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Particulate Trace Element Export in the North Atlantic (GEOTRACES GA01 Transect, GEOVIDE Cruise)

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Abstract :

Vertical export of particulate trace elements (pTEs) is a critically underconstrained aspect of their biogeochemistry. Here, we combine elemental analyses on large (>53 μm) particles and ^{234}Th measurements to determine downward export fluxes from the upper layers (40–110 m) of pTEs (Al, Cd, Co, Cu, Fe, Mn, Ni, P, Ti, V, Zn) and mineral phases (lithogenic, Fe- and Mn-oxides, calcium carbonate, and opal) in the North Atlantic along the GEOVIDE transect (Portugal–Greenland–Canada; GEOTRACES GA01 cruise). The role of lithogenic particles in controlling TE fluxes is obvious at proximity of the Iberian margin where the highest pTE export fluxes were estimated (up to 3912 $\mu\text{g}/\text{m}^2/\text{d}$ for pFe). However, high lithogenic and pTE fluxes are also observed up to 1700 km off this margin in the west European and Icelandic basins (up to 931 $\mu\text{g}/\text{m}^2/\text{d}$ for pFe). The lowest pTE export fluxes are determined in the Labrador Sea (as low as 501 $\mu\text{g}/\text{m}^2/\text{d}$ for pFe). High Mn- and Fe-oxide fluxes are estimated at the open ocean stations, suggesting that authigenic particles are an important vector of pTEs. All along the transect, biogenic particles also drive the pTE export fluxes, as shown by the similar pTE/POC ratios between exports and phytoplankton quotas. The shortest residence times (dissolved + particulate) are generally observed where lithogenic particles control the pTE fluxes (as low as 2 days for Fe) whereas pTEs seem to be longer retained when the contribution of biogenic particles become greater (residence times up to 147 days for Fe).

Keywords : particulate trace elements, export fluxes, multiple carrier phases, residence times, GEOTRACES

40 1. INTRODUCTION

41 Bioactive trace elements (TEs: Cd, Co, Cu, Fe, Mn, Ni, Zn, etc.) are important for the marine
42 primary productivity¹, as they are required for numerous metabolic processes^{2,3}. Sometimes
43 in line with other bioactive trace elements, depleted Fe concentrations in the surface waters can
44 limit the phytoplankton, thus influencing the community structure and, as a result, the overall
45 marine carbon cycle^{4,5}. Therefore, the quantification of biogeochemical processes regulating
46 the internal cycle of TEs is essential to better understand the carbon cycle and in particular the
47 biological carbon pump^{6,7}.

48 Many TEs reach the ocean through particles, either via atmospheric dusts⁸, rivers⁹, margins
49¹⁰ or sediments¹¹. Marine particles also participate in the removal of TEs, either through
50 scavenging onto particle surfaces¹², precipitation of authigenic minerals such as barite¹³⁻¹⁵
51 and Mn-Fe oxyhydroxides¹⁶, or sinking to the deep ocean due to lithogenic and biogenic ballast
52 minerals¹⁷⁻¹⁹. Small (suspended; 1-53 μ m diameter) particles mainly trap TEs via scavenging,
53 though they have been shown to slowly sink after coagulation to other particles^{20,21}. Large
54 (sinking; >53 μ m diameter) particles export TEs from the biologically active upper water
55 column down to the interior ocean²², with the remineralization length scale controlling the
56 release of TEs into solution and their subsequent return to the surface. Earlier studies have
57 revealed that particulate phosphorous (pP), nickel (pNi), zinc (pZn) and organic carbon (POC)
58 are remineralized faster than particulate iron (pFe) because of a stronger scavenging of
59 dissolved Fe onto particles^{23,24}. Thus, particle-solute interactions determine the residence times
60 of TEs in the water column. However these residence times are presently not well known
61 because of scarce estimates of TE inventories and fluxes into or out of the water column²⁵.
62 Despite an increasing number of studies addressing TE export, this process remains still poorly
63 understood^{23,26,35,36,27-34}. Besides the strong temporal and spatial variability, another reason
64 likely resides in the difficulty in measuring particulate trace element (pTE) fluxes, as TEs are

65 present at very low concentrations in the ocean and are easily prone to contamination. Sediment
66 traps are used to directly quantify the pTE export fluxes^{29,30,37,38} but their deployment tends to
67 be time- and effort-intensive. They also can be biased because of lateral advection or because
68 of possible TE contamination from the preservative solution added into the cups to avoid
69 zooplankton and microbial activities³⁹. One alternative for determining particulate export
70 fluxes is the clean but indirect ²³⁴Th-²³⁸U method⁴⁰⁻⁴². ²³⁴Th is a highly particle-reactive
71 element with a short half-life ($t_{1/2} = 24.1$ days) compared to its radioactive parent ²³⁸U ($t_{1/2} =$
72 4.47 billion years). While both isotopes are usually at secular equilibrium in subsurface waters,
73 a deficit of ²³⁴Th relative to ²³⁸U can be observed in the upper ocean, where sinking particles
74 carry ²³⁴Th downward. This deficit of ²³⁴Th relative to ²³⁸U can be converted into an elemental
75 export flux when multiplied with the ratio of the element to ²³⁴Th (element:²³⁴Th hereafter) in
76 the particulate material at a given depth^{34,41}. This method has the benefit to allow flux
77 determination at multiple stations and for a large suite of elements and mineral phases.

78 The presence of lithogenic and biogenic minerals, as well as oxyhydroxides, are identified as
79 phases liable to control the settling of particles with depth¹⁹. In the temperate north Atlantic,
80 advection of lithogenic material from continental margins and pronounced seasonal
81 phytoplankton blooms strongly enhance the pTE distributions and downward export fluxes⁴³⁻
82 ⁴⁷. However, occasional lack of nutrients such as dissolved iron (dFe)⁴⁸ can limit the primary
83 productivity, the magnitude of the downward fluxes and thus the strength of the biological
84 carbon pump^{5,49,50}. This is well illustrated in the subtropical north Atlantic, which is
85 characterized by oligotrophic conditions leading to low primary production⁵¹ and to low export
86 fluxes of POC^{52,53} and pTEs⁴³. In this region, exports of POC⁵⁴⁻⁵⁸ and pTEs²⁸ show episodic
87 fluctuations along the season due to nutrient and/or light limitations but also due to lithogenic
88 inputs mainly originating from margins or associated with atmospheric dust depositions
89 ^{28,43,44,59}. The more productive subpolar Atlantic is characterized by lower lithogenic inputs

90 because of the decreasing influence of the Saharan dust plume ⁴³. Nevertheless, lateral supplies
91 of lithogenic material from continental shelves have been reported and could enhance the
92 export fluxes ^{28,34}.

93 In this study, we aim to better understand the processes controlling the TE distributions in the
94 upper layers of the North Atlantic Ocean by focusing on particulate TE export. The different
95 particulate substrates (authigenic, lithogenic and biogenic) liable to carry the pTEs are
96 investigated and the export efficiencies are evaluated by estimating the residence times of TEs
97 within the upper ocean.

98

99 **2. METHODS**

100 2.1. Biogeochemical characteristics of investigated stations

101 Fieldwork was conducted on board the French *R/V Pourquoi Pas?* along the GEOTRACES
102 GA01 section during the GEOVIDE expedition (Fig. 1). The cruise was carried out in May-
103 June 2014. We sampled a total of 11 stations located in five different biogeochemical domains
104 described in details in Lemaitre et al. (2018) ⁶⁰ and in Table 1. Briefly, the Iberian basin was
105 sampled after the spring bloom and was characterized by a low primary productivity (PP) ⁶¹.
106 Station #13 had the highest proportion of cyanobacteria (12% of phytoplankton abundance) of
107 the all transect ⁶². Particulate organic carbon (POC) export was high at Station #1 while low at
108 Station #13, reflecting the low nutrient availability in subtropical waters ⁶⁰. The west European
109 (Stations #21 and #26) and Icelandic (Stations #32 and #38) basins were sampled during the
110 bloom development and were the most productive areas with the highest PP observed along
111 the transect ⁶⁰. Diatoms dominated the phytoplankton community (41% of phytoplankton
112 abundance) but dinoflagellates and haptophytes (including coccolitophorids) also contributed
113 significantly in the west European basin (~20% of phytoplankton abundance ⁶²). Conversely,
114 nano-phytoplankton and mainly haptophytes dominated the community in the Icelandic basin.

115 High POC exports were determined in both basins and particularly at Station #32 ⁶⁰. The
116 Irminger basin (Stations #44 and #51) was sampled close to the bloom maximum and PP values
117 were high, with a clear dominance of diatoms (between 55 and 77% of phytoplankton
118 abundance ⁶²). Because of the accumulation of biomass in the surface waters, POC export
119 fluxes were low, with Station #44 having the lowest one of the entire cruise ⁶⁰. The Labrador
120 basin (Stations #64, #69 and #77) was sampled after the PP peak, at the onset of the bloom
121 decline ⁶⁰. Productivity was relatively low compared to the other studied basins. Diatoms were
122 also dominating, contributing up to 62% of the phytoplankton abundance ⁶². POC export fluxes
123 were relatively high, likely because of the increasing number of rapidly sinking particles ⁶⁰.

124

125 2.2. Particle sampling

126 Total ²³⁴Th activities were determined from 4L unfiltered seawater sampled with 12L Niskin
127 bottles mounted on CTD rosette and were processed following the method of Pike et al. (2005)
128 ⁶³. Samples were acidified and spiked with a ²³⁰Th yield monitor in order to estimate the ²³⁴Th
129 recovery during sample processing. After a 12h equilibration, pH was increased and KMnO₄
130 and MnCl₂ solutions were added. After a further 12h equilibration, samples were filtered on
131 quartz-microfiber discs (QMA, Sartorius, nominal porosity=1 μm, diameter=25 mm) and the
132 ²³⁴Th activities were measured on-board using a low-level beta counter (RISØ®, Denmark).
133 Residual beta activities were measured ~6 months after the cruise after which samples were
134 processed for Th recoveries using ²²⁹Th as a second yield tracer. Export fluxes of ²³⁴Th were
135 then calculated using a 1-D box model ⁶⁴ under steady state assumptions and neglecting
136 advection and diffusion ⁴¹. Export fluxes of ²³⁴Th are presented in Lemaitre et al (2018) ⁶⁰.

137 Particulate matter for biogenic silica (BSi), calcium carbonate (CaCO₃) and pTE analyses was
138 collected on the same *in-situ* pump (Challenger Oceanics® and McLane® pumps, ISP) filter,
139 whereas particles for POC were collected using a separate filter holder. The later was mounted
140 either on a second flow path when modified McLane ISP heads were used, or with a separate

141 ISP unit ⁶⁰ attached 10 to 50 m apart from the ISP dedicated to TEs (see Table S1). Particulate
142 ²³⁴Th activity in the large size particle fraction (LSF, >53µm) was determined on particles
143 collected with each ISP system (Fig. S1).

144 Particulate organic carbon (POC) LSF was collected on a 53-µm mesh polyester screen (Petex),
145 which was cut into quarters. Particles present on one quarter of the Petex screen were rinsed-
146 off using 0.45 µm filtered seawater obtained during the cruise and subsequently collected on a
147 silver filter (SterliTech, nominal porosity=0.45 µm, diameter=25 mm) for one quarter, and on
148 a GF/F filter (Whatman, nominal porosity=0.7 µm, diameter=25 mm) for another quarter,
149 before being Beta-counted on board. Back in the home laboratory, samples were prepared for
150 POC analyses: filters were fumed with HCl vapor, dried, packed in pre-combusted silver cups
151 and analysed with an elemental analyser (EA-IRMS, Delta V Plus, Thermo Scientific). More
152 details on POC and particulate ²³⁴Th (p²³⁴Th) analyses can be found in Lemaitre et al. (2018)
153 ⁶⁰.

154 Particulate matter for BSi, CaCO₃ and pTE determinations was filtered on a 142mm-diameter
155 53-µm mesh polyester screen (Petex) for the LSF upstream of a 142mm-diameter 0.8-µm
156 polyethersulfone filter (Supor®) for the small size particle fraction (SSF). Before use, filters
157 were soaked in 1.2M HCl (Suprapur grade, Merck), heated overnight at 60°C and subsequently
158 rinsed with Milli-Q grade water. On board, filters were processed under a laminar flow unit
159 within a customized clean “bubble” to prevent contamination. Before and after the ISP
160 recoveries, pump heads were protected with plastic bags to minimize contamination. After
161 pump recoveries, filter heads were dismantled and carried inside the clean bubble.

