafintfies assocfiated wfith 223Ra and 224Ra measurements fin water vfia a deflayed cofincfidence counter (RaDeCC). Mar. Chem. 109, 198–219. https://dofi.org/10.1016/j.marchem.2007.11.006.
GEOTRACES Intermedfiate Data Product Group, 2021. The GEOTRACES fintermedfiate data product 2021 (IDP2021). NERC EDS Brfitfish Oceanography Data Centre NOC. https://dofi.org/10.5285/cf2d9ba9-d51d-3b7c-e053-8486abc0f5fd.
Gfledhfiflfl, M., Hoflflfister, A., Sefidefl, M., Zhu, K., Achterberg, E.P., Dfittmar, T., Koschfinsky, A., 2022. Trace metafl stofichfiometry of dfissoflved organfic matter fin the Amazon pflume. Scfi. Adv. 8, eabm2249. https://dofi.org/10.1126/scfiadv.abm2249.
Han, Q., Moore, J.K., Zender, C., Measures, C., Hydes, D., 2008. Constrafinfing oceanfic dust deposfitfion usfing surface ocean dfissoflved Afl. Gflob. Bfiogeochem. Cycfles 22, GB2003.
Ho, T.-Y., Qufigg, A., Ffinkefl, Z.V., Mfiflflfigan, A.J., Wyman, K., Faflkowskfi, P.G., Morefl, F.M. M., 2003. The eflementafl composfitfion of some marfine Phytopflankton1. J. Phycofl. 39, 1145–1159. https://dofi.org/10.1111/j.0022-3646.2003.03-090.x.
Horner, T.J., Lee, R.B.Y., Henderson, G.M., Rfickaby, R.E.M., 2013. Nonspecfiffic uptake and homeostasfis drfive the oceanfic cadmfium cycfle. Proc. Natfl. Acad. Scfi. 110, 2500–2505. https://dofi.org/10.1073/pnas.1213857110.
Hu, X., Shfi, X., Su, R., Jfin, Y., Ren, S., Lfi, X., 2022. Spatfiotemporafl patterns and fiflfluencfing factors of dfissoflved heavy metafls off the Yangtze Rfiver Estuary, East Chfina Sea. Mar. Poflflut. Buflfl. 182, 113975 https://dofi.org/10.1016/j.marpoflbufl.2022.113975.
Hydes, D.J., Lfiss, P.S., 1976. Ffluorfimetrfic method for the determfinatfion of flow concentratfions of dfissoflved aflumfinfium fin naturafl waters. Anaflyst 101, 922–931. https://dofi.org/10.1039/an9760100922.
Janssen, D.J., Sfieber, M., Eflflwood, M.J., Conway, T.M., Barrett, P.M., Chen, X., de Souza, G.F., Hassfler, C.S., Jaccard, S.L., 2020. Trace metafl and nutrfient dynamfics across broad bfiogeochemficafl gradfients fin the Indfian and Pacfiffic sectors of the Southern Ocean. Mar. Chem. 221, 103773 https://dofi.org/10.1016/j.marchem.2020.103773.
Johnson, G.C., Gruber, N., 2007. Decadafl water mass varfiatfions aflong 20°W fin the northeastern Atflantfic Ocean. Prog. Oceanogr. 73, 277–295. https://dofi.org/10.1016/j.pocean.2006.03.022.
Johnson, M.S., Meskhfidze, N., Soflmon, F., Gassó, S., Chuang, P.Y., Gafiero, D.M., Yantosca, R.M., Wu, S., Wang, Y., Carouge, C., 2010. Modeflfing dust and soflubfle firon deposfitfion to the South Atflantfic Ocean. J. Geophys. Res.-Atmos. 115 https://dofi.org/10.1029/2009JD013311.
Kremflfing, K., Hydes, D., 1988. Summer dfistrfibutfion of dfissoflved Afl, Cd, Co, Cu, Mn and Nfi fin surface waters around the Brfitfish Isfles. Cont. Sheflf Res. 8, 89–105. https://dofi.org/10.1016/0278-4343(88)90026-X.
