1 Trace element biogeochemistry in the high latitude North Atlantic Ocean: seasonal 2 variations and volcanic inputs

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18 Key Points:

- Bio-essential element concentrations in surface waters decreased from spring to summer with removal ratios reflecting biological uptake
- Effects of volcanic inputs from Eyjafjallajökull in spring 2010 were pronounced for Al,
 Mn and Zn but returned to typical levels in summer
- Deep winter convection dominated trace element supply to surface waters with
 minor contributions from atmospheric and diffusive mixing

25 Abstract

We present dissolved and total dissolvable trace elements for spring and summer cruises in 26 2010 in the high latitude North Atlantic. Surface and full depth data are provided for AI, Cd, 27 28 Co, Cu, Mn, Ni, Pb, Zn in the Iceland and Irminger Basins, and consequences of biological uptake and inputs by the spring Eyjafjallajökull volcanic eruption are assessed. Ash from 29 30 Eyjafjallajökull resulted in pronounced increases in Al, Mn and Zn in surface waters in close proximity to Iceland during the eruption, whilst 3 months later during the summer cruise 31 levels had returned to more typical values for the region. The apparent seasonal removal 32 33 ratios of surface trace elements were consistent with biological export. Assessment of supply of trace elements to the surface mixed layer for the region, excluding volcanic inputs, 34 indicated that deep winter mixing was the dominant source, with diffusive mixing being a 35 36 minor source (between 13.5% (dissolved Cd (DCd)) and -2.43% (DZn) of deep winter flux), and atmospheric inputs being an important source only for DAI and DZn (DAI up to 42% and 37 DZn up to 4.2% of deep winter+diffusive fluxes) and typically less than 1% for the other 38 elements. Elemental supply ratios to the surface mixed layer through convection were 39 comparable to apparent removal ratios we calculated between spring and summer. Given 40 41 that deep mixing dominated nutrient and trace element supply to surface waters, predicted 42 increases in water column stratification in this region may reduce supply, with potential consequences for primary production and the biological carbon pump. 43

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45 **1 Introduction**

Primary productivity, standing stock, species composition and trophic structure of planktonic communities in the oceans are controlled by the availability of light, macronutrients (nitrogen (N), phosphorus (P) and silicon (Si)) and the micronutrient iron (Fe), in association with loss processes by viral lysis and zooplankton grazing (Boyd et al., 2007; Graziano et al., 1996; Martin, 1991; Nelson et al., 2001; Wu et al., 2000). These controls influence export production and thereby impact the global carbon cycle (Brix et al., 2006). Trace elements other than Fe also play an important role in the functioning of microbial organisms, with the

next most abundant trace elements in marine phytoplankton after Fe being (in order) zinc (Zn), manganese (Mn), copper (Cu), nickel (Ni), cadmium (Cd) and cobalt (Co) (Twining and

55 Baines, 2013).

These micronutrient trace metals play key roles in a range of cellular processes that ultimately determine rates of oceanic primary productivity (Morel and Price, 2003). The availability of these micronutrient elements can therefore influence the fixation of CO_2 , generation of O_2 , uptake of N, P and Fe, with enhanced levels potentially resulting in toxic effects (Morel and Price, 2003). The involvement in biological processes results in a removal of micronutrients like Cd, Cu, Ni and Zn from the surface ocean by microbial organisms, with release at depth following remineralisation of sinking particles (Bruland and Lohan, 2004).

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The supply and removal processes of the oceanic micronutrients can be elucidated with the 64 65 use of tracers, such as aluminium (AI) for dust inputs (Vink and Measures, 2000), Mn for benthic supply (Laès et al., 2007), and lead (Pb) for scavenging (Kadko, 1993). We still have 66 a limited understanding of the oceanic distributions and cycling of trace elements, despite 67 their important biogeochemical roles. In recent years, large new datasets have emerged as 68 part of the international GEOTRACES programme (Henderson et al., 2007; Schlitzer et al., 69 70 2018). The availability of oceanic Fe data has substantially improved (e.g. (Fitzsimmons and others, 2017; Milne et al., 2017; Tagliabue et al., 2012)), with also some new datasets for 71 e.g. Zn (Middag et al., 2019; Wyatt et al., 2014), Al (Measures et al., 2015; Menzel 72 73 Barraqueta et al., 2018), Pb (Noble et al., 2015; Rusiecka et al., 2018), Cd (Middag et al., 2018; Wu and Roshan, 2015) and Ni (Middag et al., 2020). 74

The high latitude North Atlantic Ocean features a pronounced annual spring bloom (Sanders 75 76 et al., 2005) and has areas of deep water formation, and therefore forms an important component of the oceanic carbon cycle (Broecker, 1991; Pickart et al., 2003). The typical 77 78 annual phytoplankton bloom in the high latitude North Atlantic starts in early April and lasts 79 towards mid-May, with a second peak towards the end of June, followed by chlorophyll a 80 levels decreasing afterwards (Sanders et al., 2005; Achterberg et al., 2013). The region has become a focus for research into the role of Fe in ocean productivity, community structure 81 and carbon export (Browning et al., 2019; Giering et al., 2012; Le Moigne et al., 2014; Moore 82 83 et al., 2006; Nielsdottir et al., 2009; Ryan-Keogh et al., 2013). Residual nitrate concentrations have been observed during late spring and summer in surface waters of the high latitude 84 North Atlantic (Moore et al., 2006; Nielsdottir et al., 2009), indicating a reduced efficiency of 85 the biological carbon pump (Sarmiento and Toggweiler, 1984). Limitation of phytoplankton 86 87 growth, resulting in the residual nitrate levels, has been attributed to a limited supply and availability of Fe (Achterberg et al., 2013, 2018; Nielsdottir et al., 2009; Ryan-Keogh et al., 88 89 2013).

90 This study is part of the Irminger Basin Iron Study (IBIS) and presents the distributions of 91 dissolved and total dissolvable AI, Cd, Cu, Mn, Ni, Pb and Zn, and the quantification of their 92 various sources to and removal mechanisms from the surface ocean of the high latitude North Atlantic. The geographical focus of IBIS was the Iceland Basin (IB) and Irminger Basin 93 94 (IRB). Research cruises in different seasons (spring and summer) as part of IBIS were conducted during and after an eruption of the Eyjafjallajökull volcano which impacted the 95 96 study region (Achterberg et al., 2013). The study therefore allowed for a unique seasonal perspective of the effects of trace element cycling in the study region, including a direct 97 assessment of volcanic inputs, for which some indirect but few direct observations exist, e.g. 98 99 (Duggen et al., 2007; Hamme et al., 2010; Lin et al., 2011). A recent paper has reported on the distributions of dissolved and dissolvable Fe in the study region as part of IBIS 100 Programme (Achterberg et al., 2018). Here we present multiple elements other than Fe, 101 102 providing a thorough comparison of their biogeochemical cycles in this study region.

104 2 Materials and Methods

105 2.1 Sample collection

Water samples were obtained in the high latitude North Atlantic at 41 full depth CTD casts 106 107 and 195 underway surface stations during cruises D350, D351 and D354 on board RRS Discovery. The cruises took place in spring and summer 2010 (Spring: April 26-May 9 (D350) 108 and May 10-28 (D351); Summer: July 4-August 11 (D354)) (cruise tracks in Supporting 109 Information (SI) Fig. S1). The samples were collected in the shelf regions off Iceland (D350, 110 D351, D354) and Greenland (D354), and in the IB (D350, D351, D354) and IRB (D350, 111 D354) (Fig. 1). The spring cruises D350 and D351 were conducted during the explosive 112 eruption phase of the Eyjafjallajökull volcano, and the summer cruise sailed following the 113 eruption (Achterberg et al., 2013). All data are available from the British Oceanographic Data 114 115 Centre.

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Figure 1. Circulation in the North Atlantic, redrawn from graph originally from IFM-GEOMAR 118 SFB460 overlaid with sampling stations of cruises D350, D351 and D354 (black: CTD, cyan: 119 underway) and the location of the volcano Eyjafjallajökull (black triangle). Red, orange and 120 yellow: near-surface currents. Dashed black and white: intermediate currents. Blue: near-121 bottom currents. Abbreviations are: LSW: Labrador Sea Water, NAC/NAD: North Atlantic 122 Current/Drift, ISOW: Iceland Scotland Overflow Water, DSOW: Denmark Strait Overflow 123 Water, NASPG: North Atlantic Sub-Polar Gyre, RT: Rockall Trough, HRP: Hatton-Rockall 124 Plateau, IC: Irminger Current, RR: Reykjanes Ridge, IrB: Irminger Basin and IcB: Iceland 125 Basin. Map was produced using Ocean Data View (Schlitzer, R., Ocean Data View, 126 odv.awi.de, 2017). 127

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Samples were collected using trace metal clean 10 L OTE (Ocean Test Equipment) Niskin samplers mounted on a Ti CTD rosette frame. The OTE bottles were immediately transferred into a pressurized clean container (class 1000) for sub-sampling. In addition, surface
seawater (~3 m depth) was pumped from a tow fish into the clean container using a Teflon
diaphragm pump (Almatec A15) connected to a clean oil-free air compressor (JunAir)
(Achterberg et al., 2001) and samples taken every two hours whilst the ship was in transit.

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Samples for trace metal analysis were collected in acid-cleaned 125 or 250 ml low-density 136 137 polyethylene bottles (LDPE, Nalgene) after on-line filtration with a 0.2 µm cartridge filter (with 0.45 µm pre-filter, Sartobran 300, Sartorius). The samples from the OTE bottles were filtered 138 under pure N₂ pressure (filtered 99.99% N₂, 1 bar), whereas those from the tow fish were 139 140 filtered using the pressure from the Teflon pump. Additional samples were collected without filtration. Each sample was acidified to pH ~1.9 on board in a laminar flow hood (class 100) 141 142 with nitric acid (UpA HNO₃, Romil, UK) and stored in double bags until analysis at the National Oceanography Centre Southampton. The storage of the acidified (pH ~1.9) 143 144 unfiltered samples with subsequent analysis after 18 months yielded total dissolvable metal 145 (TDAI, TDCd, TDCo, TDCu, TDMn, TDNi, TDPb, TDZn) concentrations, which include the 146 dissolved (0.2 µm filtered) and an acid leachable fraction of the particulate pool (no TDAI data available for tow fish surface samples). In order to verify that sampling and sample 147 148 handling procedures were trace metal clean, samples were analysed for dissolved Fe (DFe) at sea using a flow injection technique (Obata et al., 1993). 149

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151 **2.2 Trace metal and nutrient analysis**

Concentrations of trace metals were determined by isotope dilution inductively coupled mass 152 spectrometry (ID-ICP-MS), whilst the mono-isotopic elements Co and Mn were analysed 153 154 using a standard addition approach followed by ICP-MS detection; all according to methods described in (Rapp et al., 2017). Full details are supplied in the in SI (Text S1). The values 155 determined using the ICP-MS method showed good consistency with the reported 156 consensus values for the elements (SI, Table S1). Aluminium in seawater was determined 157 158 using a flow injection lumogallion method with fluorescence detection (Brown and Bruland, 2008); full details in SI (Text S1). Nitrate+nitrite (Total Oxidised Nitrogen: TON), silicic acid 159 and phosphate were analysed at sea using standard auto-analyser techniques (Grasshoff et 160 161 al., 1983) on a Skalar instrument, following the best practice guide for performing nutrient measurements at sea (Hydes et al., 2010). 162

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164 **2.3 Aerosol sampling and analysis**

During the spring, aerosol samples were collected onto single 20 x 25 cm Whatman 41 filters 165 (Fisher) using a high volume aerosol collector (Tisch TSP) operating at a flow rate of ca. 1 m³ 166 min⁻¹ (Baker et al., 2007) and located on the deck above the bridge of RRS *Discovery*. 167 Separation of particles into aerodynamic diameters greater than or less than 1 µm was 168 achieved during the summer cruise using a Sierra-type cascade impactor, also using 169 Whatman 41 (Fisher) slotted substrates and filters. Collection filters and slotted substrates 170 171 were acid-washed before use with 0.5 M HCI (Aristar Grade, Fisher), followed by 0.1 M HCI (Aristar Grade, Fisher). Collection times for most samples were relatively long (2-3 days) 172 because of low aerosol trace metal concentrations in the high latitude North Atlantic, but 173 174 samples collected under the Eyjafjallajokull ash plume (spring TM07-09; locations of aerosol sampling depicted in Fig. S2 (SI)) were only collected for 1–3 hours. The collector was only 175 used when the ship was heading into the prevailing wind in order to avoid contamination from 176 177 the vessel.

