Ocean acidification in the Subpolar North Atlantic: rates and mechanisms controlling pH changes

Maribel I. García-Ibáñez[1], Patricia Zunino[2], Friederike Fröb[3], Lidia I. Carracedo[4], Aida F. Ríos[†], Herlé Mercier[5], Are Olsen[3], Fiz F. Pérez[1]

[1]Instituto de Investigaciones Marinas, IIM-CSIC, Vigo, E36208, Spain.
[2]Ifremer, Laboratoire d'Océanographie Physique et Spatiale, UMR 6523 CNRS/Ifremer/IRD/UBO, Ifremer Centre de Brest, Plouzané, CS 10070, France.
[3]Geophysical Institute, University of Bergen and Bjerknes Centre for Climate Research, Bergen, N5007, Norway.
[4]Faculty of Marine Sciences, University of Vigo, Vigo, E36200, Spain.
[5]CNRS, Laboratoire d'Océanographie Physique et Spatiale, UMR 6523 CNRS/Ifremer/IRD/UBO, Ifremer Centre de Brest, Plouzané, CS 10070, France.
[†]Deceased.

Correspondence to: Maribel I. García-Ibáñez (maribelgarcia@iim.csic.es)

Abstract. Repeated hydrographic sections provide critically needed data on, and understanding of, changes in basin-wide ocean CO_2 chemistry over multi-decadal timescales. Here, high-quality measurements collected at twelve cruises carried out along the same track between 1991 and 2015 have been used to determine long-term changes in ocean CO_2 chemistry and ocean acidification in the Irminger and Iceland basins of the North Atlantic Ocean. Trends were determined for each of the main water masses present and are discussed in the context of the basin-wide circulation. The pH has decreased in all water masses of the Irminger and Iceland basins over the past 25 years, with the greatest changes in surface and intermediate waters (between -0.0010 ± 0.0001 pH units·yr^{-1} and -0.0018 ± 0.0001 pH units·yr^{-1}). In order to disentangle the drivers of the pH changes, we decomposed the trends into their principal drivers: changes in temperature, salinity, total alkalinity (A_T) and total dissolved inorganic carbon (both its natural and anthropogenic components). The increase in anthropogenic CO_2 (C_{ant}) was identified as the main agent of the pH decline, partially offset by A_T increases. The acidification of intermediate waters caused by C_{ant} uptake has been reinforced by the aging of the water masses over the period of our analysis. The pH decrease of the deep overflow waters in the Irminger basin was similar to that observed in the upper ocean, and was mainly linked to the C_{ant} increase, thus reflecting the recent contact of these deep waters with the atmosphere.

Keywords. Ocean acidification; C_{ant}; water masses; Subpolar Gyre.

1 INTRODUCTION

The oceanic uptake of a fraction of the anthropogenic CO_2 (i.e., C_{ant}; CO_2 released from humankind's industrial and agricultural activities) has resulted in long-term changes in ocean CO_2 chemistry, commonly referred to as ocean acidification, OA (e.g., Caldeira and Wickett, 2003, 2005; Raven et al., 2005; Doney et al., 2009; Feely et al., 2009). The changes in the ocean CO_2 chemistry result in declining pH and reduced saturation states for $CaCO_3$ minerals (e.g., Bates et al., 2014). The average pH (-$\log_{10}$[H$^+$]) of ocean surface waters has decreased by about 0.1 pH units since the beginning of the industrial revolution (1750), and based on model projections we expect an additional drop of 0.1–0.4 by the end of this century, even under conservative CO_2 emission scenarios (Caldeira and Wickett, 2005; Orr, 2011; Ciais et al., 2013). The rate of change in pH is at

40   least a hundred times faster than at any time since the last Ice Age (Feely et al., 2004; Raven et al., 2005), clearly

41   outpacing natural processes in ocean chemistry that have occurred in the past due to geological processes (Raven

42   et al., 2005). These changes in ocean CO_2 chemistry will most likely have adverse effects on organisms,

43   particularly calcifying ones, on ecosystems (e.g., Langdon et al., 2000; Riebesell et al., 2000; Pörtner et al.,

44   2004) and on major marine biogeochemical cycles (e.g., Gehlen et al., 2011; Matear and Lenton, 2014).