162 Using a clean ceramic scalpel, one quarter of the Petex screen, dedicated to p²³⁴Th and BSi
163 analyses, was cut out. Particles were washed off the Petex screen using 0.45-µm filtered
164 seawater obtained during the cruise. Particles were then collected on polycarbonate filters (PC;
165 Nuclepore®, porosity=0.4µm, diameter=25mm) mounted on a polysulfone filtration unit.

166 Filters were left to dry at room temperature inside the laminar flow unit and subsequently
167 prepared for Beta counting. Activities of $p^{234}\text{Th}$ were also determined on a second quarter of
168 the Petex screen: particles were washed off, using the 0.45- μm filtered seawater, and collected
169 on a polyethersulfone filter (Supor®, porosity=0.45 μm , diameter=25 mm) mounted on a
170 Nalgene filtration unit (Fig. S1). Because Beta counting of samples is probably incompatible
171 with trace metal clean stringent conditions, the two last quarters of the Petex screen, dedicated
172 to pTEs, particulate calcium (pCa) and sodium (pNa), were stored in a clean petrislide (Pall
173 Gelman) and kept at -20°C until sample processing and analysis in the home laboratory. Since
174 Supor filters with the SSF were not Beta counted, there are no data for the SSF $p^{234}\text{Th}$ activity.
175

176 2.3. Particulate matter analyses

177 The methods used here have been approved during a GEOTRACES intercalibration exercise
178 and our elemental concentrations have been submitted to the GEOTRACES Intermediate Data
179 Product (IDP) 2021. The concentrations obtained from ISP sampling (this study) have been
180 compared to those obtained by GO-FLO sampling at the same locations (from Gourain et al.,
181 2019⁶⁵ and from Planquette et al., personal communication, 2019). Both datasets were obtained
182 after using exactly the same digestion and analytical methods. Although similar element
183 profiles were obtained from both datasets, highlighting data consistency, we note that pTE
184 concentrations obtained from ISP sampling were generally lower than those obtained from GO-
185 FLO bottles. This discrepancy could possibly result from particle washout during ISP recovery,
186 since our ISPs were not systematically equipped with anti-washout systems, or due to some
187 loss when transferring particles from the Petex screens to other filters (see above). To limit
188 these effects, our study focuses on elemental ratios and on element: ^{234}Th ratios, rather than on
189 concentrations or activities.

190 2.3.1. Trace and major elements

191 In the home laboratory the two remaining quarters of Petex screen saved for pTEs, pCa and
192 pNa analyses were washed off with 0.45- μm filtered, low TE surface seawater collected during
193 the GEOVIDE cruise (Station #77, 40m, filtered through a Supor filter, 0.45 μm) and
194 subsequently collected on acid cleaned 47-mm diameter mixed cellulose esters filters (MF-
195 Millipore® filters, 0.8 μm), using Nalgene® filtration units (Fig. S1). Then, filters were
196 processed following the protocol of Planquette and Sherrell (2012)⁶⁶. Briefly, one half of the
197 MF filter was kept in a clean petrislide while the other half was placed along the wall of an
198 acid cleaned Teflon vial (Savillex®) and digested with a HNO₃ 8 M - HF 2.3 M mix solution
199 (Ultrapur and Suprapur grades, respectively, Merck®), refluxing at 130°C during 4h. After
200 gentle evaporation close to near dryness, 200 μL of concentrated HNO₃ (Ultrapur grade,
201 Merck) was added in order to drive off the fluorides. The residue was brought back into solution
202 with 0.32M HNO₃ spiked with 1 $\mu\text{g/L}$ of indium and stored in acid cleaned centrifuge tubes
203 (Corning®). Measurements of pTEs were performed using a sector field inductively coupled
204 mass spectrometer (SF-ICP-MS, Element 2, Thermo). External calibration curves were run at
205 the start, middle and end of the sequence. The precision and accuracy of our measurements
206 were assessed by analysing the certified reference material (CRM) BCR-414. Recoveries were
207 typically within 10% of the certified values and the precision, given by the relative standard
208 deviation of the five CRM analyses, was between 0.2 and 24% depending on the element (Table
209 2). Gourain et al. (2019) analysed two other CRM (PACS-3 and MESS-4) by using the exact
210 same analytical method and found similar accuracy and precision results⁶⁵. The reproducibility
211 of our analyses was assessed by analytical replicates of 17 samples and differences between
212 replicates were less than 6% from the mean value.

213 Aluminium (Al) is usually used as a tracer of lithogenic particles because of its high crustal
214 abundance (Upper Continental Crust or UCC Al = 8.04% by weight⁶⁷) and its stable

215 concentrations among lithogenic sources. However, Al has been shown to be removed from
216 the surface waters via scavenging onto particles, especially diatom cells ⁶⁸. During GEOVIDE,
217 scavenging onto sinking opal-containing particles was defined as a sink for Al, especially in
218 the Irminger and Labrador basins where diatoms dominate the phytoplankton community ⁶⁹.
219 Removal of aluminium via other types of particles (i.e. carbonates, lithogenics, organics, fecal
220 pellets) was not observed in this study, although it cannot be excluded ⁶⁹. Using Al as a
221 lithogenic tracer can thus be questioned, especially for the Irminger and Labrador basins.
222 Another lithogenic tracer that can be used is titanium (Ti) but it is less abundant in the UCC
223 (UCC Ti=0.3% ⁶⁷) and its concentrations strongly vary between geological materials. We thus
224 calculated the lithogenic mass (litho) using both tracers:

$$225 \quad \text{Litho } (\mu\text{g/L}) = (p\text{Al} \times 27 \times 10^{-6}) / 0.0804 \quad (1)$$

$$226 \quad \text{or Litho } (\mu\text{g/L}) = (p\text{Ti} \times 47.9 \times 10^{-6}) / 0.003 \quad (2)$$

227 where *pAl* and *pTi* are the particulate Al and Ti concentrations in pmol/L; *0.0804* and *0.003* are
228 the mass fractions of Al and Ti in the UCC; and *27* and *47.9* are the molar masses of Al and Ti
229 in g/mol, respectively.

230 The GEOVIDE transect, and the north Atlantic in general, is characterized by multiple
231 lithogenic sources (atmospheric, sediment or continental inputs) with different geological
232 characteristics. For example, basaltic rocks present close to Iceland and Greenland have a
233 different Ti concentration than gabbro from the Iberian margin, potentially leading to wrong
234 lithogenic estimations. The flux estimates of MnO₂, Fe(OH)₃ and CaCO₃ are lower, if not
235 negative, when Ti is used to correct the lithogenic fraction (Fig. S2). We believe that Ti
236 significantly overestimates the lithogenic fraction when its contribution is low (i.e. at all
237 stations except close to the Iberian margin). In the following, we therefore use Al-calculated
238 fluxes, yet keeping in mind that our mineral fluxes might be overestimated, especially in
239 diatom-rich areas like the Irminger and Labrador basins.

240 Oxyhydroxides of Fe and Mn were calculated by subtracting Fe and Mn associated with
 241 lithogenic and biogenic materials from total Fe and Mn. Assuming that Fe oxyhydroxides are
 242 ferrihydrite (Fe(OH)₃ or Fe-oxides hereafter) and Mn oxyhydroxides are birnessite (MnO₂ or
 243 Mn-oxides hereafter), with formula weights 106.9 g Fe(OH)₃/mol Fe and 86.9 g MnO₂/mol Mn
 244 ⁷⁰, it is possible to calculate:

$$245 \quad \text{Fe(OH)}_3 \text{ (}\mu\text{g/L)} = [\text{pFe} - (\text{pAl} \times 0.21) - (\text{POC} \times 0.042)] \times 106.9 \times 10^{-3} \quad (3)$$

$$246 \quad \text{MnO}_2 \text{ (}\mu\text{g/L)} = [\text{pMn} - (\text{pAl} \times 0.00367) - (\text{POC} \times 0.003)] \times 86.9 \times 10^{-3} \quad (4)$$

247 where *pFe*, *pAl* and *pMn* are the total particulate concentrations in nmol/L; POC is the
 248 particulate organic carbon concentration in $\mu\text{mol/L}$; 0.21 and 0.00367 are respectively the UCC
 249 *pFe:pAl* and *pMn:pAl* ratios in mol/mol ⁶⁷; 0.042 and 0.003 are respectively the average Fe:C
 250 and Mn:C quota of bulk phytoplankton in nmol/ μmol in the North Atlantic (Table 5 in Twining
 251 et al., 2015 ⁷¹).

252 Analyses of *pCa* and *pNa* were made using an inductively coupled plasma atomic emission
 253 spectrometer (ICP-AES, ULTIMA 2, Horiba Jobin Yvon). As for *pTEs*, the accuracy and
 254 precision were assessed by analysing the CRM BCR-414 (Table 2). Recovery for *pCa* reached
 255 80%, keeping in mind that only an indicative value for the CRM reference is available.
 256 Replicate analyses were made for 6 samples and differences from the mean value averaged 1.3
 257 and 1.2% for *pCa* and *pNa*, respectively. As a mineral forming the shells of coccolithophorids,
 258 pteropods or foraminifers, we estimate the calcium carbonate (CaCO₃) concentrations by
 259 correcting for sea-salt and lithogenic Ca:

$$260 \quad [\text{Ca}]_{\text{CaCO}_3} \text{ (}\mu\text{g/L)} = [\text{pCa} - (\text{Ca:Na})_{\text{sw}} \times \text{pNa} - (\text{Ca:Al})_{\text{UCC}} \times \text{pAl}] \times 100.1 \quad (5)$$

261 where *pCa*, *pNa* and *pAl* are respectively the total particulate calcium, sodium, and aluminium
 262 concentrations in $\mu\text{mol/L}$; (*Ca:Na*)_{sw} is equal to 0.022 mol/mol and represents the mean

263 seawater ratio ⁷²; $(Ca:Al)_{UCC}$ is equal to 0.251 mol/mol and represents the mean UCC ratio ⁶⁷;
264 100.1 is the molar mass of $CaCO_3$ in g/mol.

265

266 2.3.2. Biogenic silica and opal

267 Following the method of Ragueneau et al. (2005), BSi concentrations were estimated using an
268 alkaline digestion with correction of the lithogenic silica (LSi) ⁷³. A 25mm diameter Nuclepore
269 filter (carrying the LSF) previously counted for Beta activity was inserted in a
270 polymethylpentene centrifuge tube and digested with a 0.2 M NaOH solution (Merck) at 95°C
271 for 1h. After cooling, the pH was neutralized by adding 1 M HCl (Analar Normapur, Merck)
272 and the supernatant was separated from the remaining suspended material by centrifugation.
273 Silicic acid concentrations were determined following an automated acid/molybdate
274 colorimetric method ⁷⁴, using an AutoAnalyzer3 Bran&Luebbe®. Dissolved aluminium
275 released during the digestion process was determined by fluorimetric analysis of an Aluminium-
276 Lumogallion complex (fluorimeter MITHRAS LB 940) ⁷⁵. At the end of the digestion, all the
277 BSi is converted into silicic acid, but some lithogenic Si may have dissolved as well, inducing
278 a bias in the BSi concentration. This bias was resolved by applying a second digestion, similar
279 to the first one, allowing the determination of a Si:Al ratio exclusively related to the lithogenic
280 material present in the samples. As a mineral forming the shells of diatoms, sponges or
281 radiolarians, we estimate the mass of opal assuming a hydrated form of silica: $SiO_2 \cdot (0.4 H_2O)$
282 ⁷⁶, or 67.2 g opal/mol BSi:

$$283 \quad \text{Opal } (\mu\text{g/L}) = ([Si_1] - [Al_1] \times (Si:Al)_2) \times 67.2 \quad (6)$$

284 where $[Si_1]$ and $[Al_1]$ are the concentrations of silicic acid and aluminium determined during
285 the first digestion in $\mu\text{mol/L}$; $(Si:Al)_2$ is the ratio of the concentrations of silicic acid and
286 aluminium determined during the second digestion; and 67.2 is the molar mass of opal in g/mol.

287

288 2.4. Component:²³⁴Th ratios and export fluxes

289 Trace element and mineral (lithogenics, Fe- and Mn-oxides, CaCO₃, opal) export fluxes were
290 determined using the ²³⁴Th-based approach by multiplying the TE:²³⁴Th or mineral:²³⁴Th ratio
291 of sinking particles with the total ²³⁴Th export flux⁶⁰, both determined at the same depth:

$$292 \quad \text{Component export flux} = (\text{component:}^{234}\text{Th})_{\text{particulate}} \times ^{234}\text{Th flux} \quad (7)$$

293 with *component* being either a TE or a mineral phase.