Following collection, samples were sealed in plastic bags and immediately frozen at -20°C 178 179 for return to the land-based laboratory. Trace elements were leached from the filters using a 180 1 M ammonium acetate solution (pH 4.7) and filtered through 0.2 µm filters (Minisart, Sartorius) (Baker et al., 2007) and their soluble concentrations were determined by ICP-OES 181 182 and ICP-MS (Baker and Jickells, 2017). Total element concentrations were determined on portions of the filters by instrumental neutron activation analysis (INAA), with the two size 183 fractions for the summer cruise samples combined together to give a single measurement 184 (Sholkovitz et al., 2012) (Pb cannot be determined by INAA). Here we report on the dry 185 deposition fluxes of soluble elements (F_{dry}, nmol m⁻² d⁻¹) as the product of their aerosol 186

187 concentrations (C_{aero} , pmol m⁻³) and a dry deposition velocity (v_d) ($F_{dry} = C_{aero} v_d$). Values of v_d 188 were set to 1 and 0.1 cm s⁻¹ for the coarse (> 1 µm) and fine (< 1 µm) aerosol modes, 189 respectively for summer cruise, and 0.7 cm s⁻¹ for the spring cruise (Baker et al., 2007; 190 Ganzeveld et al., 1998). Deposition velocities vary strongly as a function of particle size and 191 wind speed (Ganzeveld et al., 1998) and are highly uncertain. An uncertainty in v_d of plus or 192 minus a factor of 2 – 3 has been reported (Duce et al., 1991).

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194 Diffusive flux measurements and calculations

Turbulent kinetic energy dissipation (ɛ) was measured during summer cruise only using a 195 196 free-fall microstructure shear profiler (MSS90L, Sea and Sun Technology GmbH). The rate of ε was calculated from the variance of the measured vertical microstructure shear by 197 198 integration of the vertical microstructure shear power spectrum (Forryan et al., 2012) and assuming isotropic turbulence (Yamazaki and Osborn, 1990). Turbulent diffusivity (K) was 199 200 estimated from ε and buoyancy frequency, full details of the approach are provided in 201 (Painter et al., 2014). The top 8 m of data in the water column were omitted in order to 202 remove near-surface influences prior to binning the diffusivity data into 4 m depth bins. Vertical diffusive fluxes of trace elements into surface mixed layer were subsequently 203 204 determined from the turbulent diffusivity and profiles of the trace elements. The mixed layer depths (MLD) were obtained at the depth of the local maximum in the Brunt-Väisälä 205 buoyancy frequency profile (MLD range 17-49 m, mean ± 1 standard deviation: 28±8 m) 206 (Painter et al., 2014). 207

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209 2.5 Winter Convective fluxes

210 Winter convective fluxes were obtained from examination of individual Argo float profiles from the IRB and IB in winter 2010, which allowed determination of the MLD using criteria by (de 211 Boyer Montégut et al., 2004). The obtained mean winter MLD were 170±100 m for the IRB 212 and 355±144 m for the IB, rounded to 200 and 350 m, respectively; full details are provided 213 214 elsewhere (Painter et al., 2014). Dissolved metal concentrations from spring profiles in each basin were then integrated to the respective depth of winter mixing to obtain a mean estimate 215 of convective inputs as reported previously (Nielsdottir et al., 2009). Limited spatial coverage 216 217 of the IRB and IB by Argo floats introduced some uncertainty around the mean winter MLD which appeared spatially heterogenous whereas metal concentrations measured during the 218 spring cruise at the mean winter MLD were more spatially homogenous. This latter 219 observation suggests that convective fluxes obtained by blending mean winter MLD with 220 spring metal concentrations is unlikely to be significantly in error due to the time gap between 221 222 the two datasets.

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3 Results and Discussion

225226 **3.1 Hydrography**

The study region in the high latitude North Atlantic Ocean includes the IB and IRB, Hatton-227 Rockall Plateau, and Rockall Trough and Reykjanes Ridge regions (Fig. 1). The cyclonic 228 229 subpolar gyre of the North Atlantic flows around the IRB and IB. The North Atlantic Drift 230 (NAD) is part of the southern region of the subpolar gyre and flows as the main near-surface current northward into the central region of the high latitude North Atlantic (between ca. 10°W 231 to 30°W) with depths in the IB of up to 1 km (Bower et al., 2002). The NAD is bounded by the 232 cooler Irminger Current to the west, with the southern and eastern boundaries weakly 233 234 constrained by extensions of the NAC (Rossby et al., 1998). The NAD has a salinity range of 235 35.2-35.7 and is warmer than surrounding waters (Rossby et al., 1998). The Irminger Current 236 is prominent in the east IRB, and turns west in the north IRB before moving south in the subpolar give flow. Trajectories of Argo floats released in our study region during RRS 237 238 Discovery cruise D321 (June 2007) indicate the described upper ocean current movements (in SI, Fig. S3). The western IRB features a fresh and cold western boundary current (East 239 240 Greenland Current (EGC)) with a southerly flow, and salinity and temperature ranges of 30-34 and 3.5-5.5°C, respectively (Bacon et al., 2002). 241

Details of the water masses in our research area are discussed in the SI and shown in Table
S2 (SI), and were used to support the interpretation of the potential temperature-salinity (θ-S)
plot (SI, Fig. S4), optimum multiparameter (OMP) water mass analysis (Tomczak, 1999) for
an east-west section along 60°N (SI, Fig. S5) and trace metal distributions.

249 3.2 Surface water distributions of dissolved and total dissolvable trace elements

A total of 195 surface samples were collected using the tow fish in the IB and IRB during the cruises. For off shore stations (water depth >400 m) the ranges and average surface water concentrations of nitrate+nitrite (TON), dissolved and total dissolvable trace elements for the spring and summer cruises are presented in Table 1, for the whole region and separately for the IB and IRB.





Mn, Ni, Cd, Pb, Zn, Cu, Al and nitrate+nitrite (TON), silicic acid and phosphate during spring 261 2010 (D350&D351). Figures were produced using Ocean Data View (Schlitzer, R., Ocean 262 Data View, odv.awi.de, 2017).



Figure 3: Surface water concentrations (as labelled) of dissolved and total dissolvable Co, Mn, Ni, Cd, Pb, Zn, Cu, Al and nitrate+nitrite (TON), silicic acid and phosphate during

summer 2010 (D354). Figures were produced using Ocean Data View (Schlitzer, R., Ocean
 Data View, odv.awi.de, 2017).

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In surface waters, a gradient of decreasing TON and phosphate concentrations from 272 273 northwest to southeast was observed for the spring cruises (Fig. 2). This trend was also observed for DAI, DCd, DCo, DCu, DNi, DPb, DMn, DZn and was likely due to their active 274 and/or passive biological uptake in relation to the general spatial progression of the spring 275 276 bloom from east to west in the subpolar North Atlantic (Olsen et al., 2008), which was consistent with in situ and satellited derived chlorophyll data for 2013 (Ryan-Keogh et al., 277 278 2013). In addition, ash-derived metal inputs from the Eyjafjallajökull volcanic eruption phase during spring could have contributed to an increase in concentrations for a range of elements 279 280 associated with the ash particles (Achterberg et al., 2013). There were elevated 281 concentrations for a range of elements (DAI: 45 nM; DMn: 3.20 nM, TDMn 8.78 nM; DZn: 282 0.625 nM, TDZn 1.30 nM) directly under the volcanic plume (63.1°N, 18.5°W) in the immediate vicinity of the Icelandic coast (Table 1), but with no increases for Co, Cd, Cu, Ni 283 284 and Pb compared with surface waters that were not influenced by the volcanic ash inputs 285 (further discussion is provided in aerosol section below). Enhanced DAI, DCd, DCo, DCu, 286 DPb, DNi, DMn, DZn concentrations were also observed on the Scottish Shelf (Fig. 2), likely due to continental and benthic inputs; indeed the elevated DMn (8.73 nM) on this shelf 287 288 provided a strong indication of benthic release (Birchill et al., 2019; Burdige, 1993).

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290 Spatial variability in open ocean areas during spring was observed for surface water concentrations of trace metals (Fig. 2), which may be related to the temporal and spatial 291 292 variability in ash deposition (Achterberg et al., 2013) and possibly (sub-) mesoscale processes, including fronts and eddies (Lévy et al., 2012). The total dissolvable metals 293 294 showed similar patterns to dissolved metals, with generally lower concentrations in the southeast of the area where the bloom was already well progressed (Ryan-Keogh et al., 295 2013), but a less pronounced concentration increase towards the northwest (Fig. 2). The 296 297 strongest relationships between dissolved and labile particulate elements (total dissolvable minus dissolved) were observed for Cd (-0.51), Cu (-0.57) and Ni (-0.54) (bivariate Pearson 298 Correlation) indicating a transfer of the dissolved forms of these elements to particulate 299 300 forms. 301

302 During the summer cruise (Fig. 3), phosphate and TON still showed a west to east decrease in concentrations, with anomalously high TON depletion in the IB, potentially as a result of 303 the relief in Fe limitation of primary productivity by the additional Fe supply from volcanic ash 304 305 inputs (Achterberg et al., 2013). Open ocean concentrations in the study region of DAI, DCd, DCo, DCu, DMn, DPb, DZn were lower than in spring (Figs. 2 and 3, Table 1). The coastal 306 307 stations off Scotland and Iceland (Fig. 3) did not show elevated dissolved metal concentrations as observed during the spring cruises, with the reduction in concentrations 308 likely the consequence of biological and physico-chemical removal (precipitation and 309 scavenging for AI, Pb, Mn), and lower atmospheric inputs in the Icelandic waters following 310 the termination of the Eviafiallajökull eruption (May 22, 2010; (Gudmundsson et al., 2012)). 311 Total dissolvable metal concentrations in the overall study region also showed reductions in 312 average summer concentrations relative to spring (Fig. 2 and 3, Table 1), likely related to 313 export of particles from the surface ocean. For the summer cruise strongest relationships 314 315 between dissolved and labile particulate elements were observed for Cu (-0.70) with the rest 316 of the elements showing r < 0.29.

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Contributions of average dissolved to total dissolvable elemental concentration ratios for spring (first number) and summer (second number) were: Co (54%, 50%), Mn (50.5%, 60%), Ni (85%, 74%), Cd (69%, 21%), Pb (76%, 75%), Zn (43%, 16%), Cu (96%, 89%). This indicates that in the surface ocean Ni, Pb, Cu, (Cd spring only) were largely present in the dissolved forms, but around half or more of Co, Mn, Zn and Cd (Cd summer only) were in the particulate form, and likely incorporated in biogenic material (Cd, Zn; (Bruland et al., 2014)),
 or onto biogenic material through bacterial mediated precipitation (Mn, Co; (Moffett and Ho,
 1996; Tebo et al., 2004)).

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We compared average surface water dissolved and total dissolvable metal concentrations 327 328 between the IB and IRB, as well as between spring and summer for the individual basins 329 (Table 1). We included TON to determine the effects of biological uptake. The t-tests 330 indicated significant differences in spring between the IB and IRB for DCd and DPb, and in summer for DCo, DCd, DCu and DNi, with lower concentrations in the IB compared with the 331 332 IRB. Nitrate was also significantly lower in the IB compared to the IRB (by 1.34 fold in spring and 5 fold in summer), with the depleted levels in the IB explained by enhanced TON 333 334 removal as a result of the ash-derived Fe inputs (Achterberg et al., 2013) resulting in Fe and TON co-limited microbial communities (Ryan-Keogh et al., 2013). 335

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For both the IRB and IB, all of the dissolved metals measured showed significant reductions in average summer concentrations relative to spring (Table 1). Furthermore, the t-tests indicated significant differences in spring between the IB and IRB for TDNi, and in summer for TDCd, TDNi and TDPb, with lower concentrations in the IB compared with the IRB (Table 1). Total dissolvable metal concentrations showed significant reductions for the individual basins in average summer concentrations relative to spring for Cd, Ni, Zn (IB only), Co, Cu, Pb (IB and IRB); but not for Mn (Table 1).