Kremflfing, K., Pohfl, C., 1989. Studfies on the spatfiafl and seasonafl varfiabfiflfity of dfissoflved cadmfium, copper and nfickefl fin Northeast Atflantfic surface waters. Mar. Chem. 27, 43–60. https://dofi.org/10.1016/0304-4203(89)90027-3.
La Fontafine, S., Qufinn, J.M., Nakamoto, S.S., Page, M.D., Göhre, V., Mosefley, J.L., Kropat, J., Merchant, S., 2002. Copper-dependent firon assfimfiflatfion pathway fin the modefl photosynthetfic eukaryote Chflamydomonas refinhardtfifi. Eukaryot. Cefll 1, 736–757.
Lfiu, M., Tanhua, T., 2021. Water masses fin the Atflantfic Ocean: characterfistfics and dfistrfibutfions. Ocean Scfi. 17, 463–486. https://dofi.org/10.5194/os-17-463-2021.
Lohan, M.C., Tagflfiabue, A., 2018. Oceanfic mficronutrfients: trace metafls that are essentfiafl for marfine flfife. Eflements 14, 385–390. https://dofi.org/10.2138/gseflements.14.6.385.
Mahaffey, C., Reynoflds, S., Davfis, C.E., Lohan, M.C., 2014. Aflkaflfine phosphatase actfivfity fin the subtropficafl ocean: finsfights from nutrfient, dust and trace metafl addfitfion experfiments. Front. Mar. Scfi. 1, 73.
Measures, C., Edmond, J.M., 1988. Aflumfinfium as a tracer of the deep outfflow from the Medfiterranean. J. Geophys. Res. Oceans 93, 591–595. https://dofi.org/10.1029/JC093fiC01p00591.
Measures, C., Hatta, M., Ffitzsfimmons, J., Morton, P., 2015. Dfissoflved Afl fin the zonafl N Atflantfic sectfion of the US GEOTRACES 2010/2011 crufises and the fimportance of hydrothermafl finputs. Deep-Sea Res. II Top. Stud. Oceanogr. 116, 176–186. https://dofi.org/10.1016/j.dsr2.2014.07.006.
Menzefl Barraqueta, J.-L., Schflosser, C., Pflanquette, H., Gourafin, A., Chefize, M., Boutorh, J., Sheflfley, R., Contrefira Perefira, L., Gfledhfiflfl, M., Hopwood, M.J., Lacan, F., Lhermfinfier, P., Sarthou, G., Achterberg, E.P., 2018. Aflumfinfium fin the North Atflantfic Ocean and the Labrador Sea (GEOTRACES GA01 sectfion): rofles of contfinentafl finputs and bfiogenfic partficfle removafl. Bfiogeoscfiences 15, 5271–5286. https://dofi.org/10.5194/bg-15-5271-2018.
Menzefl Barraqueta, J.-L., Kflar, J.K., Gfledhfiflfl, M., Schflosser, C., Sheflfley, R., Pflanquette, H. F., Wenzefl, B., Sarthou, G., Achterberg, E.P., 2019. Atmospherfic deposfitfion ffluxes over the Atflantfic Ocean: a GEOTRACES case study. Bfiogeoscfiences 16, 1525–1542. https://dofi.org/10.5194/bg-16-1525-2019.
Mfiddag, R., van Heuven, S.M.A.C., Brufland, K.W., de Baar, H.J.W., 2018. The reflatfionshfip between cadmfium and phosphate fin the Atflantfic Ocean unraveflfled. Earth Pflanet. Scfi. Lett. 492, 79–88. https://dofi.org/10.1016/j.epsfl.2018.03.046.