294 As we do not have p²³⁴Th activities available for the SSF, we only consider the
295 component:²³⁴Th ratios from the LSF in this study. Large particles (>53μm) are generally
296 assumed to represent the sinking particulate matter and are thus responsible for the particulate
297 export flux⁷⁷⁻⁷⁹. Using the component:²³⁴Th ratios from the LSF to calculate export fluxes is
298 the most common approach^{36,80-83}. However, recent studies have shown that the SSF could
299 also contribute to the export flux of particulate carbon or nitrogen in oligotrophic regions^{20,21,84}.
300 Black et al. (2019) reported no significant differences in SSF and LSF pP:²³⁴Th, pCo:²³⁴Th and
301 pCd:²³⁴Th ratios contrasting with the higher pMn:²³⁴Th ratios in the LSF compared to the SSF,
302 leading to a greater contribution of the LSF to the total pMn flux³⁶.

303 Vertical export fluxes were determined at the depth where total ²³⁴Th is back to secular
304 equilibrium with ²³⁸U (equilibrium depth or Eq hereafter; Table 3). The ²³⁴Th export at Eq
305 represents the fully-integrated depletion of total ²³⁴Th in the upper waters⁶⁰. To collect
306 particles, three to four depths were sampled per ISP in the upper 150m while in that same depth
307 range, Niskin casts sampled nine depths. Because of this difference of depth resolution we use
308 an interpolation method to estimate the component:²³⁴Th ratios for the layer between surface
309 and Eq. The depth-weighted average (DWA) was chosen as this method yields similar TE:²³⁴Th
310 or mineral:²³⁴Th ratios than those obtained from sediment traps³¹ (DWA;
311 $\text{element:}^{234}\text{Th} = [\sum(\text{element}_i \times Z_i) / \sum(Z_i)] / [\sum(^{234}\text{Th}_i \times Z_i) / \sum(Z_i)]$ where Z_i are the depth intervals

312 sampled above Eq). Uncertainties of ratios and fluxes were obtained using error propagation
313 law.

314

315 2.5. Residence times

316 We also investigated the total residence time (τ) of TEs, which was obtained by dividing the
317 TE inventory within a specific reservoir by the TE flux into or out of this reservoir, thereby
318 assuming steady state with removal rates equalling supply rates (Equation 8). We focused on
319 total (dissolved+particulate) residence time (τ_{total}) within the surface-Eq layer depth (Table 5)
320 and we considered the particulate export flux as the main output flux of TE from the upper
321 ocean. Advective and diffusive circulation fluxes are generally slow processes compared to the
322 vertical export processes and were neglected here ^{25,35}. However these processes have been
323 shown to have impact, though limited, on measured ²³⁴Th export fluxes along the GEOVIDE
324 transect ⁶⁰, and therefore τ_{total} of TE might represent a higher end estimation in the present
325 study.

$$326 \quad \tau = \frac{\text{total TE inventory}}{\text{particulate TE export flux}} \quad (8)$$

327 with the particulate TE export flux in $\mu\text{g}/\text{m}^2/\text{d}$ at Eq (from this study), and the total TE
328 inventory in $\mu\text{g}/\text{m}^2$ obtained by summing the particulate ($>0.45 \mu\text{m}$) and dissolved ($<0.45 \mu\text{m}$)
329 TE phases, both being collected using GO-FLO bottles (Planquette et al., personal
330 communication, 2019 and ^{65,69,85}). Inventories were calculated using a depth-weighted
331 integration in the surface-Eq layer. Uncertainties in Table 5 represent the highest deviation
332 between the residence time obtained at Eq and those obtained at Eq+20m or Eq-20m (20m
333 being the average error on the determination of the Eq depth).

334

335 3. RESULTS

336 3.1. Activities of $p^{234}\text{Th}$ and concentrations of TEs, lithogenic, authigenic and biogenic
337 phases in the large size fraction ($>53\mu\text{m}$)

338 Distributions of $p^{234}\text{Th}$ vary along the transect (Fig. S3, Table S1) with the lowest activities
339 being determined in the Iberian basin (as low as 0.006 dpm/L in subsurface of Station #1) and
340 the highest in surface waters of the Irminger basin (up to 0.2 dpm/L in surface of Station #51).
341 In general, activities are high in surface and decrease with depth but some subsurface maxima
342 also occur, such as at 100m of Station #64 where activities reach 0.16 dpm/L.

343 As shown in Figure S3 and Table S1, $>53\mu\text{m}$ concentrations vary between elements, with
344 values ranging from 10^{-6} to 10^1 nmol/L in the suite of Cd, Co < Cu, Mn, Ni, Ti, Zn < Fe < Al,
345 P. Similarly to $p^{234}\text{Th}$ activities, concentrations and distributions also vary significantly for
346 each pTE along the transect, like those of the lithogenic, authigenic and biogenic phases.

347 Concentrations of pAl or lithogenic material, like that of pFe and pTi, which are known to be
348 associated with lithogenic material, generally increase with depth and are highest at proximity
349 of the Iberian margin (Station #1) reaching up to 15 nmol/L, 5.2 $\mu\text{g/L}$, 3.2 nmol/L and 0.2
350 nmol/L at 550m respectively. Similarly, pMn and pZn show maximal concentrations over the
351 transect at 550m at Station #1 (0.05 and 0.9 nmol/L, respectively) though high concentrations
352 are also observed at 100m at Station #64 (0.03 and 0.07 nmol/L, respectively) like pCd, pCu,
353 pNi and pV (7.1 pmol/L, 0.04, 0.02 and 0.05 nmol/L, respectively; Table S1). Lithogenic
354 material is also strongly enriched at 100m at Station #64 and 200m at Station #77 ($> 0.8 \mu\text{g/L}$).
355 Except for these stations located closer to margins, concentrations of lithogenic material are
356 low, averaging 0.2 $\mu\text{g/L}$.

357 Particulate Cd, Co and P are characterized by biogenic distributions, with higher concentrations
358 in surface waters, especially in the productive west European basin (Stations #21 and #26).

359 Other pTEs are characterized by high surface concentrations such as pV and pZn in the

360 Irminger and Labrador basins or pCd, pCu, pFe pNi and pZn in the west European and Icelandic
361 basins. These coincide with elevated concentrations of both opal and CaCO₃ in the upper 100m,
362 where they are produced: highest CaCO₃ concentrations mainly occur within the west European
363 and Icelandic basins (up to 14 µg/L) whereas highest opal concentrations occur within the west
364 European, Irminger and Labrador basins (up to 95 µg/L). In general, both biogenic phases
365 display nutrient-like profiles with highest concentrations in surface waters, but deeper CaCO₃
366 maxima occur at Station #32 at 100m, Station #38 at 60m and Station #64 at 100m while deeper
367 opal maxima occur at Stations #38 and #64 at 100m.

368 Slight increase of pFe, pMn, pCd, pCo, pCu, pNi and pZn concentrations are observed in
369 subsurface, such as at 60m and 100m at Station #64, in the upper 200m at Stations #32 and #38
370 and below 100m at Station #26. Iron and manganese oxide contents follow similar trends. Both
371 authigenic minerals are obtained after correction of the contribution of lithogenic and biogenic
372 fractions, and therefore show low concentrations along the section, with exceptions at the
373 depths cited just above. At 60m at Station #64, Fe(OH)₃ and MnO₂ concentrations reach 0.16
374 and 0.003 µg/L respectively, but are also relatively high at 100m, coinciding with elevated
375 lithogenic contents (0.05 and 0.002 µg/L respectively). High Fe(OH)₃ concentrations are also
376 observed in the upper 200m of the Icelandic basin (from 0.01 to 0.03 µg/L at Stations #32 and
377 #38) while high MnO₂ concentrations are seen below 100m of Station #26 (up to 0.002 µg/L).

378 Overall, our >53µm pTE concentrations are comparable with those of the world ocean literature
379 ^{31,36,86}. If we compare more closely to data from the GA03 cruise, which also took place in the
380 North Atlantic (GEOTRACES IDP2017 ⁸⁷), our concentrations of pP are slightly higher,
381 reaching 24 nmol/L during GEOVIDE (4.7 nmol/L during GA03), likely because of the higher
382 productivity observed in the subpolar compared to the subtropical North Atlantic. On the other
383 hand, both cruises have similar order of magnitudes in the whole water column for pCd (up to
384 7.1 and 1.5 pmol/L for GEOVIDE and GA03, respectively), pCo (up to 1.5 and 8.3 pmol/L for

385 GEOVIDE and GA03, respectively), pCu (up to 36 and 28 pmol/L for GEOVIDE and GA03,
386 respectively), pNi (up to 70 and 158 pmol/L for GEOVIDE and GA03, respectively) pV (up to
387 92 and 87 pmol/L for GEOVIDE and GA03, respectively) and pZn (up to 0.9 and 0.3 nmol/L
388 for GEOVIDE and GA03, respectively). However, concentrations during GEOVIDE of pAl
389 (0.1-15 nmol/L), pFe (0.02-3.2 nmol/L) and pTi (0.004-0.2 nmol/L) are lower than those
390 observed during GA03 (0.1-98, 0.04-25 and 0.004-3.6 nmol/L, respectively⁴⁴). This might be
391 due to the fact that both cruises took place at different latitudes, with the GA03 transect located
392 in the dust rich region of the Atlantic.

393

394 3.2. Particulate TE:²³⁴Th and mineral:²³⁴Th ratios in the large size fraction (>53 μ m)

395 Magnitudes of ratios differ among elements (pCd:²³⁴Th, pCo:²³⁴Th < pCu:²³⁴Th, pNi:²³⁴Th,
396 pV:²³⁴Th < pMn:²³⁴Th, pTi:²³⁴Th, pZn:²³⁴Th < pFe:²³⁴Th < pAl:²³⁴Th, pP:²³⁴Th) and vary
397 between basins as described below. Profiles of pTE:²³⁴Th and mineral:²³⁴Th ratios in the >53
398 μ m fraction generally follow those observed for the concentrations (Fig. S4).

399 Ratios of pAl:²³⁴Th (1204 nmol/dpm) or lithogenic:²³⁴Th (404 μ g/dpm) reach highest values at
400 250m at Station #1. Similarly, highest pCo:²³⁴Th (0.08 nmol/dpm), pCu:²³⁴Th (0.4 nmol/dpm),
401 pFe:²³⁴Th (245 nmol/dpm), pMn:²³⁴Th (4 nmol/dpm) and pTi:²³⁴Th (18 nmol/dpm) occur at
402 250m at Station #1. Lithogenic:²³⁴Th ratios generally increase with depth but also show
403 elevated values at the surface (15-30m) of Stations #1, #21 and #32.

404 High pP:²³⁴Th and pV:²³⁴Th ratios are observed in the upper 100m of the Irminger and Labrador
405 basins (reaching 121 and 0.9 nmol/dpm, respectively), like high opal:²³⁴Th ratios (750 μ g/dpm
406 at 30m of Station #69). In the west European and Icelandic basins, ratios of pCd:²³⁴Th,
407 pCo:²³⁴Th, pCu:²³⁴Th, pFe:²³⁴Th, pNi:²³⁴Th, pP:²³⁴Th and pZn:²³⁴Th increase towards the
408 surface, similarly to CaCO₃:²³⁴Th (reaching 271 μ g/dpm at 109m at Station #38).

409 Some exceptions are observed at 60m at Station #64 and in the Icelandic basin, especially at
410 200m at Station #32, where we determined high ratios of pCo:²³⁴Th (0.01 and 0.04 nmol/dpm
411 at Stations #64 and #32, respectively), pCu:²³⁴Th (0.17 nmol/dpm at Station #32), pNi:²³⁴Th
412 (0.14 and 1.04 nmol/dpm at Stations #64 and #32, respectively) and pZn:²³⁴Th (from 1.5 to 5.2
413 nmol/dpm in the upper 60m of the Icelandic basin). These high values correspond to the highest
414 Fe(OH)₃:²³⁴Th ratios (6.5 µg/dpm at 60m at Station #64, and 1.04-2.25 µg/dpm in the upper
415 200m at Station #32). The highest MnO₂:²³⁴Th ratios are also observed at 60m at Station #64,
416 and at 153m at Station #26, coinciding with a slight increase of the pZn:²³⁴Th ratio (1.2
417 nmol/dpm).

418

419 3.3. Export fluxes

420 Export fluxes at Eq (between 40 and 110m) significantly vary between elements and between
421 basins (Table 3, Fig. 2). The most striking results are the maximal flux of pAl or lithogenic
422 material (9207 µg/m²/d and 115 mg/m²/d, respectively) and of some pTEs in vicinity of the
423 Iberian margin (Station #1), with extreme values for pCo, pFe, pMn, pP and pTi (3.6, 3912,
424 55, 8141 and 340 µg/m²/d, respectively). Such high fluxes evidence particulate inputs from the
425 Iberian margin, leading to the export of pTE out of the surface layer.