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There is a paucity of surface ocean data for elements other than Fe and Al for our study region; comparison between our summer DAI data set (0.94 ± 0.837 nM (not influenced by volcanic ash inputs), Table 1) and that from a CLIVAR cruise (A16N in 2003, Al < 2 nM) indicates a reasonable agreement (Measures et al., 2008).

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Mean values of the significant differences between spring and summer dissolved 350 351 concentrations for multiple elements (Table 1), including Fe (Achterberg et al., 2018), could be used to calculate a net removal ratio (Table 2; in mmol metal:mol P). This apparent net 352 export stoichiometry was very similar between the two basins for the majority of elements 353 and, for the bio-essential metals (Fe, Ni, Zn, Cu, Fe, Cd, Mn, Co), was broadly consistent 354 with what might be expected on the basis of biological dominance of removal (Twining and 355 356 Baines, 2013). Interestingly, apparent Fe removal stoichiometry was higher in the IB than the IRB, potentially due to the more Fe limited status of the latter (Ryan-Keogh et al., 2013) and 357 358 higher Fe inputs to the former (Achterberg et al., 2013). 359

360 **3.3 Concentration profiles of dissolved and total dissolvable elements**

361 Depth profiles of dissolved and total dissolvable elements for a station in the IRB are 362 presented in order to illustrate the similarities and contrasts in their behaviours in the water 363 column in the high latitude North Atlantic (Fig. 4).

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Figure 4: Depth profiles for nitrate+nitrite (TON), phosphate, silicic acid, and dissolved (filled circles) and total dissolvable (open circles) Co, Mn, Ni, Cd, Pb, Fe, Zn, Cu, AI (as labelled) for station 17 (63.01°N, 34.97°W) sampled in IRB during summer 2010 (D354).

The overall trend in dissolved AI, Cd, Co, Cu, Ni, and Zn shows depleted surface ocean 370 concentrations with an increase with depth. This behaviour is similar to that of the 371 macronutrients (TON, phosphate and silicic acid; Fig. 4) and indicates involvement of 372 373 biological processes in cycling of these elements, with surface water uptake (passive or 374 active) by microbial organisms and deep water remineralisation following vertical transfer of biogenic material to depth (Bruland et al., 2014; Menzel Barraqueta et al., 2018) and/or 375 376 transport of nutrient-rich deep waters that have collected particles upstream (Middag et al., 2018, 2019); further discussion provided in section on convective supply. The depth 377 distribution of Cd shows strong similarities to those of TON and phosphate, in agreement 378 379 with other observations (Middag et al., 2018). The distributions of DZn, and to a large extent DAI, showed similarities to silicic acid (Menzel Barraqueta et al., 2018; Middag et al., 2019), 380 381 potentially suggesting an involvement in processes related to opal production and dissolution (e.g. by diatoms). The surface removal at station 17 for DCo, DCu and DNi (Fig. 4) was not 382 383 as pronounced as for DCd and DZn, which is in agreement with other reports and indicated a 384 less pronounced uptake by phytoplankton relative to available stocks in conjunction with a 385 sufficient supply and/or the presence of a fraction of the element which is difficult to assimilate due to ligand binding or slow kinetic dissociation processes (Bruland and Franks, 386 387 1983; Martin et al., 1993; Middag et al., 2020). Some combination of these processes is also likely to be responsible for observed residual DCo, DCu and DNi concentrations at depleted 388 389 nutrient concentrations (non-zero intercepts in element-nutrient plots Figs. S6-8). Iron is presented here to allow comparison to other elements, and shows DFe surface depletion and 390 391 relatively constant DFe concentrations (0.7-0.9 nM) at depth, with increasing TDFe levels 392 (Achterberg et al., 2018). DMn and DPb also have low surface water concentrations and 393 feature increases in concentrations in the first tens to hundreds of meters of the water column. These trends are likely associated with photoreduction (Mn only; (Sunda et al., 394 395 1983)) and remineralisation of sinking material with release of the elements, and the presence of waters perturbed by atmospheric anthropogenic Pb inputs and ventilated over 396 397 the last decades (mode waters in IRB (0-1000 m), Labrador Seawater (500-2500 m); (Boyle et al., 1986; Zurbrick et al., 2018). A decrease in DMn and DPb concentrations is evident at 398 399 greater depths and linked to DMn removal through MnO_x formation (Wu et al., 2014), and 400 scavenging of DPb onto particles in addition to presence of water masses less perturbed by historical anthropogenic Pb inputs (Boyle et al., 1986; Echegoyen et al., 2014). High DAI 401 concentrations near the seafloor most likely represents the influence of the nepheloid layer of 402 403 resuspended sediments, which is also reflected by the very high TDAI and TDFe concentrations (up to 27.2 nM Al and 8.39 nM Fe; Fig. 4) in that part of the water column. 404

The difference between dissolved and total dissolvable concentrations was relatively small 405 406 for the so-called 'nutrient-type' elements (Cd, Co, Cu, Ni, Zn) and also Pb, and more pronounced for AI, Mn and Fe (Fig. 4). This is reflected in the contributions of average 407 dissolved to total dissolvable elemental concentration ratios for the full IBIS data set: Al 408 409 (23%), Mn (66%), Co (74%), Ni (89%), Cd (85%), Pb (88%), Zn (85%), Cu (96%). These findings indicate that in the water column the bio-essential elements (Cd, Cu, Ni, Zn) that are 410 411 directly involved in microbial functioning, occur largely in the dissolved phase in waters below 412 the euphotic zone as a consequence of rapid remineralisation of sinking biogenic matter with only a minor fraction forming part of biogenic particles. Whereas elements that form an 413 important part of lithogenic (Al), skeletal (Al; (Gehlen et al., 2002)), metal oxide (Mn, Co; 414 (Moffett and Ho, 1996)) material had a larger labile particulate fraction as also reported for Fe 415 (14%; (Achterberg et al., 2013)). The oceanic Pb concentrations are dominated by 416 anthropogenic aerosol inputs (Bridgestock et al., 2016; Wu and Boyle, 1997), with an 417 418 apparent high solubility of the land-derived combustion related atmospheric aerosols 419 (Chester et al., 1993), and a large fraction of Pb in the dissolved phase in our study region.

A recent GEOTRACES section in the South Pacific (GP16; (Schlitzer et al., 2018)) allows a
comprehensive comparison to our study and reports dissolved to total (dissolved+particulate)
elemental concentration ratios for open ocean regions remote from land: Zn (ca. 50-98%), Pb
(ca. 80-95%), Mn (ca. 66-90%), Cu (90-95%), Co (ca. 80-98%), Cd (ca. 95-99%), Ni (92-

99%). Our dissolved:total ratio observations are in good agreement with these South Pacific
findings. Particulate elemental concentrations (Co: up to ca. 2-3 pM, Mn: up to ca. 90 pM,
Cd: up to ca. 2-3 pM, Al: up to ca. 4 nM) for a mid-latitude North Atlantic GEOTRACES
transect (GA03) (Twining et al., 2015) were also in good agreement with our labile particulate
values.

429

430 **3.4 Ocean sections of dissolved and total dissolvable trace elements**

Four transects were sampled at a high spatial resolution in 2010, the first during the spring 431 cruise (D350) and the others during the summer cruise (D354). Sections for dissolved 432 elements for the D354 transects are presented here, and the dissolved elements for D350 433 and total dissolvable elements for all transects are presented in the SI. The first and second 434 transect were along ca. 60°N, between 20 to 35°W (D350) and 19 to 43°W (D354), 435 436 respectively, crossing the Reykjanes Ridge at ca. 29°W (Fig. 5, and SI, Fig. S9). The third transect was from 20 to 35°W and 60 to 63°N and crossed the Reykjanes Ridge at about 437 438 62°N (Fig. 6). The fourth section was along 60°N from 41.4°W onto the Greenland shelf (Fig. 439 7).

Figure 5 and Fig. S9 (SI) allow for a comparison between subsurface concentrations (down to ca. 600-800 m) in the IB between spring and summer cruises, during and after the volcanic eruption. In the case of TDFe (Achterberg et al., 2018), higher concentrations were observed in the IB in the top ca. 600 m in spring during the eruption compared to the summer cruise. For the elements which showed a surface water enhancement due to the ash inputs (AI, Mn, Zn; see Fig. 2, and SI Figs. S9-S10), there was no clear evidence of increases in dissolved or total dissolvable concentrations in subsurface waters.

Deep ocean water masses in the study area are all relatively young (i.e. recently ventilated) 447 and have not yet accumulated much remineralised elements and therefore elemental 448 449 signatures of the water masses are not as pronounced as further south in the Atlantic (e.g. 450 Middag et al., 2018). The nutrient-type elements (Cd, Cu, Ni, Zn) showed increases in dissolved concentrations with depth, also reflected by total dissolvable distributions (see SI 451 Figs. S10, S11, S12). Concentrations of DZn were lowest in Modified North Atlantic Water 452 453 (MNAW (see SI): 0.3-0.8 nM) and increased gradually (to ca. 1.8-2.0 nM) in deeper Labrador 454 Seawater (LSW), Iceland-Scotland Overflow Water (ISOW) and Denmark Strait Overflow Water (DSOW) (Fig. 5, 6, and SI Text S2 for water masses), in agreement with reports from 455 the GEOTRACES GA02 section (Middag et al., 2019). A shallower increase in DCd was 456 457 observed, relative to Zn, as also indicated in Fig. 4, with concentrations in the deeper waters reaching ca. 0.24 nM; these observations agree with those (0.2-0.26 nM for North Atlantic 458 459 Deep Water (NADW) in IRB north of 60°N) reported for the GEOTRACES GA02 section (Middag et al., 2018). Dissolved Cu showed a concentration increase with depth that was 460 intermediate between Zn and Cd, likely related to its hybrid behaviour associated to 461 scavenging upon release following remineralisation (Bruland et al., 2014). Similar DCu trends 462 in the water column are also shown in Cu isotope studies indicating preferential removal of 463 lighter isotopes onto particles (Little et al., 2018; Takano et al., 2014). Nevertheless, the 464 difference between TDCu and DCu was small in deep waters (Fig. 4) indicating a small 465 particulate Cu stock. Deep water DCu concentrations ranged between 1.40-1.60 nM and 466 agree with those reported for the NW Atlantic of 1.70 nmol kg⁻¹ (Bruland and Franks, 1983). 467 Maxima in DCu of ca. 1.70 nM in bottom waters (e.g. Fig. 5), also reflected in TDCu maxima 468 469 of up to ca. 1.9 nM, were associated with DSOW and ISOW with likely additional benthic inputs of Cu as suggested by (Boyle et al., 1977), and also indicated in a Cu isotope study 470 (Little et al., 2018). Similar to DCu, the surface water concentrations of DNi were not strongly 471 depleted with concentrations always >1.4 nM. DNi showed a shallower remineralisation 472 compared to DCu, and lower concentrations in the MNAW than the LSW or DSOW/ISOW. 473 474 The DNi concentration in our study agree well with values ranging between 3.6 and 4.2 nM in 475 DSOW and LSW reported by (Middag et al., 2020). As indicated in Fig. 4, the difference

476 between TDNi and DNi was noticeable and showed that Ni has a larger particulate stock compared with Cd, Cu or Zn. Between ca. 5-20% of TDNi occurred in a reactive particulate 477 form in the water column, with highest fractions in the top of the water column, likely 478 associated with biogenic material. Nevertheless, the remnants of a particulate Ni fraction at 479 480 depth, indicates that not all Ni is associated with a biogenic fraction that can be readily 481 remineralised by microbial processes. The particulate fraction is unlikely to be lithogenic, as 482 much higher particulate Fe values would be expected throughout the water column than reported for this study (Achterberg et al., 2018). Assuming congruent dissolution of Fe and Ni 483 from crustal origin (Wedepohl, 1991) or ash from the Eyjafjallajökull volcano (Achterberg et 484 485 al., 2013), this would supply between 1300 and 1600 times more Fe relative to Ni, and there is no evidence of this (see Fig. 5). Particulate Ni therefore appears to be locked up in an 486 487 unknown organic fraction.