45   The global ocean has absorbed ~30% of the C_{ant} emitted to the atmosphere between 1750 and the present

46   (Sabine et al., 2004; Khatiwala et al., 2013; DeVries, 2014; Le Quéré et al., 2015). This C_{ant} is not evenly

47   distributed throughout the oceans (Sabine et al., 2004), but enters the interior ocean preferentially in regions of

48   deep convective overturning and subduction (Maier-Reimer and Hasselmann, 1987; Sarmiento et al., 1992;

49   Lazier et al., 2002). This explains why the Meridional Overturning Circulation (MOC) makes the North Atlantic

50   Ocean one of the most important C_{ant} sinks of the global ocean, storing 25% of the global oceanic C_{ant} (Sabine et

51   al., 2004; Khatiwala et al., 2013) despite being only 11% of the global ocean volume (Eakins and Sharman,

52   2010). The MOC transports C_{ant}-laden surface waters from the Equator to the northern North Atlantic Ocean

53   (e.g., Wallace, 2001; Anderson and Olsen, 2002; Olsen et al., 2006; Zunino et al., 2015), where deep water

54   formation provides a pathway for C_{ant} into the interior ocean (Lazier et al., 2002; Pérez et al., 2008, 2013;

55   Steinfeldt et al., 2009). Being regions close to deep water formation areas and where water mass transformation

56   occurs (Sarafanov et al., 2012; García-Ibáñez et al., 2015), the Irminger and Iceland basins are geographically

57   well placed to monitor temporal changes in the Atlantic MOC (Mercier et al., 2015), and to determine the rates

58   of C_{ant} penetration to the deep ocean and its consequence for OA.

59   In this paper, we examine high-quality direct measurements of ocean CO_2 chemistry from twelve cruises

60   conducted across the Irminger and Iceland basins between 1991 and 2015. Previous studies focused on C_{ant}

61   uptake and its storage and effect on pH in the Irminger and Iceland basins (e.g., Pérez et al., 2008; Olafsson et

62   al., 2009; Bates et al., 2012; Vázquez-Rodríguez et al., 2012b). Here we quantify the pH change for a 25-year

63   period and identify its chemical and physical drivers by decomposing the observed pH change into five

64   numerically estimated factors (temperature, salinity, alkalinity, anthropogenic CO_2 and non-anthropogenic CO_2),

65   all based on direct measurements.

2 MATERIALS and METHODS

2.1 Datasets

2.1.1 Cruise Information

69   We used data from twelve cruises along the same track across the Irminger and Iceland basins, with the cruise

70   dates spanning 25 years (1991–2015; Table 1, Fig. 1a). The bottle data were accessed from the merged data

71   product of the Global Data Analysis Project version 2 (GLODAPv2; Olsen et al., 2016) at

72   http://cdiac.ornl.gov/oceans/GLODAPv2, except for more recent unpublished data collected during the OVIDE

73   2012 and 2014 cruises and the 2015 cruise (58GS20150410). The data of the 1991 cruises (64TR91_1 and

74   06MT18_1) were merged and treated as a single cruise.

2

2.1.2 Ocean CO₂ chemistry measurements

The twelve cruises selected for our study have high-quality measurements of the seawater CO_2 system variables (Table 1). Total alkalinity (A_T) was analysed by potentiometric titration and determined by developing either a full titration curve (Millero et al., 1993; Dickson and Goyet, 1994; Ono et al., 1998) or from single point titration (Pérez and Fraga, 1987; Mintrop et al., 2000), and were calibrated with Certified Reference Materials (CRMs), with an overall accuracy of 4 $\mu mol \cdot kg^{-1}$. For samples without direct A_T measurements, it was estimated using a 3D moving window multilinear regression algorithm (3DwMLR), using potential temperature (θ), salinity, nitrate, phosphate, silicate and oxygen as predictor parameters (Velo et al., 2013). The total dissolved inorganic carbon (DIC) samples were analysed with coulometric titration techniques (Johnson et al., 1993), and were calibrated with CRMs, achieving an overall accuracy of 2 $\mu mol \cdot kg^{-1}$. For the cruises where direct DIC measurements had not been performed, it was computed from A_T and pH using the thermodynamic equations of the seawater CO_2 system (Dickson et al., 2007) and the CO_2 dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987). These calculated DIC values have an associated uncertainty of 4 $\mu mol \cdot kg^{-1}$, calculated by random propagation of the reported A_T and pH accuracies. pH was determined at 25°C and 1 atm with a spectrophotometric method (Clayton and Byrne, 1993) using diode array spectrophotometers and m-cresol purple as an indicator. The spectrophotometric pH determination has a typical precision of 0.0002–0.0004 pH units (Clayton and Byrne, 1993; Liu et al., 2011). However, Carter et al. (2013) reported an inherent uncertainty of spectrophotometric pH determinations of 0.0055 pH units, associated to the tris-buffer used for calibration. When direct pH measurements were not performed, it was computed from A_T and DIC using the thermodynamic equations of the seawater CO_2 system (Dickson et al., 2007) and the CO_2 dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987). For these calculated pH values, we estimated an uncertainty of 0.006 pH units by random propagation of the reported A_T and DIC accuracies. A_T values differing by more than two times the standard deviation (7 $\mu mol \cdot kg^{-1}$) of the difference between measured A_T and 3DwMLR predicted A_T were replaced with the predicted A_T value. Note that the effect of A_T corrections on pH trends is negligible, since A_T corrections of 4 $\mu mol \cdot kg^{-1}$ lead to pH changes lower than a thousandth. The pH values reported here are at in situ conditions (of temperature and pressure) and on the total scale (pH_{Tis}).