426 The highest CaCO₃ export fluxes occur within the west European and Icelandic basins, where
427 blooms of coccolithophorids were observed during GEOVIDE ⁶². There, we also observe high
428 fluxes of pCd, pCu, pNi or pP, which at Station #21 reach values of 11, 18, 84 and 4648
429 µg/m²/d, respectively. Opal fluxes are the highest in the Irminger and Labrador basins, where
430 diatom blooms were declining during GEOVIDE ⁶⁰ (568 mg/m²/d at Station #64). Surprisingly,
431 the settling of diatoms in these basins is characterized by low pTE export fluxes.

432 High Fe(OH)₃ export flux is observed in the Icelandic basin (Station 32) and in the western
433 Labrador basin (Station #64). At Station #32, the high Fe(OH)₃ flux (1.3 mg/m²/d) goes with

434 high fluxes of pAl, pCd, pCo, pCu, pFe, pMn, pNi, pP, pV and pZn (469, 5.1, 2.7, 10, 931, 13,
435 33, 4145, 1.7 and 396 $\mu\text{g}/\text{m}^2/\text{d}$, respectively). Export fluxes of MnO_2 are small compared to
436 other mineral fluxes (0.007 $\text{mg}/\text{m}^2/\text{d}$ compared to 0.36 $\text{mg}/\text{m}^2/\text{d}$ for $\text{Fe}(\text{OH})_3$ on average). In
437 general, high fluxes of MnO_2 and $\text{Fe}(\text{OH})_3$ coincide but MnO_2 fluxes are particularly high in
438 the west European (Station #26) and Irminger (Station #44) basins where we can observe a
439 slight increase of pCo, pMn and pV fluxes (reaching 0.4, 9.3 and 0.4 $\mu\text{g}/\text{m}^2/\text{d}$, respectively, at
440 Station #26).

441 Particulate TE export fluxes determined using the ^{234}Th approach are still scarce in the
442 literature. Comparing different biogeochemical areas is difficult because of differences in
443 sampling periods (and different productivities), export depths (surface versus deep or Eq depth
444 versus fixed depth) or locations (shelf versus open-ocean). However, the overall ranges of pTE
445 export fluxes between GEOVIDE and the literature are comparable. The pFe export flux at
446 proximity of the Iberian margin (3912 $\mu\text{g}/\text{m}^2/\text{d}$) is by far the highest observed along the
447 GEOVIDE transect but is still lower than fluxes determined on the Scotian shelf (7874 $\mu\text{g}/\text{m}^2/\text{d}$
448 ⁸⁸), or close to the Crozet island (8098 $\mu\text{g}/\text{m}^2/\text{d}$ ³²), where lithogenic inputs are even higher.
449 Conversely, the lower pAl export fluxes in the Labrador Sea (67-281 $\mu\text{g}/\text{m}^2/\text{d}$ at GEOVIDE
450 Stations #64, #69 and #77 and 432-594 $\mu\text{g}/\text{m}^2/\text{d}$ in 2005 ³⁴) indicate lower lithogenic inputs,
451 which seem to drive lower pFe export fluxes (41-501 $\mu\text{g}/\text{m}^2/\text{d}$ at GEOVIDE Stations #64, #69
452 and #77 and 480-614 $\mu\text{g}/\text{m}^2/\text{d}$ in 2005 ³⁴). Even though GEOVIDE took place during the spring
453 bloom, export of pP (266-8141 $\mu\text{g}/\text{m}^2/\text{d}$) is lower than observed along the GP16 transect, from
454 the Peruvian shelf to the subtropical Pacific gyre (254-27876 $\mu\text{g}/\text{m}^2/\text{d}$ ³⁶) likely due to high
455 productivities and high biogenic exports induced by the coastal upwelling there. Similarly,
456 particulate organic carbon (POC) export reaches 960 $\text{mg}/\text{m}^2/\text{d}$ during GP16 compared to 139
457 $\text{mg}/\text{m}^2/\text{d}$ during GEOVIDE ⁸³. For that same Pacific ocean area, Black et al. (2019)³⁶ reports
458 similar pCo fluxes (0.1-4 $\mu\text{g}/\text{m}^2/\text{d}$) but much higher pCd (0.2-112 $\mu\text{g}/\text{m}^2/\text{d}$) and pMn export

459 fluxes ($6\text{-}549 \mu\text{g}/\text{m}^2/\text{d}$) compared to fluxes in the North Atlantic reaching up to $4 \mu\text{g pCo}/\text{m}^2/\text{d}$,
460 $11 \mu\text{g pCd}/\text{m}^2/\text{d}$, $55 \mu\text{g pMn}/\text{m}^2/\text{d}$ for the present GEOVIDE section and $3 \mu\text{g pCd}/\text{m}^2/\text{d}$ for the
461 Scotian shelf area ⁸⁸. Finally, Smith et al. (2014) ⁸⁸ reports similar pCu export fluxes for the
462 Scotian shelf ($1\text{-}22 \mu\text{g}/\text{m}^2/\text{d}$) compared to those observed for the GEOVIDE transect ($1\text{-}16$
463 $\mu\text{g}/\text{m}^2/\text{d}$).

464

465 3.4. Residence times

466 Along the GEOVIDE transect, TE inventories and exports, and consequently residence times,
467 vary considerably (Table 5). Trace element residence times in the surface-Eq depth layer range
468 from 2 to 13297 days: Al ($4\pm 0.2 - 106\pm 3$ days), Fe ($2\pm 0.1 - 147\pm 5$ days) < Mn ($89\pm 25 -$
469 626 ± 80 days), Zn ($4\pm 0.4 - 582\pm 18$ days) < Co ($64\pm 3 - 3427\pm 209$ days), Cu ($236\pm 11 - 3646\pm 698$
470 days) < Ni ($339\pm 15 - 13297\pm 407$ days).

471 High particulate and dissolved inventories, high export fluxes and short τ_{total} are observed at
472 Station #1, close to the Iberian margin, for all TEs. There, we observe the shortest residence
473 times for Al ($\tau_{\text{total}}=4$ days), Co ($\tau_{\text{total}}=64$ days), Cu ($\tau_{\text{total}}=236$ days) and Fe ($\tau_{\text{total}}=2$ days).
474 However, τ_{total} values for Mn, Zn and Ni at Station #1 are not the shortest ones along the
475 transect.

476 The Icelandic and western European basins are also characterized by short element residence
477 times. For example, the residence time for Fe is only 3 days (at Stations #32 and #38) and Ni
478 and Zn residence times are shorter there (Ni: $\tau_{\text{total}}=339$ days at Station #21; Zn: $\tau_{\text{total}}=4$ days at
479 Station #32) than near the Iberian margin. A major difference with the Iberian margin is the
480 generally lower surface water particulate and dissolved inventories for most TEs in the
481 Icelandic and west European basins (Table 5).

482 Finally, τ_{total} for all TEs are much longer, generally of the order of years (5, 9, 7, 36 and 2 years
483 for Co, Cu, Mn, Ni and Zn respectively) within the Labrador and Irminger basins, while they

484 are less than a year or even only a few days, within the west European/Icelandic and Iberian
485 basins. For example, Fe residence times average 47 days within the Labrador and Irminger
486 basins compared to an average of 10 days for the west European/Icelandic basins and 2 days
487 for Station #1 at the Iberian margin. For all TEs, except Co, τ_{total} is maximal at Station #77 in
488 the Labrador Sea. For Co, the maximum τ_{total} is reached at Station #64, also in the Labrador
489 Sea.

490

491 **4. DISCUSSION**

492 Since particulate ^{234}Th was not analysed on filters dedicated to trace metal analyses in the SSF,
493 element: ^{234}Th ratios could only be determined for the LSF, which is assumed to be
494 representative of sinking particles ⁸⁹. To our knowledge, this assumption has been used in all
495 studies dedicated to TE export fluxes and using ISP ^{31,32,34-36}. We are aware though, that small
496 particles may contribute to the TE export.

497

498 4.1. Statistical analyses

499 In order to gain more insight about the vector phases carrying each elemental flux, we examined
500 the Spearman rank correlation coefficients between TE and mineral exports (XLStat software;
501 Table 4). The analysis was conducted on log-transformed export fluxes to ensure that input
502 variables are more normally distributed and to reduce the influence of extreme values. The
503 influence of lithogenic materials on the pTE export fluxes is highlighted by the significant
504 correlations, especially for pCu, pFe and pZn (p-value < 0.05 and $R \geq 0.9$; Table 4). At a lesser
505 extent but still significantly, pCd, pCo, pNi and pTi export fluxes are also correlated to
506 lithogenic fluxes (p-value < 0.05 and $R \geq 0.6$; Table 4). Biogenic (opal and CaCO_3) and oxide
507 ($\text{Fe}(\text{OH})_3$ and MnO_2) phases do not show any significant correlations with the pTEs, likely due
508 to the significance of lithogenic particles in controlling TE fluxes in the North Atlantic (Table

509 4). In order to disentangle the roles of the biogenic and oxide phases on pTE fluxes, we used a
510 principal component analysis (PCA; XLStat software) considering excess pTE exports (ie. pTE
511 export fluxes corrected from the lithogenic fraction; Fig. 3). Recent studies have applied a PCA
512 approach for large datasets of element concentrations, including small and large particle size
513 fractions^{19,44,65,90}, but we only consider here export fluxes at the Eq depth based on the large
514 particle size fraction (with GEOVIDE particulate concentrations being reported and discussed
515 elsewhere; Planquette et al., personal communication, 2019 and Gourain et al., 2019⁶⁵). To
516 only comment on the distribution of the pTEs, neither mineral exports nor chemical variables
517 are included in the PCA. The PCA has been conducted after a Varimax rotation which appeared
518 to clarify the relationship among variables by better capturing known dynamics of the water
519 column^{19,91}. This analysis is also conducted on log-transformed export fluxes to limit the
520 influence of extreme values and to ensure a more normal distribution of the variables^{19,92}. We
521 identified four principal components that together explain 95% of the total dataset variance
522 (Fig. 3).

523 The first principal component (33 % of the total variance) likely describes the biological
524 influence as it explains 84 and 81% of the excess pCd and pP flux variances, respectively. This
525 component also explains 55% of the excess pCu flux and between 9 and 17% of the excess
526 pCo, pNi and pZn fluxes. In Table 4, pP appears to be correlated with most pTEs (p-value <
527 0.05 and $R > 0.65$ for pCd, pCo, pCu and pMn fluxes and $R > 0.45$ for pAl, pNi and pZn). To
528 investigate the biological influence on pTE fluxes, we also examined their correlations with
529 POC, CaCO₃ and opal. No significant correlation was observed.

530 The second component (30% of the total variance) explains 74% of both excess pCo and pZn
531 fluxes variances and also explains, at a lesser extent, the export fluxes of other pTEs (12-41%
532 of excess pCd, pCu, pNi variances and 6% of excess pP variance). Interestingly, Ohnemus et
533 al. (2019) also found a factor strongly driven by pCo abundances, with additional - smaller -

534 contributions for other pTEs. They related this factor to a secondary (heterotrophic) biomass
535 phase¹⁹.

536 The third principal component (19% of the total variance) is strongly indicative of authigenic
537 Fe oxides, as it explains 89% of the variability of excess pFe fluxes. In addition, this third
538 component also explains 21% of the variance of excess pNi flux and between 4 and 9% of the
539 variances of excess pCo, pCu, pMn, pP and pZn fluxes, reflecting the scavenging of these TEs
540 onto this authigenic phase⁹³. Furthermore, the correlation analysis highlights links between
541 authigenic Fe oxide and Mn oxide fluxes ($R=0.77$), CaCO_3 fluxes ($R=0.63$) and pTEs,
542 especially pNi, pCu and pZn fluxes ($R = 0.30 - 0.46$; Table 4).

543 Finally, the fourth component (14% of the total variance) probably describes the influence of
544 authigenic Mn oxides as it explains 90% of the variance of excess pMn fluxes. It is associated
545 at 6-8% with excess pFe and pNi fluxes, and at 1-3% with pCd, pCo, pCu and pP fluxes.

546

547 4.2. Lithogenic contribution to fluxes

548 Lithogenic particles play a central role in the North Atlantic (Table 4). They can originate from
549 different sources such as atmospheric deposition, glacial meltwater, advection of sediment-
550 enriched water masses or lateral mixing with shallow coastal waters under continental
551 influence. The importance of lithogenic sources is particularly clear for Station #1, suggesting
552 an input from the Iberian margin (Fig. 2) in agreement with the literature^{44,59}. There, we
553 determined the highest fluxes for lithogenic material and some pTEs, which were accompanied
554 by pTE:pAl ratios close to UCC⁶⁷ (Fig. 4; Fig. S5). This is especially the case for pFe and pMn
555 for which the respective ratios show only 2 and 20% offset relative to UCC ratios (Fig. 4). For
556 other pTEs, these ratios are slightly greater than for UCC, pointing to the presence of another
557 driver of export fluxes. Such TE enrichments relative to the UCC have also been reported in
558 the estuary of the Tagus river⁹⁴ for which the plume has been shown to reach Station #1^{69,85}.