The DAI concentrations ranged between ca. 2 nM in surface waters to 24 nM at depth, with 488 some spatial variability and highest concentrations in the ISOW and DSOW (e.g. Fig. 5), and 489 are in good agreement with those reported (ca. 1.7-23 nM) for the IB and IRB (Menzel 490 Barraqueta et al., 2018). Increases of DAI with depth have been related to sinking opaline 491 492 material and dissolution at depth as reflected in Si distributions (Gehlen et al., 2002; Menzel 493 Barraqueta et al., 2018), and agree with observations in the Mediterranean (Rolison et al., 2015). Our observations contrast with distributions displaying elevated DAI in surface waters, 494 associated with atmospheric inputs, and decreases with depth related to scavenging, as has 495 496 been observed in the low latitude North Atlantic (Measures et al., 2015) and Pacific Ocean (Orians and Bruland, 1986). 497

Enhanced DPb was observed in LSW with concentrations up to ca. 30-40 pM (e.g. Figs. 5 498 and 7). Similar observations of elevated DPb in LSW have previously been reported 499 (Zurbrick et al., 2018), and attributed to historical atmospheric anthropogenic Pb inputs to the 500 N Atlantic. Lower DPb concentrations in ISOW and DSOW (5-15 pM; Figs. 5 and 6), agree 501 502 with those reported by (Zurbrick et al., 2018). The dynamic behaviours of Co and Mn, with strong input and removal processes, coupled to the presence of relatively young water 503 504 masses in the high latitude North Atlantic, meant that no distinct elemental signatures could 505 be observed in the various water masses (Fig. 5, 6).

506 An important feature along the three deep ocean sections is the elevated concentrations of DMn (up to 0.96 nM), TDMn (up to 3.25 nM), DCo (up to 94 pM), TDCo (up to 135 pM), DAI 507 508 (up to 19 nM) and TDAI (up to 104 nM) over the Reykjanes Ridge (also associated with enhanced DFe (up to 1.03 nM) and TDFe (up to 57 nM) (Achterberg et al., 2018)). 509 particularly on the eastern flank. The elevated concentrations are likely largely driven by 510 511 enhanced turbulent mixing over the Reykjanes Ridge with resuspension of sunken particles, with perhaps a contribution by hydrothermal inputs (Achterberg et al., 2018). Internal tides, 512 near-inertial waves and mean flows cause the deep turbulent mixing over the rough 513 514 topography of mid-ocean ridges (Clément et al., 2017; St Laurent and Thurnherr, 2007). The 515 mixing over the Reykjanes Ridge will transfer sedimented particulate material into the water column, with associated dynamic exchange of dissolved Mn, Co, Al (and Fe). Removal of 516 DPb through particle scavenging is evident in the vicinity of the Reykjanes Ridge, with 517 concentrations down to 16.5 pM. Similar observations of depleted DPb (ca. 7 pM) have been 518 519 reported over the mid-Atlantic Ridge (at TAG) for GEOTRACES cruise GA03 (Noble et al., 520 2015).





Figure 5: Section plots of dissolved trace elements, nitrate+nitrite (TON), silicic acid and salinity on a transect along 60°N with data from summer 2010. Main water masses indicated in salinity panel and explained in SI Text S2. MNAW: Modified North Atlantic Water; LSW: Labrador Seawater; ISOW: Iceland-Scotland Overflow Water; DSOW: Denmark Strait Overflow Water. Figures were produced using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2017).



531

532 Figure 6: Section plots of dissolved trace elements, nitrate+nitrite (TON), silicic acid and

salinity on a transect across the Reykjanes Ridge at 62°N with data from summer 2010. Main

water masses indicated in salinity panel and explained in SI Text S2. MNAW: Modified North 534

Atlantic Water: LSW: Labrador Seawater: ISOW: Iceland-Scotland Overflow Water: DSOW: 535

Denmark Strait Overflow Water. Figures were produced using Ocean Data View (Schlitzer, 536

537 R., Ocean Data View, odv.awi.de, 2017).

538



539 540

Figure 7: Section plots of dissolved trace elements, nitrate+nitrite (TON), silicic acid and 541 salinity on a transect along 60°N onto the Greenland shelf with data from summer 2010. Main 542 543 water masses indicated in salinity panel and explained in SI Text S2. ECG: East Greenland Current; LSW: Labrador Seawater. Figures were produced using Ocean Data View 544

- (Schlitzer, R., Ocean Data View, odv.awi.de, 2017). 545
- 546

The fourth section was from 41.4°W along 60°N onto the Greenland shelf (Fig. 7). The redox 547 sensitive element Mn showed elevated surface dissolved concentrations of 0.35 nM at ca. 60 548 km off the coast and increasing to >1.35 nM at ca. 30 km off the coast (also see Fig. 3). The 549 DMn increase in coastal waters was coincident with a reduction in salinity indicating the 550 occurrence of EGC waters with reduced temperatures (from 9.14 to 5.83°C) and salinities 551 552 (from 34.99 to 33.84) as a consequence of freshwater advection south through Fram Strait in addition to local glacier and iceberg melt water inputs from Greenland (Sutherland et al., 553 554 2009). The DMn concentrations on the Greenland shelf (200 m water depth) reached >2 nM 555 and were fairly constant below ca. 40 m depth, coinciding with elevated DFe values (up to 1 556 nM; (Achterberg et al., 2018)) indicating a benthic release of these elements following reductive dissolution (Burdige, 1993). Concentrations of TDMn were also elevated in the 557 Greenland shelf waters and showed an increase near the seafloor to values of 6.83 nM, as a 558 consequence of scavenging/precipitation of DMn diffusing out of the sediments and/or 559 560 sediment resuspension (SI Fig. S13). The dissolved concentrations of the redox sensitive element Co on the Greenland shelf in the EGC (0.03-0.12 nM) were lower or comparable to 561 subsurface waters off shelf (ca. 0.09-0.11 nM), indicating a low continental and Arctic Ocean 562 supply with limited benthic release and/or important scavenging removal. The TDCo 563 concentrations on the Greenland shelf were between 30% and 300% higher than DCo. 564 565 indicating an important role for transfer of DCo onto particles (Moffett and Ho, 1996).

Trends in DCd and DZn along this section showed similarities to nutrients, with lower surface levels and an increase with depth. Dissolved Cd showed a pronounced difference between surface and deep water concentrations (e.g. station 13: 0.024 nM surface and 0.22 nM at 300 m). Dissolved Cu and DNi showed elevated concentrations on the Greenland shelf in the EGC, with invariable concentrations with depth and an absence of surface water depletion, likely as a result of enhanced supply and a minimal removal through biological activity.

572 Dissolved Pb concentrations along the section were similar to other parts of the IB and IRB, 573 and ranged between 0.017-0.03 nM, including concentrations up to 0.024 nM in the EGC, 574 with little depth-related variation, and >80% of Pb in the dissolved phase. The surface water 575 concentrations of DAI ranged between ca. 0.9-2.8 nM with TDAI being up to 10 times higher, 576 and deep water DAI levels increased to 7 nM on shelf and 14 nM off shelf with TDAI being 577 several fold higher.

Clear differences are apparent between the distributions of the various elements. We used 578 579 principal component analysis (PCA) with the full dataset to determine relationships between various oceanographic variables and hence suggest which processes dominate observed 580 combined trace element distributions in an overall statistical sense (Fig. 8). The first principal 581 component axis (PC1) explains 48% of the variance and represents mainly depth dependent 582 increases in nutrients and trace elements involved in biological processes and controlled by 583 584 organic matter production and remineralisation, including DCd, DZn, DCu and DNi but potentially also DPb and DAI. Phosphate and DCd correlate as does Si with both DZn and 585 DAI, in accordance with previous studies (Bruland et al., 2014; Menzel Barraqueta et al., 586 2018; Middag et al., 2019; Xie et al., 2015). The PCA results also agree with elevated 587 Pearson correlations for the relationships of DCd, DZn, DCu and DNi with depth (r=0.50, 588 0.59, 0.45 and 0.32, resp.), TON (r=0.91, 0.51, 0.28 and 0.39, resp.), phosphate (r=0.90, 589 0.58, 0.42 and 0.39, resp.) and silicic acid (r=0.83, 0.67, 0.43 and 0.46, resp.) (SI, Table S3). 590 Enhanced Pearson correlations were observed for the relationships of DPb and DAI with 591 592 TON (r=0.46 and 0.53, resp.), phosphate (r=0.46 and 0.51, resp.) and silicic acid (r=0.29 and 0.75, resp.) (SI, Table S3). Whilst DPb and DAI distributions are known to be influenced by 593 atmospheric inputs, sediment supply, and scavenging (Measures and Vink, 2000; Menzel 594 595 Barraqueta et al., 2019; Rusiecka et al., 2018), an association of AI with diatom frustules (Menzel Barraqueta et al., 2018) and Pb with organic matter remineralization and sediment 596 597 supply (Rusiecka et al., 2018) has recently been reported. A role of Mn and Fe in DPb cvcling (but not DAI) is suggested by negative Pearson correlations (r = -0.45 and -0.35 for 598 DPb with TDMn and TDFe, resp.) indicating lower DPb at elevated particulate Mn and Fe 599 600 concentrations related to scavenging.

601 Dissolved Mn, Co and Fe are micronutrients, and in Fig. 8 fall on the trajectory of the other nutrient-type elements (e.g. Cd), but less of their variance is explained by PC1, indicating 602 that processes other than biological uptake and remineralization influenced their 603 604 distributions. Whilst these redox sensitive elements have elevated concentrations in oxygen 605 minimum zones as a result of benthic supply (Bruland et al., 2005; Rapp et al., 2019; Schroller-Lomnitz et al., 2019), no association with low oxygen is notable in Fig. 8 and their 606 variance is not explained by the oxygen/salinity correlated PC2. As might be expected, the 607 dissolved concentrations of Mn, Co and Fe therefore appear to be determined by a 608 609 combination of factors including supply strength, biological uptake and remineralization, 610 characteristics and abundance of particles, and water mass age and mixing.

Plots of nutrients versus trace elements (Figs. S6-S8) confirm the findings of the PCA and 611 Pearson correlations, and show the strong relationships between Si and DZn, and 612 TON/phosphate and DCd. The slopes of the DZn-Si (DZn-PO₄) relationship were 0.084 613 (0.50) for <5 µM Si (<0.75 µM PO₄) and 0.201 (2.79) for >5 µM Si (>0.75 µM PO₄), and 614 compare fairly well with slopes of 0.14 (3.0) for waters between 57.5°N and 64°N reported by 615 (Middag et al., 2019) for cruise GA02. Furthermore, the slope of the DNi-PO₄ relationship 616 was 1.04 and compares well with slopes of 1.4 for N Atlantic Central Waters between 50°N 617 618 and 64°N and 0.6 for North Atlantic Subpolar Mode Waters reported by (Middag et al., 2020).

The slope of the DCd-PO₄ relationship was 0.217 and compares well with slopes between 0.2-0.24 for the waters between 50°N and 64°N for GA02 reported by (Middag et al., 2018). The DCd-PO₄ slope is indicative of surface waters and relatively young Atlantic waters with <1.3 μ M PO₄ and a regression through the origin, with Indian, Pacific and Southern Ocean sourced waters providing a steeper slope and a resulting kink at >1.3 μ M PO₄ and a regression with a non-zero intercept (de Baar et al., 1994).



Figure 8: Principal component analysis for IBIS data set. Component scores of each sample are shown as grey circles. Principal component loadings for each variable are shown by black vectors. Loadings/scores have been scaled symmetrically by the square root of eigenvalues.

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631 **3.5 Trace element supply to surface waters of the IB and IRB.**

The transfer of trace elements to surface waters for the following sources has been estimated: (i) atmospheric inputs, (ii) winter convective supply, (iii) diffusive fluxes, whilst it is assumed that the horizontal fluxes are small as the horizontal concentration gradients off shelf were relatively minor (also see (Achterberg et al., 2018)).