2.1.3 Anthropogenic CO₂ (i.e., C$_{ant}$) estimation

C_{ant} concentrations were estimated using the back-calculation method φC_T^0 (Pérez et al., 2008; Vázquez-Rodríguez, 2009a) that has previously been applied for the entire Atlantic Ocean (Vázquez-Rodríguez et al., 2009b). Back-calculation methods determine C_{ant} for any sample in the water column as the difference between DIC concentration at the time of the measurement and the DIC concentration it would have had in preindustrial times. Following Gruber et al. (1996), this is represented as the difference in preformed DIC between the time of observation and the preindustrial as:

$$C_{ant} = DIC_{meas} - \Delta C_{bio} - DIC_{preind} - \Delta C_{diseq}, \tag{1}$$

where the preformed DIC for the time of observation is represented as the measured DIC (DIC_{meas}) minus any DIC added to the water due to organic matter remineralisation and calcium carbonate dissolution (ΔC_{bio}), and the preindustrial preformed concentration is represented by the DIC concentration the water would have if in equilibrium with the preindustrial atmosphere (DIC_{preind}) minus any offset from such an equilibrium value, known as the disequilibrium term (ΔC_{diseq}). The procedure requires DIC and A_T as input parameters, and the

114   empirical parameterization of the preformed A_T (A_T^0) for the computation of the calcium carbonate dissolution

115   and of the ΔC_{diseq} term (Vázquez-Rodríguez et al., 2012a). The A_T^0 is based on the concept of potential alkalinity

116   ($PA_T = A_T + NO_3 + PO_4$) and is defined as $A_T^0 = PA_T – (NO_3^0 + PO_4^0)$ (Vázquez-Rodríguez et al., 2012a), where

117   NO_3^0 and PO_4^0 are the preformed nitrate and phosphate concentrations, respectively. NO_3^0 and PO_4^0 are

118   determined as $NO_3^0 = NO_3 – AOU/R_{ON}$ and $PO_4^0 = PO_4 – AOU/R_{OP}$. In the former equations AOU stands for

119   Apparent Oxygen Utilisation, which is the difference between the saturated concentrations of oxygen calculated

120   using the equations of Benson and Krause (1984) and the measured concentrations of oxygen; R_{ON} and R_{OP} are

121   the Redfield ratios proposed by Broecker (1974).

122   The φC_T^0 method presents two main advantages relative to the previous method proposed by Gruber et al.

123   (1996). First, the spatiotemporal variability of A_T^0 is taken into account. And second, the parameterizations of

124   A_T^0 and ΔC_{diseq} are determined using the subsurface layer as reference (Vázquez-Rodríguez et al., 2012a), where

125   the age of the water parcel and, therefore, its C_{ant} concentration is estimated using CFC measurements (Waugh et

126   al., 2006). The overall uncertainty of the φC_T^0 method has been estimated at 5.2 $\mu mol \cdot kg^{-1}$ (Pérez et al., 2008;

127   Vázquez-Rodríguez, 2009a).

128   The uncertainties and reproducibilities of the analysis and calculation methods were determined from the deep

129   waters sampled at Iberian Abyssal Plain during the seven repeats of the OVIDE line, since these waters are

130   expected to be in near-steady state. The standard deviations of those samples for each cruise (Table 2) were

131   taken as an estimate of the uncertainty at each cruise. The uncertainties of the AOU, A_T and pH_{Tis} for the seven

132   cruises were similar. The standard deviations of C_{ant} (1.2–1.6 $\mu mol \cdot kg^{-1}$) and pH_{Tis} (0.002–0.003 pH units) for

133   each of the seven cruises are lower than the inherent uncertainty of the φC_T^0 estimates (5.2 $\mu mol \cdot kg^{-1}$) and the

134   accuracy of the spectrophotometric pH measurements (0.0055 pH units), which provides confidence that these

135   data are suitable for trend determination. The standard deviations of the C_{ant} estimates are rather similar to those

136   from other regions where C_{ant} has been compared across many cruises (i.e., 2.4 $\mu mol \cdot kg^{-1}$ in the South Atlantic

137   Ocean, Ríos et al. (2003); 2.7 $\mu mol \cdot kg^{-1}$ in the Equatorial Atlantic Ocean, 24ºN, Guallart et al. (2015); and 2.7

138    $\mu mol \cdot kg^{-1}$ reported from a transect along the western boundary of the Atlantic Ocean from 50ºS to 36ºN, Ríos et

139   al. (2015)). The standard deviations of the mean values of the Iberian Abyssal Plain samples across all (last row

140   of Table 2) were taken as an estimate of the reproducibility of the methodologies. The high reproducibility of the

141   pH measurements, an order of magnitude better than the uncertainty (0.0055 pH units, Carter et al. (2013)), is

142   suggestive of high quality data. Using these standard deviations for the seven cruises, and taking into account the

143   25 years considered in this study, the threshold of detectability of pH trends at 95% of confidence is 0.00012 pH

144   units $\cdot yr^{-1}$, which renders confidence to the estimated trends.