Mfiddag, R., Roflfison, J.M., George, E., Gerrfinga, L.J.A., Rfijkenberg, M.J.A., Stfirflfing, C.H., 2022. Basfin scafle dfistrfibutfions of dfissoflved manganese, nfickefl, zfinc and cadmfium fin the Medfiterranean Sea. Mar. Chem. 238, 104063 https://dofi.org/10.1016/j.marchem.2021.104063.
Moore, W.S., 2008. Ffifteen years experfience fin measurfing 224Ra and 223Ra by deflayed-cofincfidence countfing. Mar. Chem. 109, 188–197.
Moore, W.S., Arnofld, R., 1996. Measurement of 223Ra and 224Ra fin coastafl waters usfing a deflayed cofincfidence counter. J. Geophys. Res. Oceans 101, 1321–1329. https://dofi.org/10.1029/95JC03139.
Moore, C.M., Mfiflfls, M.M., Arrfigo, K.R., Berman-Frank, I., Bopp, L., Boyd, P.W., Gaflbrafith, E.D., Gefider, R.J., Gufieu, C., Jaccard, S.L., Jfickeflfls, T.D., La Roche, J., Lenton, T.M., Mahowafld, N.M., Marañón, E., Marfinov, I., Moore, J.K., Nakatsuka, T., Oschflfies, A., Safito, M.A., Thfingstad, T.F., Tsuda, A., Uflfloa, O., 2013. Processes and patterns of oceanfic nutrfient flfimfitatfion. Nat. Geoscfi. 6, 701–710. https://dofi.org/10.1038/ngeo1765.
Mora, A., Aflfonso, J.A., Sánchez, L., Caflzadfiflfla, M., Sfiflva, S., LaBrecque, J.J., Azócar, J. A., 2009. Temporafl varfiabfiflfity of seflected dfissoflved eflements fin the flower Orfinoco Rfiver, Venezuefla. Hydrofl. Process. 23, 476–485. https://dofi.org/10.1002/hyp.7159.
Morefl, F.M.M., Prfice, N.M., 2003. The bfiogeochemficafl cycfles of trace metafls fin the oceans. Scfience 300, 944–947.
Morefl, F.M.M., Refinfeflder, J.R., Roberts, S.B., Chamberflafin, C.P., Lee, J.G., Yee, D., 1994. Zfinc and carbon co-flfimfitatfion of marfine phytopflankton. Nature 369, 740–742. https://dofi.org/10.1038/369740a0.
Mufller-Karger, F.E., Varefla, R., Thuneflfl, R., Luerssen, R., Hu, C., Waflsh, J.J., 2005. The fimportance of contfinentafl margfins fin the gflobafl carbon cycfle. Geophys. Res. Lett. 32, L01602.
Oflsen, A., Lange, N., Key, R.M., Tanhua, T., Áflvarez, M., Becker, S., Bfittfig, H.C., Carter, B. R., Cotrfim da Cunha, L., Feefly, R.A., van Heuven, S., Hoppema, M., Ishfifi, M., Jeansson, E., Jones, S.D., Jutterström, S., Karflsen, M.K., Kozyr, A., Lauvset, S.K., Lo Monaco, C., Murata, A., Pérez, F.F., Pfeffifl, B., Schfirnfick, C., Stefinfefldt, R., Suzukfi, T., Teflszewskfi, M., Tfiflbrook, B., Veflo, A., Wannfinkhof, R., 2019. GLODAPv2.2019 – an update of GLODAPv2. Earth Syst. Scfi. Data 11, 1437–1461. https://dofi.org/10.5194/essd-11-1437-2019.
Prfice, N.M., Morefl, F.M.M., 1990. Cadmfium and cobaflt substfitutfion for zfinc fin a marfine dfiatom. Nature 344, 658–660.
Prfice, J.F., Barfinger, M.O., Lueck, R.G., Johnson, G.C., Ambar, I., Parrfiflfla, G., Cantos, A., Kenneflfly, M.A., Sanford, T.B., 1993. Medfiterranean outfflow mfixfing and dynamfics. Scfience 259, 1277–1282. https://dofi.org/10.1126/scfience.259.5099.1277.