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3.5.1 Atmospheric supply. Atmospheric concentrations of soluble and total trace elements 637 638 determined using direct aerosol sampling on the spring and summer cruises are presented in Tables 3 and SI Table S4, respectively. The summer cruise observations (fine and coarse 639 640 fractions combined; Table 3) for soluble AI, Mn, Cu and Ni were within the range of concentrations reported for these elements in remote North Atlantic aerosols from the AMT 641 18-21 cruises (soluble AI: 25-862 pmol m⁻³, soluble Mn: 0.4-46 pmol m⁻³, soluble Cu, 1.8-642 22.3 pmol m⁻³, soluble Ni: 1.2-18.4 pmol m⁻³), using the same leaching procedure as our 643 study (Baker and Jickells, 2017). Soluble Zn concentrations were a little lower than those 644 reported by Baker and Jickells (2017) (36-530 pmol m⁻³). Aerosol concentrations in the 645 vicinity of Iceland (between 59.1°N and 62.8°N, 20°W; CLIVAR A16) for deionised water 646 soluble AI ranged between 70-125 pmol m⁻³, Mn between 1.6-2.2 pmol m⁻³ and Pb 0.4-0.6 647 pmol m⁻³ (Buck et al., 2010), and were therefore similar to our summer cruise observations 648 (fine and coarse fractions combined; Table 3). Reported aerosol concentrations (Shelley et 649 al., 2018) from GEOTRACES cruise GA01 in the high latitude North Atlantic (sample G13, 650 59.6°N and 38.9°W) for soluble AI (45.9 pmol m⁻³), Ni (0.322 pmol m⁻³), Co (0.005 pmol m⁻³), 651 Cd (0.002 pmol m⁻³) and Pb (0.290 pmol m⁻³) (25% acetic acid leach) were similar to our 652 summer cruise observations (fine and coarse fractions combined; Table 3), but their Mn 653

654 (0.133 pmol m⁻³), Zn (0.330 pmol m⁻³), Cu (0.107 pmol m⁻³) concentrations were lower than 655 ours. Our observations for soluble trace element concentrations are therefore in reasonable 656 agreement with literature values, whilst recognising that individual observations made during 657 cruises do not reflect the intra-annual variability of aerosol concentrations in the high latitude 658 North Atlantic that can be important (Prospero et al., 2012).

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660 In some cases, soluble element concentrations in the spring non-volcanic samples (TM02-661 06) were up to several fold (Al, Mn, Pb) or more than an order of magnitude (Cu, Cd) higher than their respective concentrations in the summer. In particular, the concentrations for 662 663 samples TM04-06 in the IB were above background levels, probably as a result of longerrange transport of ash from the eruption, as indicated by airmass back trajectories (SI Figs. 664 665 S14-S16). The increases were not consistent with the proportions in which the elements were observed in samples collected under the ash plume, which could possibly be related to 666 667 changing properties of ejected materials during different phases of eruption, and/or contributions of additional aerosol sources to these spring samples. Size fractionated aerosol 668 soluble Cu, Ni, Co, Cd concentrations for the < 1 μ m and > 1 μ m fractions observed during 669 the summer cruise were approximately equal at some stations. For soluble Pb, the < 1 μ m 670 fraction was ca. 2-6 times higher than the > 1 μ m fraction, and for soluble Zn between 1.5-9 671 times, as also reported by (Arimoto and Duce, 1986; Fomba et al., 2013) and related to their 672 673 industrial sources from high temperature combustion processes. Concentrations of the soluble Mn fraction of < 1 μ m were between 1.1 and 6 times smaller than the > 1 μ m fraction, 674 and for soluble AI ranging from equal to 17 times smaller, in accordance with the lithogenic 675 nature of these elements (Arimoto and Duce, 1986; Baker and Jickells, 2017; Fomba et al., 676 677 2013).

678

679 Rates of dry deposition of soluble trace elements are presented in Table 4, and for many elements (Al, Mn, Co, Cd, Pb) these fluxes were higher by factors of 9 - 113 under the 680 681 Eyjafjallajokull volcanic ash plume (spring TM07-09) than for all other samples (ratios of median volcanic to median non-volcanic fluxes). The spatial extent of the direct volcanically-682 derived input fluxes thus appeared to be restricted to waters in the vicinity of Iceland 683 (Achterberg et al., 2013; Gudmundsson et al., 2012). Chemical analysis of Eyjafjallajokull 684 ash collected at sea during cruise D350 indicated 7.91% Al and 0.17% Mn by weight, 173 µg 685 g⁻¹ Zn, 55.2 µg g⁻¹ Ni, 4.53 µg g⁻¹ Pb (sample EYJ 04; SI, Table S5; data from (Achterberg et 686 al., 2013)), consistent with other reports for this material (Gislason et al., 2011) who 687 additionally report on Cu (35 µg g⁻¹) and Co (33 µg g⁻¹). The solubilities of the aerosol 688 689 samples (defined as the ratio of soluble to total element concentration) affected by the 690 volcanic emissions were lower compared to other samples (SI, Table S6). However, it should be noted that in some cases (particularly for Ni) total element concentrations were below 691 692 detection limit and only minimum values for solubility could be determined. For example, the median solubilities of the ash plume samples were 0.92% for AI and 0.96% for Mn, compared 693 to medians of 8.8% and 27% respectively for the other samples. Similar patterns in solubility 694 between the ash and non-volcanic samples were apparent for the other trace elements, with 695 the possible exception of Cd (see SI, Table S6). The soluble trace element inputs to the 696 surface ocean related to ash deposition are likely dominated by a highly soluble salt layer (up 697 to 300 nm) of metal halides and sulphates formed on the ash particles within the volcanic 698 plumes and during their onwards transport through coagulation with aerosol (i.e. SO₄) and 699 700 the condensation of acidic gases (i.e. SO₂, HCl, HF) (Duggen et al., 2010; Gislason et al., 2011). The main ash fraction had a mean grain size of 123 µm and would have settled 701 702 through a 30 m mixed layer in ~1.5 h (Achterberg et al., 2013), and therefore the short 703 residence time and the relatively low elemental solubilities of the ash limit the inputs for a range of soluble elements including Co. Cd. Cu. Ni and Pb related to the eruption of the 704 705 Eyjafjallajokull volcano. This is also evidenced by a lack of elevated surface water concentrations for these elements in the vicinity of Iceland during the spring cruise (Fig. 2). 706 707

3.5.2 Diffusive vertical fluxes. Diffusive dissolved trace element fluxes were determined during summer 2010 at 21 stations, and the data compiled for annual fluxes in the IB and

710 IRB (Table 5). In general, there was widespread variability in the direction and magnitude of diffusive trace element fluxes, with fluxes both into and out of the mixed laver estimated. The 711 annual diffusive fluxes for the IB and IRB were similar for dissolved Cd and Pb, with three 712 713 times higher Co fluxes in the IRB and two times lower Mn fluxes in the IRB compared to the 714 IB. The annual fluxes had opposite directions in the IB and IRB for dissolved Ni, Zn, Cu and 715 Al. The variability in annual diffusive fluxes for the various elements was a function of near-716 surface elemental gradients, which is related to elemental removal by biological uptake and scavenging, and supply by organic matter remineralisation at the base of the mixed layer. 717 Consequently, the overall picture of diffusive elemental supply to surface waters in our study 718 719 area during summer is variable with no clear geographical or regional patterns.

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3.5.3 Convective supply. There is a paucity of data on the winter convective supply of trace 721 elements to surface waters of the high latitude North Atlantic. Annual convective DFe inputs 722 723 have been reported for the IB (Forryan et al., 2012), and DFe and DAI for our cruise 724 programme covering a wider geographical region, including both the IB and IRB (Achterberg 725 et al., 2018; Painter et al., 2014), and using a similar technique to Forryan et al. (2012). Here we employed the same approach, and determined convective trace elements inputs to 726 727 surface waters of the IB and IRB during winter 2010. The convective supply of dissolved Co, Mn, Ni, Cd, Cu, Pb, Zn and Al all showed positive values (Table 5), indicating that subsurface 728 729 stocks with elevated concentrations were accessed during deep winter mixing, which resulted in a replenishment of depleted surface water stocks. Consequently, the winter 730 731 mixing was deeper than for example the ferricline or nutricline (Rigby et al., 2020; Tagliabue 732 et al., 2014). This was also the case for the scavenged-type element Mn, which in many 733 ocean regions shows vertical profiles with a depletion with depth due to scavenging, resulting in a dilution by winter mixing of surface water stocks in the Atlantic between 40°S and 40°N 734 735 (Rigby et al., 2020). The positive Mn supply through convective mixing was related to the 736 surface ocean depletion observed for DMn in this study (Fig. 4) which is then resupplied 737 during winter from deeper water pools. The convective supply rates were remarkably similar for all the elements between the IB and IRB, with typically less than 10% difference, despite 738 differences in deep winter mixing depths (IB 350 m, IRB 200 m). This is in contrast to 739 740 convective DFe supply, which was nearly four times higher in the IB compared to the IRB (Painter et al., 2014), with the difference related to differences between DFe profiles. Winter 741 mixing depths also change on an interannual basis, with reported depths for the IB of 600 m 742 743 previously used (Forryan et al., 2012) for DFe convective supply calculations for winter 2007. 744

745 the magnitude of estimated convective fluxes indicated that diffusive supply of trace 746 elements was a small supply term to the surface mixed layer relative to convective mixing, 747 ranging from -2.43% for DZn to 13.5% for DCd in the IB to -0.63% for DAI to 6.87% for DCd 748 in the IRB (Table 5). The atmospheric fluxes relative to the combined convective+diffusive fluxes were largest for DAI (9.1% in IB, and 42% in IRB) which has a known atmospheric 749 supply route (Menzel Barraqueta et al., 2019). For the other elements, the atmospheric 750 fluxes were relatively small and less than 4.2% for DZn and 0.13% for DCd, and even less 751 752 than 2.57% for DPb which has a known atmospheric supply route to the oceans (Boyle et al., 753 1986, 2014). The observed atmospheric inputs and diffusive vertical fluxes are subject to temporal and spatial variability and have an inherent uncertainty, but overall indicate that 754 755 these fluxes of dissolved trace elements into the IB and IRB are significantly lower than the 756 fluxes associated with winter mixing.

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Convection thus played a dominant role in the supply of dissolved elements to the surface 758 759 waters, with total supply ratios (relative to P) that were very similar in both basins (Table 2), in agreement with the similarities between supply rates through convection (see above and 760 761 Table 5). The supply ratios of the various elements are determined by the shape of their vertical profiles and the depth of winter mixing in the respective basin. As a consequence, 762 763 the trace element: P supply ratios for Zn, Cu, Mn and Fe were similar and ca. 4 times higher than Cd, ca. 10 fold higher than Co, ca. 25-30 times higher than Pb, but ca. 4-7 times lower 764 765 than AI (Table 2). As mentioned above, the Fe supply ratio was more than 3 times higher in

the IB than the IRB, and related to differences in vertical DFe profiles (Achterberg et al., 766 2018). To first order, total elemental supply ratios were comparable to the apparent removal 767 ratios we calculated between spring and summer (Table 2), suggesting an overall balance 768 769 between multi-element supply and biologically mediated export stoichiometry in the region. 770 The reasonable agreement occurred despite the different time windows used for the ratio 771 calculations (spring to summer concentration differences for removal ratio and winter 772 convection for supply ratio). Supply ratios were however generally higher than removal ratios relative to P over the sampled periods (Table 2), with some variability between the trace 773 metals. The overall tendency for supply ratios to exceed removal from spring to summer may 774 775 reflect preferential remineralisation of the trace metals in these surface waters relative to P (Boyd et al. 2017; Rafter et al. 2017). Further elevated supply ratios relative to removal for 776 the redox sensitive and scavenged-type elements (Fe, Mn, Co, Pb) may then be related to 777 additional dissolved-particle phase processes (colloid formation and scavenging without 778 779 coinciding P removal, taking place year-round) which will ultimately influence both surface 780 retention (Boyd et al. 2017) and subsurface profiles (Fig. 4) and hence convective re-supply 781 to the surface.

4 Conclusions

This study provides a unique picture of changes from spring to summer in trace element concentrations in the high latitude North Atlantic, a region with pronounced spring blooms and deep water formation. The eruption in spring 2010 of the Eyjafjallajökull volcano resulted in pronounced increases in Al, Mn and Zn in surface waters near Iceland, with concentrations returning to more typical values for the region in summer.