559 This river is known to receive effluents from agricultural, industrial and urban sources and thus
560 represents an important discharge of dissolved and particulate TE concentrations to the estuary
561 ⁹⁵⁻⁹⁸. The slightly higher pTE:pAl ratios compared to UCC may indicate that fluxes at Station
562 #1 are under anthropogenic influence via the discharge from the Tagus estuary.

563 Stations at proximity of the Greenland and Newfoundland margins are also characterized by
564 some higher pTE:pAl ratios (i.e., pCd:pAl or pCu:pAl; Fig. 4), implying additional processes
565 in the export of these pTEs. Although lithogenic particles settle quickly through the water
566 column, they can also adsorb elements onto their surfaces ^{44,99,100}. Such scavenging processes
567 could explain the higher pTE:pAl ratios. Interestingly, the Greenland and Newfoundland
568 margin stations are characterized by much lower lithogenic and pTE flux intensities compared
569 to the Iberian margin (Fig. 2), suggesting that lithogenic material is not similarly released at all
570 margins. Such differences can depend on the morphology of the margin and on the
571 hydrodynamical forcing, providing (or not) significant amounts of lithogenic particles and
572 leading (or not) to the formation of nepheloid layers ¹⁰¹. Indeed, relatively high lithogenic
573 export fluxes are also observed at open-ocean stations beyond the Iberian margin (up to Station
574 #32). The Iberian margin is known to be an efficient exporter of particulate matter to the open
575 and deep sea ^{102,103} and during GEOVIDE, high proportions of lithogenic particulate rare earth
576 elements ¹⁰¹ and pFe ⁶⁵ were observed up to 1700 km far from the Iberian margin. These
577 enrichments were attributed to the presence of intermediate nepheloid layers transported along
578 the isopycnals, which then likely drive pTEs fluxes to the deep ocean. To a lesser extent,
579 lithogenic particles were also transported to the west of the Greenland margin ⁶⁵, in line with
580 the moderate lithogenic export fluxes observed at Station #64, in the eastern Labrador basin.
581 Conversely, lithogenic particles do not seem to spread off the Newfoundland margin, thereby
582 explaining the lower lithogenic export fluxes at Station #77.

583

584 4.3. Authigenic contribution to fluxes

585 High fluxes of Mn- and Fe-oxides were determined at some stations close to margins, also
586 under lithogenic influence (i.e. Station #64), and at open-ocean stations, which are not
587 necessarily characterized by high particulate lithogenic exports. For example, Station #26
588 presents one of the lowest lithogenic and Fe(OH)₃ fluxes, while MnO₂ fluxes are among the
589 highest at this station. This decoupling between high pMn and low pAl fluxes has already been
590 observed and was attributed to a distant shelf source of lithogenic particles³⁰. Indeed, nepheloid
591 layers sourced at the shelves lose particles by gravitational settling during lateral advection,
592 but in the case of Mn, it has been shown that dissolved Mn, remobilized from the shelf, oxidizes
593 very slowly, enriching the particulate phase during transport¹⁰⁴. Long distance transport
594 inducing a subsurface pMn maximum was observed off the Kuril/Kamchatka margin, in the
595 western subarctic Pacific¹⁸. High pMn concentrations and fluxes at Station #26 could thus have
596 originated from authigenically precipitated Mn during its transport from the American coasts,
597 via the North Atlantic Current (NAC, Fig. 1). The distance between Station #26 and North
598 Carolina coasts (USA) is around 4500km, which roughly corresponds to the distance of
599 4220km calculated by multiplying a NAC velocity of 0.4 m/s¹⁰⁵ by the inverse of the oxidation
600 rate constant of Mn ($k_{ox}=0.341 \times 10^{-3} \text{ h}^{-1}$ ¹⁰⁶). Interestingly, the high Mn-oxide fluxes determined
601 at Stations #26, #32, #44 and #64 and to a lesser extent at Stations #13 and #38 drive other pTE
602 fluxes. Indeed, Figure 3 shows that Mn oxides could be responsible for 3-8% of the excess
603 export fluxes of pCu, pFe and pNi.

604 Similarly, Fe-oxide fluxes are high at Stations #32, #38 and #64. As seen in Figures 2 and 3,
605 Fe-oxides could represent an important carrier phase for pCo, pCu, pMn, pNi and pZn (from 4
606 to 21% of the variance explained in the PCA on excess - i.e., non-lithogenic - fluxes, as already
607 discussed in other studies^{46, 107, 19}.

608

609 4.4. Biogenic contribution to fluxes

610 In addition to Figure 3 and Table 4, the comparison of pTE:POC ratios at each station with
611 those of phytoplankton cells suggests that biogenic particles partly influence pTE exports (Fig.
612 5). Despite large uncertainties associated with this approach, some pTE:POC ratios are
613 comparable to ratios reported for functional phytoplankton groups (diatoms, autotrophic
614 flagellates and autotrophic picoplankton) collected in the upper 150m of the North Atlantic ⁷¹
615 (Fig. 5; Fig. S5). This suggests that pTE exports, and especially those of pCd, pCo, pCu, pMn,
616 and pZn, can also be driven by biogenic particles. However, higher pTE:POC ratios than cell
617 ratios are also observed. Trace elements are known to be scavenged onto particles with depth
618 ^{12,108} (see previous sections) and it is usual to observe an increase of the bulk ratios compared
619 to cellular ratios ^{24,109,110}. This can be caused by the presence of detrital, authigenic and
620 lithogenic particles on the filters leading to an increase of the pTE:POC, as observed in Figure
621 5. Moreover, the intracellular TE:C considerably changes between taxa and regions depending
622 on the environmental conditions (e.g. nutrients, sunlight limitations ³): Fe:C quota usually
623 range between 10-1700 $\mu\text{g/g}$ for diatoms and coccolithophorids in natural and culture
624 experiments ^{3,111,112} but Sunda and Huntsman (1995) have measured a Fe:C ratio equalling
625 8230 $\mu\text{g/g}$ ¹¹³, highlighting the high variability of the ratio and the difficulty to generalize the
626 intracellular phytoplankton TE:C ratios. Therefore, we searched for indicators of the
627 phytoplankton community structure, such as CaCO_3 , opal and pigment analyses using
628 CHEMTAX ⁶². The highest CaCO_3 fluxes have been determined within the west European and
629 Icelandic basins (Fig. 2) where coccolithophorids were present ⁶². The contribution of
630 coccolithophorids to export pZn, pCu, pNi and pMn is indicated by relatively high correlation
631 coefficients ($0.3 < R < 0.5$) between these pTEs and CaCO_3 exports (Table 4). Opal fluxes are
632 high at Stations #51, #64 and #69 (Irminger and Labrador basins; Fig. 2) where diatoms
633 dominate the phytoplankton community ⁶². In the Labrador Sea, high POC and opal fluxes are

634 associated with surprisingly low pTE export fluxes (Fig. 2). This basin was sampled during the
635 decline of the bloom (Station #69: 7 weeks after the bloom peak) and was also characterized
636 by an important remineralization event in the mesopelagic layer, evidenced from the excess
637 barium (Ba_{xs}) proxy¹¹⁴. Both results suggest either a pTE accumulation in surface waters while
638 POC would be preferentially exported, or a limitation of dissolved TEs that would impede a
639 pTE export due to enhanced recycling in surface waters¹¹⁵.

640

641 4.5. Residence time of TEs and efficiency of export

642 Although only few TE residence times within the upper ocean are available in the literature,
643 the τ_{total} values estimated from the present dataset are comparable with those of other studies.
644 In the surface global ocean, the majority of τ_{total} for Fe fall between 10 and 100 days³⁵, which
645 corresponds to the 2-147 days range estimated in this study. Hayes et al. (2018) examined the
646 dissolved TE residence times in the upper 1000m of the North Atlantic (note the wider depth
647 layer) and found that Fe had the shortest residence time relative to other TEs, of about 30-60
648 days²⁵. The authors estimated dissolved residence times of less than 6 years for Zn, Co and
649 Mn (0.01 to 6 years in our study, except at Station #64 where τ_{total} for Co reaches 14 years) and
650 of 80-90 years for Cu (0.65-15 years in this study; Table 5). The good consistency between
651 these different studies allows us to rank the turnover rate of TEs in the upper ocean as follows:
652 $Fe < Zn < Mn < Co < Cu$.

653 In the following, our attention is mainly devoted to Fe (Fig. 6). The shortest τ_{total} (2 days) is
654 observed close to the Iberian margin, indicating an efficient Fe export. Similar short τ_{total} within
655 the upper ocean (<5 days) have been observed in coastal areas where lithogenic particles
656 probably play an important role in transporting TEs out of the upper ocean^{32,35,88}. These
657 lithogenic particles advected from margins may represent a continuous Fe input in surface
658 waters explaining the high inventories and export observed during GEOVIDE at Station #1,

659 even in post-bloom conditions. For example, they contribute for 98% of the total Fe export at
660 Station #1 (Fig. 6). As it consists of dense particles, the sinking rate of lithogenic material is
661 known to be high. Here the particle sinking rate is estimated by dividing the particulate
662 residence time by the surface-Eq depth layer. At Station 1, the sinking rate reaches 63 m/d for
663 pFe, which is in the same order of magnitude as estimated using Stokes law (88 m/d for a
664 particle of 53 μ m diameter and of density of 1860 kg/m³, representing an average density for a
665 mixed aggregate composed of lithogenic, transparent exopolymer particles (TEP), detritus,
666 opal and CaCO₃; ¹¹⁶). Similarly, high particulate and dissolved inventories, high export fluxes
667 and short τ_{total} are observed at Station #1 for other TEs, suggesting a fast supply to and removal
668 from the upper ocean by lithogenic particles (Table 5). However, τ_{total} values for Mn, Zn and
669 Ni at Station #1 are not the shortest observed along the transect, indicating that lithogenic
670 particles are not the only drivers of TE export, even at this coastal station.

671 The Icelandic and western European basins were sampled during the bloom development and
672 were thus characterized by an important productivity event ^{60,61}. In these basins, we observe a
673 τ_{total} averaging 3 days for Fe, suggesting an efficient transport to the deep ocean. As seen
674 previously, Stations #21, #32 and #38 are characterized by high export fluxes of Fe- and Mn-
675 oxides, carrying other TEs to the deep ocean. At these stations, pFe sinks faster compared to
676 the Iberian margin (up to 135 m/d at Station #32), likely because of the presence of Fe-oxides
677 (contributing to 62% of total Fe export in these basins; Fig. 6). These mineral phases are
678 presumably denser than lithogenic particles (the density of ferrihydrite is about 3.8 g/cm³
679 compared to a typical clay density of 2.7 g/cm³) but the sinking speed is also controlled by the
680 size of the particle, which might be an important factor in the west European and Icelandic
681 basins. Other TEs also have short τ_{total} and high sinking rates in these basins, confirming the
682 important contribution of oxides to export pTEs.

683 Finally, the Labrador and Irminger basins were sampled during the bloom decline and the
684 average pFe export flux is the lowest of the whole transect (182 $\mu\text{g}/\text{m}^2/\text{d}$ compared to 441 and
685 3912 $\mu\text{g}/\text{m}^2/\text{d}$ for respectively the west European/Icelandic basins and Iberian margin). Longer
686 residence times are also determined within the Labrador and Irminger basins, suggesting that
687 most of pFe is not exported as efficiently as in the eastern basins. This may be due to the more
688 important fraction of Fe carried by biogenic matter (12% compared to 1 and 3% in the Iberian
689 and west European/Icelandic basins, respectively), leading to a slower export of Fe and/or
690 active recycling processes. The median sinking rate of 3 m/d (Table 5) is similar to the rate
691 estimated by using Stokes law (3.5 m/d) for an organic particle of 53 μm diameter and a density
692 of 1060 kg/m^3 . Indeed, Fe removal rate from the upper ocean via biological processes has been
693 shown to be much smaller than via lithogenic and authigenic processes³⁵. A greater τ_{total} is also
694 estimated for other TEs. The slower removal of biogenic TEs can also be reflected by the longer
695 residence times of less detrital TEs, such as Ni, Co or Cu (from 65 days to >35 years) compared
696 to more detrital TEs (Al, Fe with $\tau_{\text{total}} < 150$ days).