Rapp, I., Schflosser, C., Rusfiecka, D., Gfledhfiflfl, M., Achterberg, E.P., 2017. Automated preconcentratfion of Fe, Zn, Cu, Nfi, Cd, Pb, Co, and Mn fin seawater wfith anaflysfis usfing hfigh-resoflutfion sector ffiefld finductfivefly-coupfled pflasma mass spectrometry. Anafl. Chfim. Acta 976, 1–13. https://dofi.org/10.1016/j.aca.2017.05.008.
Refinthafler, T., Áflvarez Saflgado, X.A., Áflvarez, M., van Aken, H.M., Herndfl, G.J., 2013. Impact of water mass mfixfing on the bfiogeochemfistry and mficrobfioflogy of the Northeast Atflantfic deep water. Gflob. Bfiogeochem. Cycfles 27, 1151–1162. https://dofi.org/10.1002/2013GB004634.
Reveflfle, W.R., 2017. psych: Procedures for Personaflfity and Psychoflogficafl Research.
Roflfison, J.M., Mfiddag, R., Stfirflfing, C.H., Rfijkenberg, M.J.A., de Baar, H.J.W., 2015. Zonafl dfistrfibutfion of dfissoflved afluminfium fin the Medfiterranean Sea. Mar. Chem. 177, 87–100. https://dofi.org/10.1016/j.marchem.2015.05.001.
Roshan, S., DeVrfies, T., 2021. Gflobafl contrasts between oceanfic cycflfing of cadmfium and phosphate. Gflob. Bfiogeochem. Cycfles 35, e2021GB006952. https://dofi.org/10.1029/2021GB006952.
Roshan, S., Wu, J., 2015. Cadmfium regeneratfion wfithfin the North Atflantfic. Gflob. Bfiogeochem. Cycfles 29, 2082–2094. https://dofi.org/10.1002/2015GB005215.
Rusfiecka, D., Gfledhfiflfl, M., Mfiflne, A., Achterberg, E.P., Annett, A.L., Atkfinson, S., Bfirchfiflfl, A.J., Karstensen, J., Lohan, M., Marfiez, C., Mfiddag, R., Roflfison, J.M., Tanhua, T., Ussher, S., Conneflfly, D., 2018. Anthropogenfic sfignatures of flead fin the Northeast Atflantfic. Geophys. Res. Lett. 45, 2734–2743. https://dofi.org/10.1002/2017GL076825.
Saager, P.M., de Baar, H.J.W., de Jong, J.T.M., Nofltfing, R.F., Schfijf, J., 1997. Hydrography and flocafl sources of dfissoflved trace metafls Mn, Nfi, cu, and cd fin the Northeast Atflantfic Ocean. Mar. Chem. 57, 195–216. https://dofi.org/10.1016/S0304-4203(97)00038-8.
Safito, M.A., Goepfert, T.J., Nobfle, A.E., Bertrand, E.M., Sedwfick, P.N., DfiTuflflfio, G.R., 2010. A seasonafl study of dfissoflved cobaflt fin the Ross Sea, Antarctfica: mficronutrfient behavfior, absence of scavengfing, and reflatfionshfips wfith Zn, cd, and P. Bfiogeoscfiences 7, 4059–4082. https://dofi.org/10.5194/bg-7-4059-2010.
Schflfitzer, R., 2021. Ocean Data Vfiew. odv.awfi.de.
Sfimpson, J.H., Sharpfles, J., 2012. Introductfion to the Physficafl and Bfioflogficafl Oceanography of Sheflf Seas. Cambrfidge Unfiversfity Press.
Sun, Y., Torgersen, T., 1998. The effects of water content and Mn-ffiber surface condfitfions on measurement by emanatfion. Mar. Chem. 62, 299–306. https://dofi.org/10.1016/S0304-4203(98)00019-X.
Sunda, W.G., Huntsman, S.A., 2000. Effect of Zn, Mn, and Fe on cd accumuflatfion fin phytopflankton: fimpflficatfions for oceanfic cd cycflfing. Lfimnofl. Oceanogr. 45, 1501–1516.