789 Convective mixing formed the dominant supply mechanism of multiple trace elements to the 790 surface waters, with elemental ratios (relative to P) of convective supply similar to ratios of 791 likely biologically dominated removal. The convective fluxes of bio-essential elements and 792 nutrients would be expected influence magnitude and duration of the high latitude North 793 Atlantic spring bloom, setting an upper bound on export potential from the system (Nielsdottir et al. 2009; Forryan et al 2012; Painter et al. 2014), although additional control by light 794 795 availability and loss process due to zooplankton grazing could potentially result in this upper 796 bound not being achieved. Interannual variability in the strength of the convective supply 797 might thus influence biological productivity in the region. Over the mid Atlantic ridge, maximum winter mixing depths along 60°N do not usually exceed 300 m (de Boyer Montégut 798 799 et al., 2004), in agreement with depths down to 400 m as observed at moorings in the central IB (de Jong et al., 2012), however extreme mixing depths of 1 km are possible in cold 800 801 winters. Therefore, during cold winters the trace element supply to surface waters by 802 convective mixing will be further enhanced. Atmospheric inputs are often considered to form an important source of bio-essential elements to the surface ocean (Duce et al., 1991). 803 804 However, we show that atmospheric and also diffusive fluxes were low compared to convective fluxes in the high latitude North Atlantic, but nevertheless they provide a 805 806 sustained trace element supply during the summer period after the winter mixing derived elements may have been depleted. 807

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In contrast, ocean warming is considered to result in upper ocean density stratification. A 809 significant strengthening of stratification (3.3-6.1% increase of mean stratification) has been 810 observed in ~40% of the global ocean since the 1960s (Yamaguchi and Suga, 2019). A 811 shoaling of the maximum depths of winter mixing is projected in climate models as a 812 consequence of the increased stratification (Capotondi et al., 2012). For our study region, 813 814 assuming it behaves as the global mean, this would likely result in a reduced supply of 815 nutrients and trace elements, and therefore a reduction in productivity and potentially carbon export. Projections for the North Atlantic subpolar avre indicated that with a 20% reduction in 816 maximum deep winter mixing depth, a reduced supply of all elements will occur, with the 817 exception of scavenged-type elements, where a reduced dilution of elevated surface ocean 818 819 stocks might result (Rigby et al., 2020).

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821 Upper ocean stratification is also considered to reduce the transfer of trace elements and

nutrients from the deep ocean to the surface mixed layer through upwelling and diapycnal diffusion, as the barrier to transfer across the main thermocline will strengthen (Yamaguchi and Suga, 2019). A reduced advective and diffusive supply of (micro-)nutrients to the surface mixed layer in the subpolar North Atlantic will further enhance the relative importance of seasonal convective mixing, provided that the (micro-) nutrient-clines remain at shallower depths than the maximum winter MLD. Future Icelandic volcanic eruptions could thus have a larger relative impact than presented here for the same deposition magnitude.

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 doi:10.5194/bg-15-4995-2018.

1178 **Table 1.** Ranges and average concentration values for TON and dissolved and total

1179 dissolvable trace elements in surface waters of the high latitude North Atlantic (excluding

1180 shelf waters). A regional concentration comparison between the Iceland (IB) and Irminger

(IRB) Basins is presented, as well as a seasonal comparison between the spring (D350/351)

and summer cruise (D354) of 2010 for each basin; Student t-test was undertaken with a 95%

1183 significance threshold. BD: below detection limit.

	Range	Average all (± SD)	Average IB (± SD)	Average IRB (±SD)	t-test (IRB vs IB)	t-test P value (seasonal comparison IB)	t-test P value (seasonal comparison IRB)
Spring cruises							-
DCo (pM)	22.9– 109	52.8 (±11.0) n = 103	52.2 (±7.49) n = 45	50.7 (±5.65) n = 20	0.40	0.00	0.00
TDCo (pM)	72.2– 336	(± 36.1) n = 64	(± 46.5) n = 29	95.6 (±5.29) n = 7	0.75	0.009	0.03
DMn (nM)	0.22– 8.73	(± 1.06) n = 103	(± 0.09) n = 45	(± 0.07) n = 20	0.025	0.015	0.006
TDMn (nM)	0.48– 10.5	(± 2.14) n = 64	(± 1.83) n = 29 118	(±0.39) n = 7 170	0.098	0.31	0.25
DCd (pM)	36.9– 197	(±41.7) n = 103 181	(±32.0) n = 45 195	(± 17.4) n = 20 170	0.00	0.00	0.00
TDCd (pM)	102– 313	(± 42.0) n = 69	(±47.6) n = 29 1 14	(±29.7) n = 7 1 16	0.098	0.00	0.19
DCu (nM)	0.70 – 2.28	(±0.19) n = 103 1 21	(±0.11) n = 45 1 17	(± 0.03) n = 20 1 21	0.26	0.00	0.00
TDCu (nM)	0.96 – 2.16	(±0.23) n = 69 3.23	(±0.15) n = 29 3.32	(±0.06) n = 7 3.18	0.30	0.015	0.002
DNi (nM)	1.41– 4.14	(±0.31) n = 103 3.80	(±0.22) n = 45 3.76	(±0.24) n = 20 3.91	0.038	0.00	0.00
TDNi (nM)	2.75– 7.05	(± 0.48) n = 69 0.32	(±0.16) n = 29 0.29	(± 0.09) n = 7 0.33	0.0046	0.04	0.85
DZn (nM)	0.07– 1.24	(±0.16) n = 97 0.74	(± 0.14) n = 41 0.64	(± 0.11) n = 20 1.62	0.23	0.00	0.00
TDZn (nM)	0.09– 7.19	(± 0.89) n = 64 3 44	(±0.36) n = 28 2.51	(± 2.46) n = 7 2.60	0.33	0.00	0.23
DAI (nM)	0.27 – 44.8	(±5.64) n = 105 23.4	(±1.87) n = 45 21 9	(±2.08) n = 20 25.0	0.88	0.00	0.00
DPb (pM)	14.8– 36.3	(±3.87) n = 103	(±3.33) n = 45	(± 2.02) n = 20	0.00	0.00	0.00
TDPb (pM)	20.9– 99.3	30.7 (±14.2) n = 69	29.3 (±15.6) n = 29	27.7 (±1.97) n = 7	0.59	0.006	0.03

NO₃ (μΜ)	4.94– 14.5	9.96 (±2.54) n = 94	9.08 (±1.82) n = 43	12.6 (±0.99) n = 19	0.00	0.00	0.00
Summe cruise	r						
DCo (pM)	20.6– 46.1	37.6 (±11.0) n = 84	32.3 (±5.69) n = 25	40.8 (±11.1) n = 42	0.00		
TDCo (pM)	5.3– 117	75.3 (±23.3) n = 35	71.4 (±9.7) n = 5	76.6 (±30.0) n = 15	0.57		
DMn (nM)	0.24 – 1.35	0.43 (±0.15) n = 84	0.46 (±0.09) n = 25	0.41 (±0.11) n = 20	0.029		
TDMn (nM)	0.03– 1.96	0.72 (±0.31) n = 35	0.76 (±0.16) n = 5	0.69 (±0.28) n = 15	0.49		
DCd (pM)	4.45– 93.7	(± 19.9) n = 87	(± 11.2) n = 26	(±17.1) n = 44	0.00		
TDCd (pM)	55.9– 274	(± 62.3) n = 41	(±31.6) n = 10	(±40.5) n = 15	0.00		
DCu (nM)	0.85 – 1.83	0.97 (±0.14) n = 87	0.93 (±0.04) n = 26	0.99 (±0.13) n = 44	0.006		
TDCu (nM)	0.97 – 1.65	1.10 (±0.11) n = 41	1.08 (±0.07) n = 10	1.09 (±0.04) n = 15	0.62		
DNi (nM)	2.09– 3.44	(± 0.23) n = 85	(±0.25) n = 26	2.65 (±0.18) n = 42 3.89	0.003		
TDNi (nM)	3.11– 4.33	(± 0.32) n = 41	(±0.29) n = 10	(±0.25) n = 15	0.004		
DZn (nM)	0.02– 0.23	(± 0.05) n = 68 0.40	(±0.06) n = 19 0.15	(±0.056) n = 37 1.09	0.59		
TDZn (nM)	0.02– 4.65	(±0.81) n = 34 0.94	(±0.13) n = 5 1.22	(±0.04) n = 15 0.056	0.15		
DAI (nM)	0.10– 4.81	(±0.84) n = 89 17.7	(±0.72) n = 26 16.0	(±0.73) n = 43 16.4	0.00		
DPb (pM)	10.1– 104	(±9.64) n = 87 23 7	(±2.86) n = 26 20.6	(±1.57) n = 44 24 6	0.55		
TDPb (pM)	16.8– 37.9	(± 4.3) n = 41 2 24	(±1.9) n = 10 0 57	(±4.3) n = 15 2 86	0.004		
NO₃ (μΜ)	BD– 6.47	(±1.66) n = 74	(±0.76) n = 21	(±1.47) n = 40	0.00		

Table 2. Removal and supply ratios (in mmol:mol P) of dissolved trace elements relative to P (phosphate) out of and into the surface waters of the Iceland Basin (IB) and Irminger Basin (IRB). Removal ratios were calculated from the differences between spring and summer 2010 surface water

1187 concentrations (Table 1), and supply ratios were determined from winter convective mixing (Table 5), which was the dominant supply mechanism

1188 for dissolved elements. Dissolved Fe data was obtained from Achterberg et al. (2018) and P supply data (convective mixing) from Painter et al.

1189 (2014).

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	Removal ratio IB	Removal ratio IRB	Supply ratio IB	Supply ratio IRB
DAI	2.43	4.16	8.24	5.93
DNi	1.26	0.57	4.49	5.03
DZn	0.43	0.43	1.01	1.10
DCu	0.39	0.28	1.24	1.54
DFe	0.27	0.06	0.94	0.25
DCd	0.19	0.22	0.25	0.28
DMn	0.10	0.11	0.81	0.79
DCo	0.037	0.016	0.10	0.11
DPb	0.011	0.014	0.04	0.04

Table 3. Atmospheric trace element soluble concentrations (pmol m⁻³) during spring and summer 2010. (Spring cruise samples were collected in a single size fraction (Bulk), summer cruise samples were fractionated into particles <1 μ m and >1 μ m. a – Probable contamination). The latitudes and longitudes are the midpoints of acrospl sample collection; dates are at start point of collection. See Fig. S2 (SI) for acrospl sampling map

and longitudes are the midpoints of aerosol sample collection; dates are at start point of collection. See Fig. S2 (SI) for aerosol sampling map.

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	Start	Lat.	Long.		AI	N	In	Z	n	C	u	
	Date											
Spring				B	Bulk		Bulk		Bulk		Bulk	
TM02	28/04/2010	58.39	-20.92	69.6	±26.7	1.67:	±0.48	22.7	±4.3	60.6	±0.3	
TM03	29/04/2010	59.70	-30.62	190)±4.6	10.7:	±0.29	5.7=	±1.3	37.0)±0.2	
TM04	02/05/2010	59.98	-30.26	479	9±8.3	9.53	±0.62	577:	£130	218	±1.1	
TM05	05/05/2010	60.97	-22.88	425	5±4.9	11.6:	±0.54	14.2	±4.2	423	±2.1	
TM06	07/05/2010	62.50	-19.97	619	9±10	10.2:	±0.73	6.8	£2.1	26.2	2±0.2	
TM07	08/05/2010	63.10	-18.75	3358	6±103	327	±9.4	193	193±31		146±1.2	
TM08	08/05/2010	63.09	-19.08	1776	0±109	252±7.3		62-	£19	289	±1.7	
TM09	09/05/2010	63.39	-21.31	1280	0±450	25.6	±4.3	<4	10	147	±1.5	
Summer				<1 µm	>1 µm	<1 µm	>1 µm	<1 µm	>1 µm	<1 µm	>1 µm	
TM10	17/07/2010	60.00	-38.59	29.7±3.2	28.4±3.6	0.34±0.06	0.38±0.08	9.4±3.4	<2.4	3.6±0.5	0.8±0.4	
TM11	19/07/2010	60.72	-38.49	22.6±7.5	67.9±6.5	0.37±0.08	2.06±0.24	14.8±5.4	9.7±2.4	4.8±0.6	6.1±0.4	
TM12	23/07/2010	61.19	-32.98	29.9±3.8	512±4	0.45±0.06	1.09±0.12	<9.8	<4.6	1.5±0.5	1.6±0.3	
TM13	26/07/2010	59.42	-33.40	95.9±3.7	188.8±4.7	0.35±0.05	1.08±0.08	11.4±2.4	5.0±1.6	1.6±0.3	1.4±0.2	
TM14	29/07/2010	63.41	-29.43	1948±96 ^a	204±1.4	6.88±0.34 ^a	0.88±0.06	27.1±2.5 ^a	3.1±0.9	1.6±0.2	0.8±0.4	
TM15	04/08/2010	61.18	-22.42	44.8±2.6	82.2±4.0	0.65±0.06	0.82±0.10	<8.7	<5.4	2.0±0.4	1.4±0.7	

Table 3 continued.