697

698 CONCLUSION

699 Using the ²³⁴Th approach and the elemental composition of large, sinking particles, this study
700 investigated the pTE export fluxes, sinking rates and residence times in the North Atlantic.

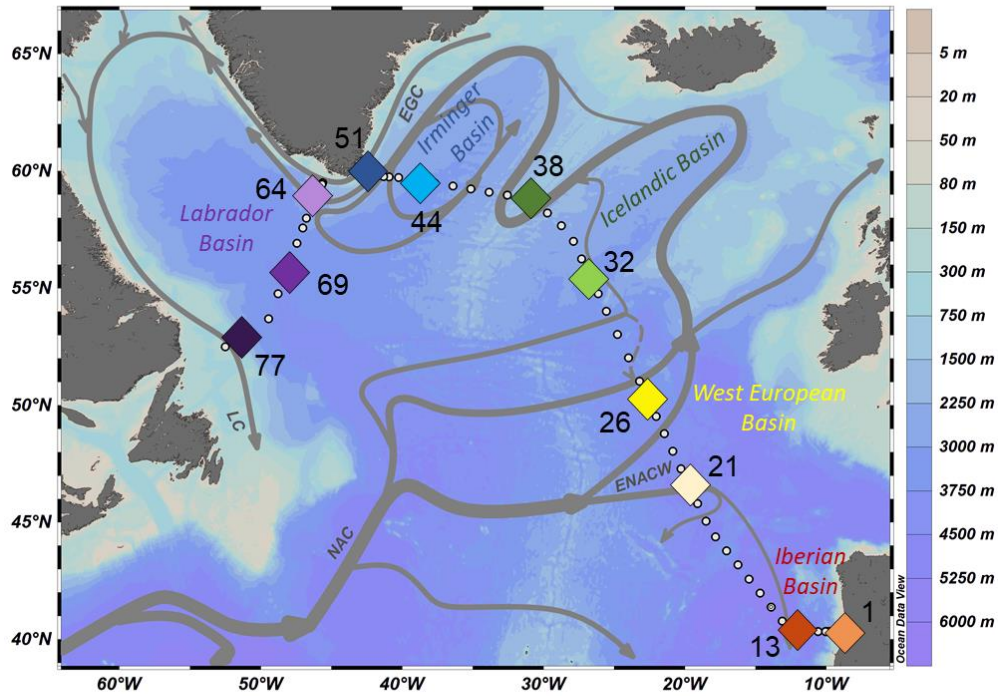
701 Lithogenic material is present everywhere along the section, but mainly controls the fluxes near
702 the Iberian margin, where the highest pTE fluxes are observed. As a result, TE residence time
703 in the upper ocean is short in vicinity of the Iberian Margin. In the open ocean, and especially
704 within the Icelandic basin, Mn- and Fe-oxides are likely the main TE carriers to the deep ocean.
705 Zinc and Ni, for example, have shorter residence times there compared to the Iberian basin
706 which is under lithogenic influence. Biogenic particles also contribute to export pTEs, as
707 reflected by the similarity of pTE:POC export ratios and TE:C cell ratios. Particulate TE export

708 fluxes especially those of pZn, pCu, pNi and pMn might be enhanced by sinking
709 coccolithophorid cells within the west European and Icelandic basins, where CaCO₃ exports
710 are the highest. Diatoms are dominating the phytoplankton community within the Irminger and
711 Labrador basins, in agreement with the highest opal fluxes. However there, pTE fluxes are low,
712 possibly suggesting TE recycling due to dissolved TE limitations in surface waters, in line with
713 the decline of the bloom. The inefficient pTE export in this area is also illustrated by the longer
714 residence times, which may be due to greater biogenic contribution.

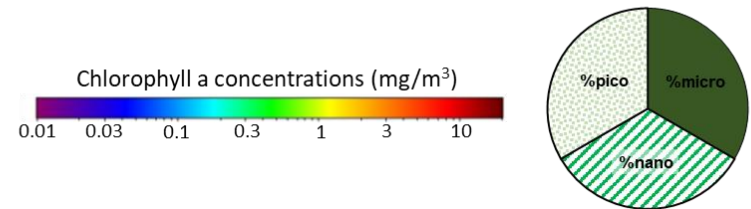
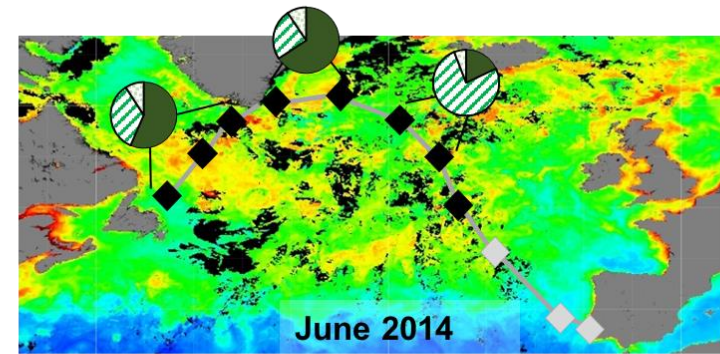
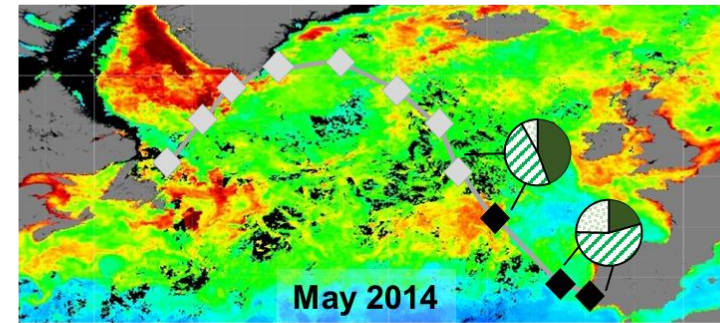
715

FIGURE 1

a)



b)

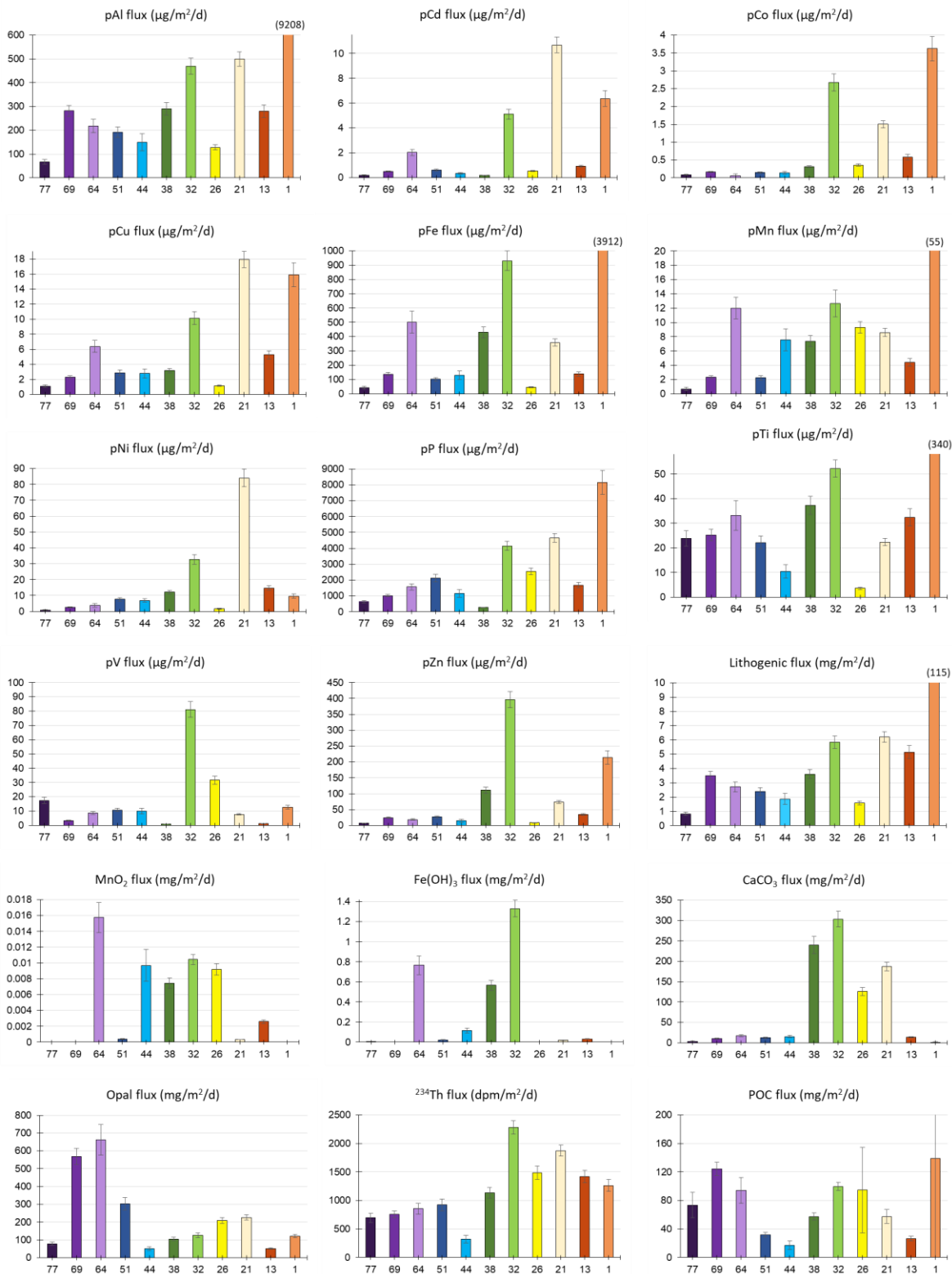


716

717 **Figure 1:** a) Schematic diagram of the surface circulation superimposed on the bathymetric map of the North Atlantic ¹¹⁷. Coloured symbols
718 represent the stations discussed in this study (red: Iberian basin; yellow: West European basin; green: Icelandic basin; blue: Irminger basin; purple:
719 Labrador basin). Abbreviations for the main surface hydrographic features in the upper 500m indicate the East North Atlantic Central Water
720 (ENACW), Labrador Current (LC), East Greenland Current (EGC) and the North Atlantic Current (NAC). b) Satellite-derived chlorophyll-*a*
721 concentrations (MODIS Aqua from oceancolor.gsfc.nasa.gov) averaged over May (top panel) and June (bottom panel) 2014. The GEOVIDE
722 transect is indicated by the grey line and black symbols indicate stations sampled during the corresponding month. The pie charts indicate the
723 proportion of micro-phytoplankton (dark green), nano-phytoplankton (hatched green) and pico-phytoplankton (dotted light green) encountered in
724 each basin during GEOVIDE ⁶².

725

FIGURE 2



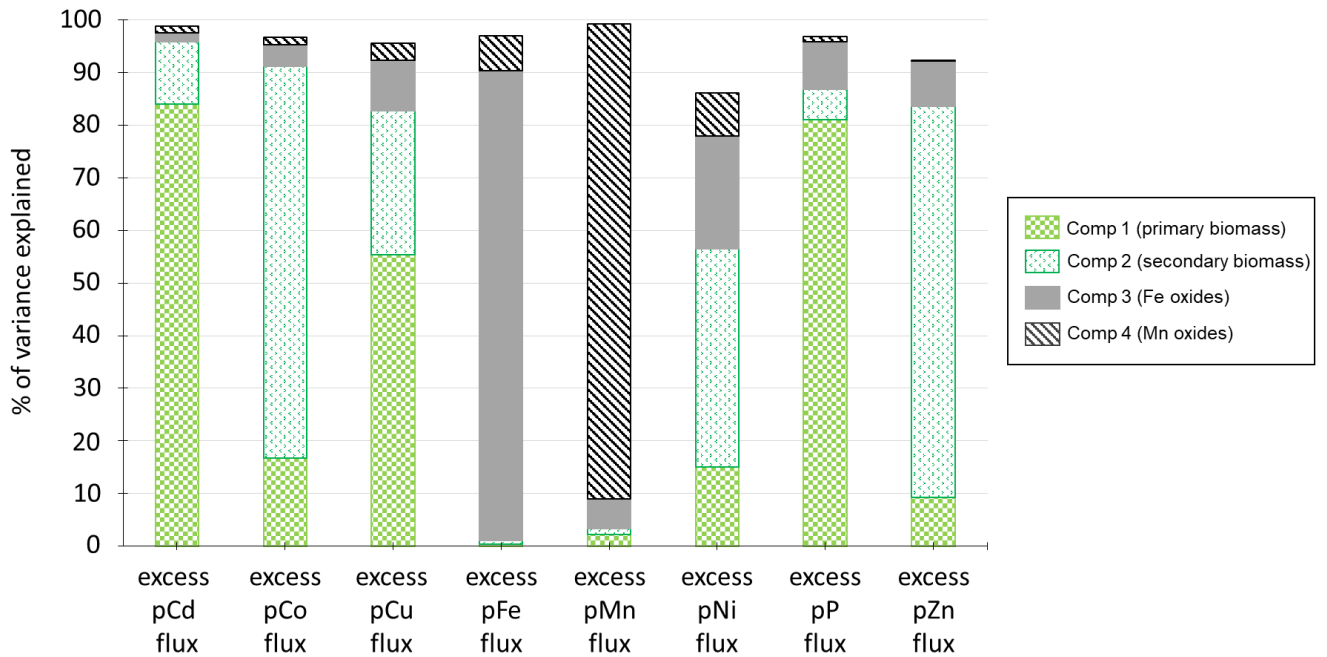
726

727

728 **Figure 2:** Particulate trace element and mineral export fluxes in $\mu\text{g}/\text{m}^2/\text{d}$ or $\text{mg}/\text{m}^2/\text{d}$ estimated
 729 in the large size fraction at the Eq depth. ²³⁴Th (in $\text{dpm}/\text{m}^2/\text{d}$) and POC (in $\text{mg}/\text{m}^2/\text{d}$) export
 730 fluxes in the large size fraction and at the Eq depth are also presented for comparison ⁶⁰.