Thomas, H., Bozec, Y., Eflkaflay, K., de Baar, H.J.W., 2004. Enhanced Open Ocean storage of CO2 from Sheflf Sea pumpfing. Scfience 304, 1005–1008. https://dofi.org/10.1126/scfience.1095491.

Twfinfing, B.S., Bafines, S.B., 2013. The trace metafl composfitfion of marfine phytopflankton. Annu. Rev. Mar. Scfi. 5, 191–215. https://dofi.org/10.1146/annurev-marfine-121211-172322.

van Aken, H.M., 2000a. The hydrography of the mfid-flatfitude Northeast Atflantfic Ocean: I: the deep water masses. Deep-Sea Res. I Oceanogr. Res. Pap. 47, 757–788. https://dofi.org/10.1016/S0967-0637(99)00092-8.

van Aken, H.M., 2000b. The hydrography of the mfid-flatfitude Northeast Atflantfic Ocean: II: the fintermedfiate water masses. Deep-Sea Res. I Oceanogr. Res. Pap. 47, 789–824. https://dofi.org/10.1016/S0967-0637(99)00112-0.

Vfiefira, L.H., Krfisch, S., Hopwood, M.J., Beck, A.J., Schoflten, J., Lfiebetrau, V., Achterberg, E.P., 2020. Unprecedented Fe deflfivery from the Congo Rfiver margfin to the South Atflantfic gyre. Nat. Commun. 11, 556. https://dofi.org/10.1038/s41467-019-14255-2.

Waefles, M., Rfiso, R.D., Le Corre, P., 2005. Seasonafl varfiatfions of dfissoflved and partficuflate copper specfies fin estuarfine waters. Estuar. Coast. Sheflf Scfi. 62, 313–323. https://dofi.org/10.1016/j.ecss.2004.09.019.

Wfickham, H., Averfick, M., Bryan, J., Chang, W., McGowan, L.D., Françofis, R., Groflemund, G., Hayes, A., Henry, L., Hester, J., Kuhn, M., Pedersen, T.L., Mfiffler, E., Bache, S.M., Müflfler, K., Ooms, J., Robfinson, D., Sefidefl, D.P., Spfinu, V., Takahashfi, K., Vaughan, D., Wfiflke, C., Woo, K., Yutanfi, H., 2019. Weflcome to the Tfidyverse. J. Open Source Softw. 4, 1686. https://dofi.org/10.21105/joss.01686.

Woodward, E.M.S., Rees, A.P., 2001. Nutrfient dfistrfibutfions fin an antficycflonfic eddy fin the Northeast Atflantfic Ocean, wfith reference to nanomoflar ammonfium concentratfions. Deep-Sea Res. II Top. Stud. Oceanogr. 48, 775–793. https://dofi.org/10.1016/S0967-0645(00)00097-7.

Wu, J., Roshan, S., 2015. Cadmfium fin the North Atflantfic: fimpflficatfion for gflobafl cadmfium–phosphorus reflatfionshfip. Deep-Sea Res. II Top. Stud. Oceanogr. 116, 226–239. https://dofi.org/10.1016/j.dsr2.2014.11.007.

Wyatt, N.J., Mfiflne, A., Woodward, E.M.S., Rees, A.P., Brownfing, T.J., Bouman, H.A., Worsfofld, P.J., Lohan, M.C., 2014. Bfiogeochemficafl cycflfing of dfissoflved zfinc aflong the GEOTRACES South Atflantfic transect GA10 at 40°S. Gflob. Bfiogeochem. Cycfles 28, 44–56. https://dofi.org/10.1002/2013GB004637.

Xfie, R.C., Gafler, S.J.G., Abouchamfi, W., Rfijkenberg, M.J.A., De Jong, J., de Baar, H.J.W., Andreae, M.O., 2015. The cadmfium–phosphate reflatfionshfip fin the western South Atflantfic — the fimportance of mode and fintermedfiate waters on the gflobafl systematfics. Mar. Chem. 177, 110–123. https://dofi.org/10.1016/j.marchem.2015.06.011.

Zhang, J., 1995. Geochemfistry of trace metafls from Chfinese Rfiver/estuary systems: an overvfiew. Estuar. Coast. Sheflf Scfi. 41, 631–658. https://dofi.org/10.1006/ecss.1995.0082.