	N	li	C	o	C	d	Pb		
	Bi	ılk	Βι	ılk	Bu	ılk	Bi	Bulk	
Spring									
TM02	1.11±0.10		<0.	031	13.2	±0.34	0.31±0.011		
TM03	<0	.25	0.084	±0.007	2.35	±0.09	1.61:	±0.01	
TM04	4.53:	±0.13	0.13:	±0.02	4.42:	±0.17	1.14	<u>+</u> 0.01	
TM05	0.96:	±0.08	0.12	±0.01	4.11:	±0.13	1.84:	±0.01	
TM06	0.73:	±0.14	0.13:	±0.02	4.48	±0.17	1.38:	±0.01	
TM07	<3	3.9	1.91±0.30		142±3.6		23.2±0.13		
TM08	2.88:	±0.78	1.97±0.17		73.3	±1.9	10.6	±0.08	
TM09	9.3:	±2.1	<0.60		14.0	±2.1	3.41:	±0.22	
					-				
Summer	<1 µm	>1 µm	<1 µm	>1 µm	<1 µm	>1 µm	<1 µm	>1 µm	
TM10	0.38±0.15	<0.11	0.086±0.015	0.055±0.013	0.087±0.003	0.011±0.002	0.85±0.06	<0.07	
TM11	0.61±0.95	0.88±0.94	<0.050	<0.071	0.15±0.005	0.11±0.003	0.48±0.10	0.32±0.03	
TM12	0.83±0.67	0.87±0.36	<0.036	<0.050	0.028±0.004	0.048±0.003	<0.21	<0.07	
TM13	0.53±0.53	.53 0.45±0.33 0.11±0		0.124±0.01	0.02±0.003	0.015±0.002	<0.15	<0.05	
TM14	1.47±0.44	0.72±0.36	0.075±0.01	0.071±0.01	0.12±0.002	0.017±0.001	<0.10	<0.04	
TM15	<0.27	0.17±0.27	<0.03	<0.043	0.08±0.003	0.016±0.003	0.24±0.06	<0.06	

	Al	Mn	Zn	Cu	Ni	Со	Cd	Pb
Spring								
TM02	42	1.0	2.0	5.2	0.096	<0.019	1.14	0.027
TM03	115	6.4	0.5	3.2	<0.018	0.051	0.20	0.139
TM04	289	5.8	49.9	18.9	0.391	0.078	0.38	0.098
TM05	257	7.0	1.2	36.5	0.083	0.074	0.35	0.159
TM06	374	6.2	0.6	2.3	<0.084	0.078	0.39	0.119
TM07	20300	198	16.7	12.6	0.218	1.16	12.2	2.00
TM08	10700	152	5.3	25.0	0.249	1.19	6.33	0.911
TM09	774	15.5	<2.9	12.7	0.803	<0.36	1.21	0.295
Summer								
TM10	27	0.4	2.3	1.0	0.105	0.055	0.017	0.115
TM11	61	1.8	9.7	5.6	0.815	<0.065	0.111	0.320
TM12	445	1.0	<4.8	1.5	0.820	<0.047	0.044	<0.080
TM13	171	1.0	5.3	1.4	0.434	0.117	0.015	<0.057
TM14	344	1.4	5.0	0.9	0.744	0.068	0.024	<0.041
TM15	75	0.8	<5.4	1.3	0.167	<0.040	0.021	0.061

Table 4. Calculated dry deposition fluxes (nmol $m^{-2} d^{-1}$) for soluble metals during the spring and summer cruises. Deposition fluxes are uncertain by a factor of 2-3 (Duce et al., 1991).

Table 5. Annual convective, diffusive and atmospheric trace element fluxes, with their uncertainties. Diffusive and atmospheric fluxes derived from observations made during summer cruise. The convective flux uncertainties are based on the use of mean and standard deviation estimates of the metal concentrations at the winter mixed layer depth of the respective basin. The uncertainties for the atmospheric fluxes are indicated as a range in brackets, with the range being the relevant flux value divided by, and multiplied by, an uncertainty of factor 2 in deposition velocity (Duce et al. 1991). The variability in atmospheric fluxes of the various elements is less than 20% for the samples collected in the respective IB and IRB, and therefore a more realistic flux range is presented based on the deposition velocity uncertainty.

	DCo	DMn	DNi	DCd	DPb	DZn	DCu	DAI
Iceland Basin								
Annual Diffusive Flux (µmol/m2/y)		2.07±0.25	-0.39±0.94			-0.89±1.44	-0.78±0	12.2±0.13
Annual Diffusive Flux (nmol/m2/y)	55.6±22.4			1198±56.1	55.6±24.6			
Convective Flux (mmol/m2/y)		0.03±0.01	0.18±0.02			0.04±0.02	0.05±0.01	0.29±0.05
Convective Flux (µmol/m2/y)	3.98±0.36			8.85±0.7	1.37±0.18			
Atmospheric Flux (µmol/m2/y)	0.011 (0.006- 0.022)	0.28 (0.14- 0.56)	0.06 (0.03- 0.12)	0.008 (0.004- 0.016)	0.012 (0.006- 0.024)	1.46 (0.73- 2.92)	0.48 (0.24- 0.96)	27.3 (13.7- 54.6)
Diffusive Flux as % Convective Flux	1.40±0.58	6.40±2.26	-0.22±0.53	13.5±1.24	4.05±1.86	-2.43±4.11	-1.55±0.93	4.24±0.73
Atmospheric Flux as % Convective+ Diffusive Fluxes	0.27±0.34	0.81±1.04	0.03±0.04	0.08±0.12	0.84±0.64	4.10±3.70	0.98±0.94	9.11±7.01
Irminger Basin								
Annual Diffusive Flux (µmol/m2/y)		1.11±1.33	0.82±1.39			2.20±2.1	0.80±0.43	-1.04±2.41
Annual Diffusive Flux (nmol/m2/y)	184±48.6			706±321	46.7±52.2			
Convective Flux (mmol/m2/y)		0.03±0.00 1	0.20±0.00 3			0.04±0.01	0.06±0.00 3	0.17±0.00 4
Convective Flux (µmol/m2/y)	4.18±0.03			10.3±1.03	1.55±0.03			
Atmospheric Flux (µmol/m2/y)	0.022 (0.011- 0.044)	0.38 (0.19- 0.76)	0.19 (0.1- 0.38)	0.014 (0.007- 0.028)	0.041 (0.02- 0.084)	1.86 (0.93- 3.66)	0.71 (0.35- 1.42)	68.4 (34.2- 137)
Diffusive Flux as % Convective flux	4.40±1.16	4.08±4.89	0.40±0.67	6.87±3.20	3.02±3.36	5.16±5.09	1.34±0.72	-0.63±1.46
Atmospheric Flux as %								
Convective+ Diffusive Fluxes	0.50±0.63	1.34±1.67	0.09±0.06	0.13±0.14	2.57±2.01	4.15± 3.27	1.16±1.75	41.7±31.3

Figure 1.



Figure 2.







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Figure 3.



DCd [pM] 100 65°N 80 60 60°N

DPb [pM] 25 65°N 20 15 60°N















Figure 4.

Figure 5.

35°W

30°W

DCo [nM]

DCd [nM]

DMn [nM]

DPb [nM]

DAI [nM]

Silicic Acid [uM]

DNi [nM]

DZn [nM]

TON (uM) [uM]

Salinity [psu]

Figure 6.

DCo [nM]

DCd [nM]

DCu [nM]

10°W

DMn [nM]

DPb [nM]

DAI [nM]

Silicic Acid [uM]

DNi [nM]

DZn [nM]

TON (uM) [uM]

Salinity [psu]

Figure 7.

DCo [nM]

DCd [nM]

DCu [nM]

80

DMn [nM]

DPb [nM]

DAI [nM]

Silicic Acid [µM]

DNi [nM]

DZn [nM]

ΤΟΝ [μΜ]

Salinity [psu]

Figure 8.

Table 1. Ranges and average concentration values for TON and dissolved and total dissolvable trace elements in surface waters of the high latitude North Atlantic (excluding shelf waters). A regional concentration comparison between the Iceland (IB) and Irminger (IRB) Basins is presented, as well as a seasonal comparison between the spring (D350/351) and summer cruise (D354) of 2010 for each basin; Student t-test was undertaken with a 95% significance threshold. BD: below detection limit.

	Range	Average all (± SD)	Average IB (± SD)	Average IRB (±SD)	t-test (IRB vs IB)	t-test P value (seasonal comparison IB)	t-test P value (seasonal comparison IRB)
Spring cruises						-	
DCo (pM)	22.9– 109	52.8 (±11.0) n = 103	52.2 (±7.49) n = 45	50.7 (±5.65) n = 20	0.40	0.00	0.00
TDCo (pM)	72.2– 336	97.4 (±36.1) n = 64	98.4 (±46.5) n = 29	95.6 (±5.29) n = 7	0.75	0.009	0.03
DMn (nM)	0.22– 8.73	0.72 (±1.06) n = 103	0.52 (±0.09) n = 45	0.48 (±0.07) n = 20	0.025	0.015	0.006
TDMn (nM)	0.48– 10.5	1.42 (±2.14) n = 64	1.12 (±1.83) n = 29	0.77 (±0.39) n = 7	0.098	0.31	0.25
DCd (pM)	36.9– 197	125 (±41.7) n = 103	118 (±32.0) n = 45	170 (±17.4) n = 20	0.00	0.00	0.00
TDCd (pM)	102– 313	(± 42.0) n = 69	(±47.6) n = 29	(±29.7) n = 7	0.098	0.00	0.19
DCu (nM)	0.70 – 2.28	(± 0.19) n = 103	(± 0.11) n = 45	(± 0.03) n = 20	0.26	0.00	0.00
TDCu (nM)	0.96 – 2.16	(± 0.23) n = 69	(± 0.15) n = 29	(± 0.06) n = 7	0.30	0.015	0.002
DNi (nM)	1.41– 4.14	3.23 (±0.31) n = 103	(± 0.22) n = 45	(± 0.24) n = 20	0.038	0.00	0.00
TDNi (nM)	2.75– 7.05	3.80 (±0.48) n = 69	3.76 (±0.16) n = 29	3.91 (±0.09) n = 7	0.0046	0.04	0.85
DZn (nM)	0.07– 1.24	(± 0.32) (± 0.16) n = 97	0.29 (±0.14) n = 41	0.33 (±0.11) n = 20	0.23	0.00	0.00
TDZn (nM)	0.09– 7.19	(± 0.89) n = 64	0.64 (±0.36) n = 28	1.62 (±2.46) n = 7	0.33	0.00	0.23
DAI (nM)	0.27 – 44.8	3.44 (±5.64) n = 105	2.51 (±1.87) n = 45	2.60 (±2.08) n = 20	0.88	0.00	0.00
DPb (pM)	14.8– 36.3	23.4 (±3.87) n = 103	21.9 (±3.33) n = 45	25.0 (±2.02) n = 20	0.00	0.00	0.00
TDPb (pM)	20.9– 99.3	30.7 (±14.2) n = 69	29.3 (±15.6) n = 29	27.7 (±1.97) n = 7	0.59	0.006	0.03