731

FIGURE 3



732

733 **Figure 3:** Variance explained for eight excess pTE export fluxes at Eq, captured by the first
 734 four principal components in principal component analysis (XLStat software). The description
 735 of the components is provided in the text. Excess pTE export fluxes are calculated by removing the
 736 lithogenic fraction of the flux (excess pTE flux = pTE flux - [pAl flux × ($\frac{pTE}{pAl}$)_{UCC}]; with the UCC ratio
 737 from ⁶⁷).

738

FIGURE 4

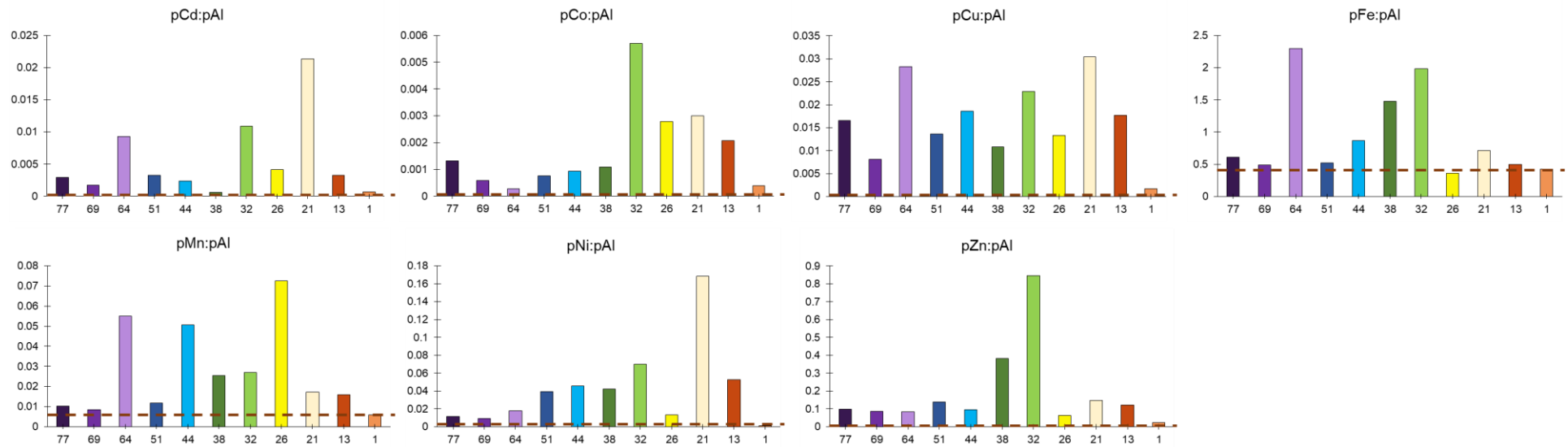


Figure 4: Ratios of the pTEs over pAl fluxes (in g/g, on y-axis) determined at Eq along the GEOVIDE transect (station numbers on x-axis). The brown horizontal dashed lines represent the ratios for the upper continental crust (UCC) ⁶⁷.

FIGURE 5

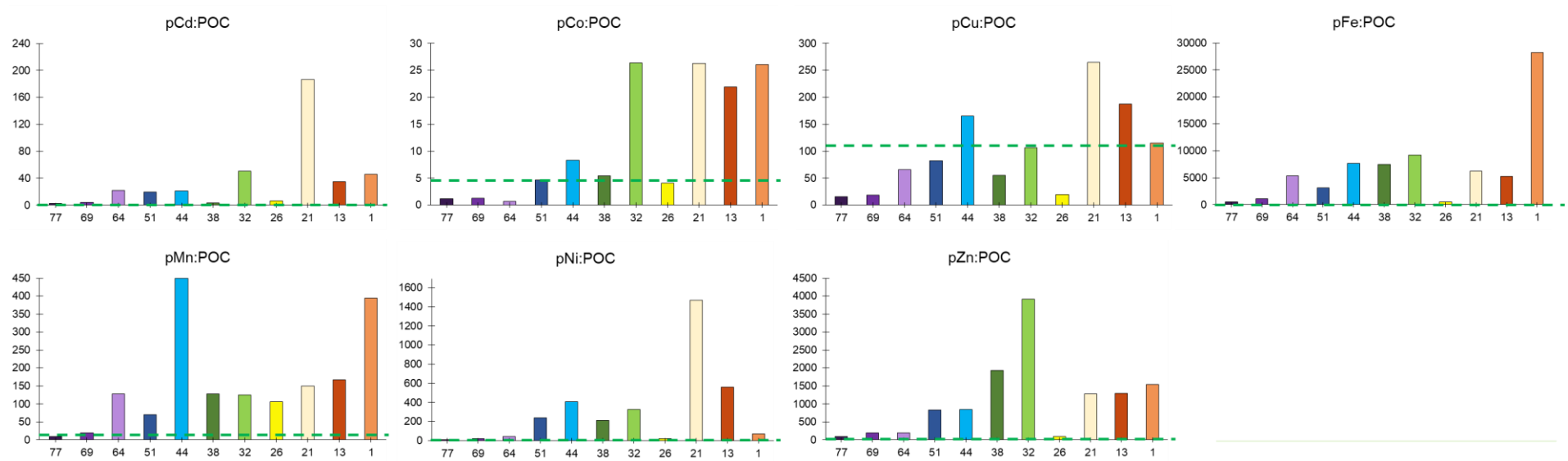


Figure 5: Ratios of the pTEs over particulate organic carbon (POC) fluxes (in $\mu\text{g/g}$, on y-axis) determined at Eq along the GEOVIDE transect (station numbers on x-axis). The green horizontal dashed lines indicate the average intracellular metal stoichiometries ⁷¹.

FIGURE 6

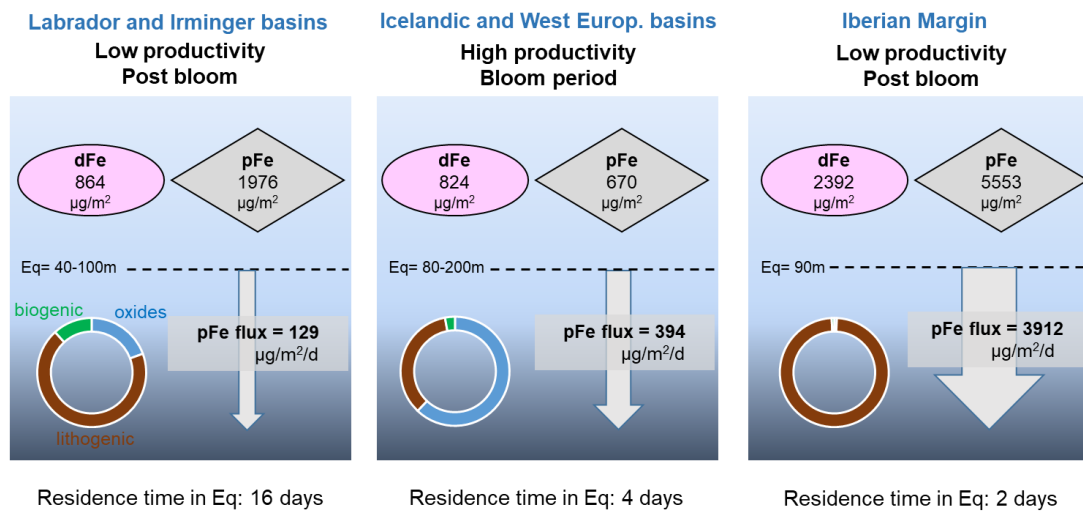


Figure 6: Biogeochemical iron budget in the upper ocean for the Labrador and Irminger basins (left box), for the Icelandic and west European basins (middle box) and for the Iberian margin (right box). For each area, we show the median inventories of dissolved iron (dFe⁸⁵; pink circles) and particulate iron (pFe⁶⁵; grey diamonds) in $\mu\text{g}/\text{m}^2$, the median particulate iron fluxes (pFe flux; grey rectangles) in $\mu\text{g}/\text{m}^2/\text{d}$ and the median total residence times (τ_{tot}) in days. The total residence time is calculated for the depth interval 0-Eq. The size of the arrows is roughly proportional to the magnitude of the pFe fluxes. The fractions of the pFe flux driven by lithogenic, authigenic or biogenic particles are represented by the brown, blue and green colours, respectively. Lithogenic pFe flux was estimated by multiplying the pAl flux by the pFe:pAl ratio in the upper continental crust (UCC, i.e., 0.44 g/g)⁶⁷. Authigenic pFe flux is equal to the Fe(OH)₃ flux (see details in section 2.3) and the biogenic pFe flux is obtained by multiplying the POC flux⁶⁰ by an average Fe:C ratio determined in phytoplankton cells of the North Atlantic (193.7 $\mu\text{g}/\text{g}$)⁷¹.

TABLE 1

	Station	Number of weeks since beginning of spring bloom	In-situ primary production (mmol/m ² /d)	Phytoplankton class	POC export (mmol/m ² /d)
Iberian basin	1	10	33	diatoms & coccolith.	12
	13	11	79	pelagophytes & cyano.	2.2
west Europ. Basin	21	9	135	diatoms	4.8
	26	8	174	diatoms	7.9
Icelandic basin	32	5	105	coccolith.	8.3
	38	4	68	coccolith.	4.8
Irminger basin	44	5	137	diatoms	1.4
	51	4	166	diatoms	2.7
Labrador basin	64	5	54	diatoms	7.8
	69	4	27	diatoms	10
	77	5	80	diatoms	6.1

Table 1: Station characteristics with the number of weeks between the sampling time and beginning of the spring bloom (obtained from satellite data products ⁶⁰), primary production (obtained from incubations ⁶¹), POC export fluxes (obtained with the ²³⁴Th approach ⁶⁰), and phytoplankton classes (from HPLC pigment analysis and CHEMTAX analysis ⁶²).

TABLE 2

	Al ⁺	Ca ⁺	Cd	Co*	Cu	Fe*	Mn	Na [^]	Ni	P ⁺	Ti ⁺	V	Zn
Blank (ppm)	1.6E-03	1.4	1.2E-06	3.2E-06	1.3E-05	1.5E-03	1.4E-04	936	3.4E-04	2.5E-03	1.0E-04	7.3E-06	2.6E-04
BCR-414 (n=5; ppm)	3112	51133	0.385	1.44	29.7	1860	301	6601	17.8	15541	95	9	112.4
RSD (%)	15	2.1	5.2	15	13	12	14	0.2	16	24	8	1	17
Recovery CRM (%)	118	80	101	101	101	101	101	/	95	113	75	111	101

Table 2: Blanks, average concentrations of the certified reference material (CRM; BCR-414), relative standard deviation (RSD) of the 5 analyses of the CRM and recoveries. Elements without any superscript sign have certified concentrations (Cd, Cu, Mn, Ni, V and Zn); elements marked with (*) have indicative concentrations reported on the official certificate (Co and Fe); elements marked with (+) have indicative concentrations reported on the GEOREM website (Al, Ca, P, and Ti) and Na has no reported concentration. The official certificate can be found at <https://crm.jrc.ec.europa.eu/p/40455/40461/By-material-matrix/Animal-materials/BCR-414-PLANKTON-trace-elements/BCR-414> .