NO₃ (μM)	4.94– 14.5	9.96 (±2.54) n = 94	9.08 (±1.82) n = 43	12.6 (±0.99) n = 19	0.00	0.00	0.00
Summe cruise	r						
DCo (pM)	20.6– 46.1	37.6 (±11.0) n = 84	32.3 (±5.69) n = 25	40.8 (±11.1) n = 42	0.00		
TDCo (pM)	5.3– 117	75.3 (±23.3) n = 35	71.4 (±9.7) n = 5	(± 30.0) n = 15	0.57		
DMn (nM)	0.24 – 1.35	0.43 (±0.15) n = 84	0.46 (±0.09) n = 25	(± 0.11) n = 20	0.029		
TDMn (nM)	0.03– 1.96	(± 0.31) n = 35 30.2	(±0.16) n = 5 18 5	(±0.28) n = 15 37.6	0.49		
DCd (pM)	4.45– 93.7	(±19.9) n = 87 144	(±11.2) n = 26 107	(±17.1) n = 44 191	0.00		
TDCd (pM)	55.9– 274	(±62.3) n = 41	(±31.6) n = 10	(±40.5) n = 15	0.00		
DCu (nM)	0.85 — 1.83	0.97 (±0.14) n = 87	0.93 (±0.04) n = 26	0.99 (±0.13) n = 44	0.006		
TDCu (nM)	0.97 – 1.65	1.10 (±0.11) n = 41	1.08 (±0.07) n = 10	1.09 (±0.04) n = 15	0.62		
DNi (nM)	2.09– 3.44	2.75 (±0.23) n = 85	2.65 (±0.25) n = 26	2.83 (±0.18) n = 42	0.003		
TDNi (nM)	3.11– 4.33	(± 0.32) n = 41	(±0.29) n = 10	(±0.25) n = 15	0.004		
DZn (nM)	0.02– 0.23	(± 0.05) n = 68 0.40	(±0.06) n = 19 0.15	(±0.056) n = 37	0.59		
TDZn (nM)	0.02– 4.65	(±0.81) n = 34 0.94	(±0.13) n = 5 1 22	(±0.04) n = 15 0.056	0.15		
DAI (nM)	0.10– 4.81	(±0.84) n = 89 17 7	(± 0.72) n = 26 16.0	(±0.73) n = 43 16 4	0.00		
DPb (pM)	10.1– 104	(±9.64) n = 87 23.7	(±2.86) n = 26 20.6	(±1.57) n = 44 24 6	0.55		
TDPb (pM)	16.8– 37.9	(± 4.3) n = 41 2 24	(±1.9) n = 10 0.57	(±4.3) n = 15 2 86	0.004		
NO₃ (μΜ)	BD– 6.47	(±1.66) n = 74	(±0.76) n = 21	(±1.47) n = 40	0.00		

Table 2. Removal and supply ratios (in mmol:mol P) of dissolved trace elements relative to P (phosphate) out of and into the surface waters of the Iceland Basin (IB) and Irminger Basin (IRB). Removal ratios were calculated from the differences between spring and summer 2010 surface water concentrations (Table 1), and supply ratios were determined from winter convective mixing (Table 5), which was the dominant supply mechanism for dissolved elements. Dissolved Fe data was obtained from Achterberg et al. (2018) and P supply data (convective mixing) from Painter et al. (2014).

	Removal ratio IB	Removal ratio IRB	Supply ratio IB	Supply ratio IRB
DAI	2.43	4.16	8.24	5.93
DNi	1.26	0.57	4.49	5.03
DZn	0.43	0.43	1.01	1.10
DCu	0.39	0.28	1.24	1.54
DFe	0.27	0.06	0.94	0.25
DCd	0.19	0.22	0.25	0.28
DMn	0.10	0.11	0.81	0.79
DCo	0.037	0.016	0.10	0.11
DPb	0.011	0.014	0.04	0.04

Table 3. Atmospheric trace element soluble concentrations (pmol m⁻³) during spring and summer 2010. (Spring cruise samples were collected in a single size fraction (Bulk), summer cruise samples were fractionated into particles <1 μ m and >1 μ m. a – Probable contamination). The latitudes and longitudes are the midpoints of aerosol sample collection; dates are at start point of collection. See Fig. S2 (SI) for aerosol sampling map.

	Start	Lat.	Long.		41	N	In	Z	n	C	u	
	Date		-									
Spring				В	Bulk		Bulk		Bulk		Bulk	
TM02	28/04/2010	58.39	-20.92	69.6	±26.7	1.67:	±0.48	22.7	±4.3	60.6±0.3		
TM03	29/04/2010	59.70	-30.62	190)±4.6	10.7:	±0.29	5.7	±1.3	37.0	±0.2	
TM04	02/05/2010	59.98	-30.26	479)±8.3	9.53	±0.62	577-	±130	218	±1.1	
TM05	05/05/2010	60.97	-22.88	425	5±4.9	11.6	±0.54	14.2	±4.2	423	±2.1	
TM06	07/05/2010	62.50	-19.97	619	9±10	10.2:	±0.73	6.8	-2.1	26.2	±0.2	
TM07	08/05/2010	63.10	-18.75	3358	6±103	327	±9.4	193	±31	146±1.2		
TM08	08/05/2010	63.09	-19.08	1776	0±109	252±7.3		62-	±19	289	±1.7	
TM09	09/05/2010	63.39	-21.31	1280)±450	25.6	±4.3	<4	10	147	±1.5	
Summer				<1 µm	>1 µm	<1 µm	>1 µm	<1 µm	>1 µm	<1 µm	>1 µm	
TM10	17/07/2010	60.00	-38.59	29.7±3.2	28.4±3.6	0.34±0.06	0.38±0.08	9.4±3.4	<2.4	3.6±0.5	0.8±0.4	
TM11	19/07/2010	60.72	-38.49	22.6±7.5	67.9±6.5	0.37±0.08	2.06±0.24	14.8±5.4	9.7±2.4	4.8±0.6	6.1±0.4	
TM12	23/07/2010	61.19	-32.98	29.9±3.8	512±4	0.45±0.06	1.09±0.12	<9.8	<4.6	1.5±0.5	1.6±0.3	
TM13	26/07/2010	59.42	-33.40	95.9±3.7	188.8±4.7	0.35±0.05	1.08±0.08	11.4±2.4	5.0±1.6	1.6±0.3	1.4±0.2	
TM14	29/07/2010	63.41	-29.43	1948±96 ^ª	204±1.4	6.88±0.34 ^a	0.88±0.06	27.1±2.5 ^a	3.1±0.9	1.6±0.2	0.8±0.4	
TM15	04/08/2010	61.18	-22.42	44.8±2.6	82.2±4.0	0.65±0.06	0.82±0.10	<8.7	<5.4	2.0±0.4	1.4±0.7	

Table 3 continued.

	N	li	C	o	C	d	P	b		
	Bu	ılk	Βι	ılk	Bu	ılk	Bi	ılk		
Spring										
TM02	1.11±0.10		<0.	031	13.2	±0.34	0.31±	0.31±0.011		
TM03	<0	.25	0.084	±0.007	2.35	±0.09	1.61:	±0.01		
TM04	4.53	±0.13	0.13:	±0.02	4.42:	±0.17	1.14	±0.01		
TM05	0.96	±0.08	0.12	±0.01	4.11:	±0.13	1.84:	±0.01		
TM06	0.73	±0.14	0.13:	±0.02	4.48	±0.17	1.38:	±0.01		
TM07	<3	3.9	1.91:	±0.30	142±3.6		23.2±0.13			
TM08	2.88	±0.78	1.97±0.17		73.3	±1.9	10.6	±0.08		
TM09	9.3	±2.1	<0	.60	14.0	±2.1	3.41:	±0.22		
Summer	<1 µm	>1 µm	<1 µm	>1 µm	<1 µm	>1 µm	<1 µm	>1 µm		
TM10	0.38±0.15	<0.11	0.086±0.015	0.055±0.013	0.087±0.003	0.011±0.002	0.85±0.06	<0.07		
TM11	0.61±0.95	0.88±0.94	<0.050	<0.071	0.15±0.005	0.11±0.003	0.48±0.10	0.32±0.03		
TM12	0.83±0.67	0.87±0.36	<0.036	<0.050	0.028±0.004	0.048±0.003	<0.21	<0.07		
TM13	0.53±0.53	0.45±0.33	0.11±0.01	0.124±0.01	0.02±0.003	0.015±0.002	<0.15	<0.05		
TM14	1.47±0.44	0.72±0.36	0.075 <u>+</u> 0.01	0.071±0.01	0.12±0.002	0.017±0.001	<0.10	< 0.04		
TM15	<0.27	0.17±0.27	< 0.03	<0.043	0.08±0.003	0.016±0.003	0.24±0.06	<0.06		

	AI	Mn	Zn	Cu	Ni	Со	Cd	Pb
Spring								
TM02	42	1.0	2.0	5.2	0.096	<0.019	1.14	0.027
TM03	115	6.4	0.5	3.2	<0.018	0.018 0.051		0.139
TM04	289	5.8	49.9	18.9	0.391	0.078	0.38	0.098
TM05	257	7.0	1.2	36.5	0.083	0.074	0.35	0.159
TM06	374	6.2	0.6	2.3	<0.084	0.078	0.39	0.119
TM07	20300	198	16.7	12.6	0.218	1.16	12.2	2.00
TM08	10700	152	5.3	25.0	0.249	1.19	6.33	0.911
TM09	774	15.5	<2.9	12.7	0.803	<0.36	1.21	0.295
Summer								
TM10	27	0.4	2.3	1.0	0.105	0.055	0.017	0.115
TM11	61	1.8	9.7	5.6	0.815	<0.065	0.111	0.320
TM12	445	1.0	<4.8	1.5	0.820	<0.047	0.044	<0.080
TM13	171	1.0	5.3	1.4	0.434	0.117	0.015	<0.057
TM14	344	1.4	5.0	0.9	0.744	0.068	0.024	<0.041
TM15	75	0.8	<5.4	1.3	0.167	<0.040	0.021	0.061

Table 4. Calculated dry deposition fluxes (nmol m⁻² d⁻¹) for soluble metals during the spring and summer cruises. Deposition fluxes are uncertain by a factor of 2-3 (Duce et al., 1991).

Table 5. Annual convective, diffusive and atmospheric trace element fluxes, with their uncertainties. Diffusive and atmospheric fluxes derived from observations made during summer cruise. The convective flux uncertainties are based on the use of mean and standard deviation estimates of the metal concentrations at the winter mixed layer depth of the respective basin. The uncertainties for the atmospheric fluxes are indicated as a range in brackets, with the range being the relevant flux value divided by, and multiplied by, an uncertainty of factor 2 in deposition velocity (Duce et al. 1991). The variability in atmospheric fluxes of the various elements is less than 20% for the samples collected in the respective IB and IRB, and therefore a more realistic flux range is presented based on the deposition velocity uncertainty.

	DCo	DMn	DNi	DCd	DPb	DZn	DCu	DAI
Iceland Basin								
Annual Diffusive Flux (µmol/m2/y)		2.07±0.25	-0.39±0.94			-0.89±1.44	-0.78±0	12.2±0.13
Annual Diffusive Flux (nmol/m2/y)	55.6±22.4			1198±56.1	55.6±24.6			
Convective Flux (mmol/m2/y)		0.03±0.01	0.18±0.02			0.04±0.02	0.05±0.01	0.29±0.05
Convective Flux (µmol/m2/y)	3.98±0.36			8.85±0.7	1.37±0.18			
Atmospheric Flux (µmol/m2/y)	0.011 (0.006- 0.022)	0.28 (0.14- 0.56)	0.06 (0.03- 0.12)	0.008 (0.004- 0.016)	0.012 (0.006- 0.024)	1.46 (0.73- 2.92)	0.48 (0.24- 0.96)	27.3 (13.7- 54.6)
Diffusive Flux as % Convective Flux	1.40±0.58	6.40±2.26	-0.22±0.53	13.5±1.24	4.05±1.86	-2.43±4.11	-1.55±0.93	4.24±0.73
Atmospheric Flux as % Convective+ Diffusive Fluxes	0.27±0.34	0.81±1.04	0.03±0.04	0.08±0.12	0.84±0.64	4.10±3.70	0.98±0.94	9.11±7.01
Irminger Basin								
Annual Diffusive Flux (µmol/m2/y)		1.11±1.33	0.82±1.39			2.20±2.1	0.80±0.43	-1.04±2.41
Annual Diffusive Flux (nmol/m2/y)	184±48.6			706±321	46.7±52.2			
Convective Flux (mmol/m2/y)		0.03±0.00 1	0.20±0.00 3			0.04±0.01	0.06±0.00 3	0.17±0.00 4
Convective Flux (µmol/m2/y)	4.18±0.03			10.3±1.03	1.55±0.03			
Atmospheric Flux (µmol/m2/y)	0.022 (0.011- 0.044)	0.38 (0.19- 0.76)	0.19 (0.1- 0.38)	0.014 (0.007- 0.028)	0.041 (0.02- 0.084)	1.86 (0.93- 3.66)	0.71 (0.35- 1.42)	68.4 (34.2- 137)
Diffusive Flux as % Convective flux	4.40±1.16	4.08±4.89	0.40±0.67	6.87±3.20	3.02±3.36	5.16±5.09	1.34±0.72	-0.63±1.46
Atmospheric Flux as %								
Convective+ Diffusive Fluxes	0.50±0.63	1.34±1.67	0.09±0.06	0.13±0.14	2.57±2.01	4.15± 3.27	1.16±1.75	41.7±31.3