TABLE 3

Basin	Station	Eq m	Al flux		Cd flux		Co flux		Cu flux		Fe flux		Mn flux		Ni flux		P flux		Ti flux		V flux		Zn flux	
			$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd
Iberian	1	90	9208	883	6.4	0.6	3.6	0.3	16	2	3912	364	55	6	9.7	1.4	8141	758	340	34	13	1	214	21
	13	110	280	26	0.9	0.1	0.58	0.08	5.0	0.5	138	15	4.4	0.5	15	1	1673	160	32	4	1.2	0.1	34	3
west Europ.	21	110	500	30	10.7	0.6	1.5	0.1	15	1	358	25	8.6	0.6	84	6	4648	278	22	1	7.8	0.5	74	5
	26	100	128	11	0.53	0.05	0.36	0.03	1.7	0.1	46	4	9.3	0.8	1.7	0.2	2537	212	3.5	0.4	32	3	8	1
Icelandic	32	130	469	35	5.1	0.4	2.7	0.2	11	1	931	69	13	2	33	3	4145	285	52	4	81	5	396	25
	38	80	290	26	0.18	0.02	0.31	0.03	3.1	0.3	429	40	7.4	0.8	12	1	266	24	37	4	1.0	0.1	111	10
Irminger	44	40	150	36	0.36	0.07	0.14	0.04	2.8	0.6	129	30	7.6	1.6	6.9	1.1	1158	237	10	3	10	2	14	6
	51	100	192	22	0.63	0.07	0.15	0.02	2.6	0.3	101	12	2.2	0.3	7.6	1.0	2105	242	22	3	11	1	26	3
Labrador	64	80	218	29	2.0	0.2	0.06	0.05	6.2	0.8	501	77	12	2	3.8	1.2	1562	185	33	6	8.6	1.0	18	2
	69	40	281	23	0.49	0.04	0.16	0.01	2.3	0.2	137	11	2.4	0.2	2.6	0.3	1017	82	25	2	3.2	0.3	24	2
	77	60	67	10	0.19	0.02	0.09	0.01	1.1	0.1	41	10	0.7	0.2	0.8	0.3	627	73	24	3	17	2	7	1

Basin	Station	Eq m	Lithogenic flux		Fe(OH) ₃ flux		MnO ₂ flux		CaCO ₃ flux		Opal flux		²³⁴ Th flux	
			$\text{mg}/\text{m}^2/\text{d}$	sd	$\text{mg}/\text{m}^2/\text{d}$	sd	$\text{mg}/\text{m}^2/\text{d}$	sd	$\text{mg}/\text{m}^2/\text{d}$	sd	$\text{mg}/\text{m}^2/\text{d}$	sd	$\text{dpm}/\text{m}^2/\text{d}$	sd
Iberian	1	90	115	11	nd	nd	nd	nd	nd	nd	122	10	1264	104
	13	110	3.5	0.3	0.032	0.003	0.0026	0.0002	14	1	52	4	1418	111
west Europ.	21	110	6.2	0.4	0.020	0.001	0.00032	0.00002	187	10	226	14	1873	97
	26	100	1.6	0.1	nd	nd	0.009	0.001	126	10	209	17	1486	117
Icelandic	32	130	5.8	0.4	1.3	0.1	0.010	0.001	303	19	127	13	2282	119
	38	80	3.6	0.3	0.57	0.05	0.007	0.001	240	21	105	9	1134	95
Irminger	44	40	1.9	0.4	0.11	0.02	0.010	0.002	15	3	51	11	321	66
	51	100	2.4	0.3	0.024	0.003	0.00038	0.00004	12	1	303	34	922	103
Labrador	64	80	2.7	0.4	0.8	0.1	0.016	0.002	17	2	661	86	855	95
	69	40	3.5	0.3	nd	nd	nd	nd	10	1	568	46	758	57
	77	60	0.8	0.1	0.0	0.0	nd	nd	3	1	79	9	696	77

Table 3: Particulate export fluxes in $\mu\text{g}/\text{m}^2/\text{d}$ for aluminum (pAl), cadmium (pCd), cobalt (pCo), copper (pCu), iron (pFe), manganese (pMn), nickel (pNi), phosphorus (pP), titanium (pTi), vanadium (pV) and zinc (pZn); in $\text{mg}/\text{m}^2/\text{d}$ for lithogenic material, iron oxides (Fe(OH)₃), manganese oxides (MnO₂), calcium carbonate (CaCO₃), opal and in $\text{dpm}/\text{m}^2/\text{d}$ for ²³⁴Th. Standard deviations (sd) were calculated by considering the standard deviations of the ²³⁴Th fluxes and pTE:²³⁴Th ratios at Eq, with all concentration and activity uncertainties estimated using error propagation law.

TABLE 4

Variables	Lithogenic flux	Fe(OH) ₃ flux	MnO ₂ flux	CaCO ₃ flux	Opal flux	POC flux	Al flux	Cd flux	Co flux	Cu flux	Fe flux	Mn flux	Ni flux	P flux	Ti flux	V flux	Zn flux
Lithogenic flux	1																
Fe(OH) ₃ flux	0.083	1															
MnO ₂ flux		0.769	1														
CaCO ₃ flux	0.200	0.633	0.706	1													
Opal flux	0.164		0.028	0.073	1												
POC flux	0.391				0.473	1											
Al flux	1.000	0.083		0.200	0.164	0.391	1										
Cd flux	0.618	0.018	0.037	0.100	0.364	0.273	0.618	1									
Co flux	0.745			0.200		0.282	0.745	0.591	1								
Cu flux	0.845	0.330	0.156	0.255	0.064	0.191	0.845	0.791	0.609	1							
Fe flux	0.855	0.395	0.220	0.273	0.145	0.455	0.855	0.591	0.527	0.900	1						
Mn flux	0.527	0.183	0.440	0.364	0.136	0.473	0.527	0.636	0.527	0.718	0.736	1					
Ni flux	0.764	0.440	0.138	0.491			0.764	0.573	0.673	0.791	0.636	0.345	1				
P flux	0.491			0.073	0.209	0.236	0.491	0.891	0.718	0.627	0.400	0.655	0.473	1			
Ti flux	0.691	0.312		0.018	0.000	0.564	0.691	0.300	0.400	0.627	0.845	0.427	0.409	0.100	1		
V flux			0.119		0.009	0.336		0.200	0.127			0.327		0.445		1	
Zn flux	0.909	0.303	0.000	0.318	0.018	0.245	0.909	0.527	0.764	0.791	0.818	0.464	0.855	0.464	0.718		1

Table 4: Spearman rank correlation coefficients between trace element and mineral export fluxes for the large size fraction at the Eq depth. The analysis was conducted on log-transformed export fluxes to ensure that input variables were more normally distributed and to reduce the influence of extreme values. Correlations with $R < 0.1$ are not shown. Values in bold are correlation coefficients with $p\text{-value} \leq 0.05$ (t-test; XLStat software).

TABLE 5

Basin	Station	Al					Co					Cu					Fe				
		diss. invent.	part. invent.	sinking rate	τ_{tot}		diss. invent.	part. invent.	sinking rate	τ_{tot}		diss. invent.	part. invent.	sinking rate	τ_{tot}		diss. invent.	part. invent.	sinking rate	τ_{tot}	
		$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd
Iberian	1	20847	12741	65	4	0.2	219	13	25	64	3	3718	28	52	236	11	2392	5553	63	2	0.1
	13	7720	6672	5	51	5	124	32	2	269	29	5002	129	4	1033	110	1564	1139	13	20	2
west	21	13038	3628	15	33	1	151	37	5	125	5	6224	186	9	422	19	861	599	66	4	0.2
Europ.	26	6181	1741	7	62	12	195	20	2	598	114	6100	133	1	3646	698	691	741	6	31	6
Icelandic	32	12630	1465	42	30	4	224	22	16	92	11	5539	202	7	534	66	1471	898	135	3	0.3
	38	6007	716	32	23	1	111	9	3	380	19	2859	113	2	944	47	786	539	64	3	0.2
Irminger	44	443	1831	3	15	4	49	7	1	401	111	1281	147	1	512	142	809	996	5	14	4
	51	9983	4558	4	76	5	312	2	7	2125	145	8128	200	1	3191	218	1983	3275	3	52	4
Labrador	64	3525	3049	6	30	2	203	4	1	3427	209	5812	160	3	966	59	2086	1976	20	8	0.5
	69	969	3314	3	15	11	31	9	1	245	175	2150	129	1	996	713	294	1915	3	16	12
	77	2621	4465	1	106	3	122	44	0.1	1873	57	3588	237	0.3	3442	105	864	5128	0.5	147	5

Basin	Station	Mn					Ni					Zn				
		diss. invent.	part. invent.	sinking rate	τ_{tot}		diss. invent.	part. invent.	sinking rate	τ_{tot}		diss. invent.	part. invent.	sinking rate	τ_{tot}	
		$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd
Iberian	1	6726	408	12	130	6	8236	23	37	854	39	5769	1174	16	32	1
	13	2606	332	1	664	70	11488	167	10	789	84	1355	951	4	67	7
west	21	2134	272	3	280	12	27694	816	11	339	15	2736	536	15	44	2
Europ.	26	2868	204	5	330	63	20682	194	1	12374	2369	1647	552	1	271	52
Icelandic	32	2505	175	9	212	26	19375	193	22	597	74	709	679	76	4	0.4
	38	1018	98	6	151	8	8152	88	11	674	33	790	400	22	11	0.1
Irminger	44	361	312	1	89	25	3611	118	2	544	151	658	757	1	99	27
	51	2317	102	2	1080	74	9212	181	4	1240	85	3668	855	3	171	12
Labrador	64	1833	113	8	162	3	15196	97	3	3987	243	4112	536	3	256	16
	69	152	152	1	129	92	4705	202	1	1902	1361	464	345	3	33	24
	77	1353	461	0.1	2626	80	9488	1006	0.05	13297	407	3177	638	1	582	18

Table 5: Dissolved inventories (diss. invent. from ^{69,85} and from Planquette et al., personal communication, 2019), particulate inventories (part. invent. from ⁶⁵ and from Planquette et al., personal communication, 2019), sinking rates calculated as the inverse of particle residence time multiplied by the Eq depth layer; total residence time (τ_{tot} , in days) calculated by dividing the total inventory (dissolved+particulate) by the

particulate flux and its standard deviation (sd) obtained by calculating τ_{tot} at Eq, Eq+20m or Eq-20m (20m being the average error on the determination of the Eq depth).

ASSOCIATED CONTENT

Supporting Information

Figure S1: Summary of the different sampling and analytical steps for the $>53\mu\text{m}$ particle size fraction, collected on in-situ pump (ISP) filters and for total ^{234}Th activities, collected via standard CTD rosette. In this figure, each filter is defined by a nominal porosity (in μm) and a diameter (corresponding to the symbol \emptyset , in mm).

Figure S2: Mineral fluxes calculated either by using Al (top panel) or Ti (bottom panel) as lithogenic tracers (in $\text{mg}/\text{m}^2/\text{d}$).

Figure S3: Vertical concentration profiles in the upper 400m (see Table S1 for deeper concentrations) of pTEs and minerals for the $>53\mu\text{m}$ size fraction along the GEOVIDE transect. There are three plots per element: Station #1 (shown alone because of the extreme values observed for few elements); Iberian, west European and Icelandic basins; Irminger and Labrador basins.

Figure S4: Vertical profiles of pTE: ^{234}Th and mineral: ^{234}Th ratios in the upper 400m for the large size fraction ($>53\mu\text{m}$) along the GEOVIDE transect. There are three plots per element: Station #1 (shown alone because of the extreme values observed for few elements); Iberian, west European and Icelandic basins; Irminger and Labrador basins.

Figure S5: Concentration profiles of the pFe:pAl (mol/mol) and pFe:POC (mmol/mol) ratios, with the Eq depth (horizontal black dotted line), the pFe:pAl ratio in the UCC (vertical brown dashed line, from Taylor and McLenan, 1985) and the pFe:POC ratio in phytoplankton bulk (vertical green dashed line, from Twining et al., 2015). Ratios at Eq determined via the concentrations and the fluxes are indicated below each graph.

Table S1: Trace element concentrations (in nmol/L), mineral concentrations (in $\mu\text{g}/\text{L}$) and ^{234}Th activities (in dpm/L) for the large size fraction ($>53\mu\text{m}$) along the GEOVIDE transect.

The (*) indicate depths where POC was collected using a separate ISP unit, 10 to 50 m apart from the ISP dedicated to TEs.

Table S2: Particulate TE:²³⁴Th (in nmol/dpm) and mineral:²³⁴Th (in µg/dpm or ng/dpm) ratios in the large size fraction (>53µm), estimated at the Eq depth, along the GEOVIDE transect.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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