145   **2.2 Water mass characterization**

146   Changes in ocean CO_2 chemistry were determined for the main water masses in the Irminger and Iceland

147   basins. These are: (1) Subpolar Mode Water (SPMW); (2) upper and classical Labrador Sea Water (uLSW and

148   cLSW, respectively); (3) Iceland–Scotland Overflow Water (ISOW) and; (4) Denmark Strait Overflow Water

149   (DSOW; Fig. 1b). The layers defining the water masses were delimited using potential density following Azetsu-

150   Scott et al. (2003), Kieke et al. (2007), Pérez et al. (2008) and Yashayaev et al. (2008). The advantage of

151   working in layers is the relatively low variability of the physical and chemical properties within the layers,

152   allowing us to assume linearity in the ocean CO_2 system.

To better determine the limits between layers and the average value of each variable in each layer, cruise bottle data were linearly interpolated onto each dbar before determining average variable values, an improvement with respect to the previous approaches of Pérez et al. (2008, 2010) and Vázquez-Rodríguez et al. (2012b). Then, the interpolated profiles were averaged over each density layer, defined in Figure 1b. Finally, the average values in each density layer were determined for each cruise taking into account the thickness of the layer and the separation between stations. The exception comes with pH_{Tis}, which is pressure sensitive, and for which we needed to define a unique reference pressure to remove pressure effects due to varying sampling strategies. pH_{Tis} was calculated using the layer average values of DIC and A_T for the considered year but using the time-averaged pressure of the layer over the studied time period as reference pressure. To reduce the influence of seasonal differences in sampling on the inter-annual trends, only samples with pressure ≥ 75 dbar were considered. The 75 dbar level was determined by the depth of the seasonal nutrients drawdown along the section. The average values of the variables for each layer and their standard deviations can be found in the Supplementary Table S1.

2.3 pH deconvolution

Changes in ocean pH may be brought about by changes in in situ temperature (T_{is}), salinity (S), A_T, and/or DIC, of which changes in the latter may be brought about by C_{ant} uptake or by natural processes (C_{nat}), such as remineralisation. C_{nat} is determined as the difference between measured DIC and estimated C_{ant}. Changes in temperature and salinity influence the equilibrium constants of the oceanic CO_2 system. Additionally, changes in salinity influence the borate concentration, whose influence is taken into account by the relationship proposed by Uppström (1974).

To estimate how much each of these altogether five factors have contributed to the observed change in pH, we assumed linearity and decomposed the observed pH changes into these potential drivers according to:

$$\left(\frac{dpH_{Tis}}{dt}\right)_{total} = \frac{\partial pH_{Tis}}{\partial T_{is}}\frac{dT_{is}}{dt} + \frac{\partial pH_{Tis}}{\partial S}\frac{dS}{dt} + \frac{\partial pH_{Tis}}{\partial A_T}\frac{dA_T}{dt} + \frac{\partial pH_{Tis}}{\partial DIC}\left(\frac{dC_{ant}}{dt} + \frac{dC_{nat}}{dt}\right), \tag{2}$$

To estimate $\frac{\partial pH_{Tis}}{\partial var}$ (where 'var' refers to each of the drivers: T_{is}, S, A_T and DIC) we calculated a pH_{Tis} for each layer and year using the layer average value of 'var' for each year but keeping the values of the other drivers constant and equal to the time-average value for the layer over the studied time period. Given that the variability of the physicochemical properties within each layer is relatively low (see standard deviations of the averaged values in Table S1), we can assume that these derivatives are constant over the studied time period and use a constant derivative value for each layer. Note that sensitivity of pH_{Tis} to changes in C_{ant} is the same as the sensitivity to changes in C_{nat} since both are DIC, and, therefore, only $\frac{\partial pH_{Tis}}{\partial DIC}$ is necessary. To estimate each $\frac{dvar}{dt}$ term we performed a linear regression between var and time for each layer.

Due to the small range of pH change to which we are working and to the relatively low pH variability within each layer, we can consider that pH follows a linear scale instead of a logarithmic scale. This causes that the contributions of each of the terms considered in Eq. (2) to pH change are equivalent to the contributions in terms of $[H^+]$.

Trends of all variables involved in Eq. (2) were calculated based on the annual interpolation of the observed values to avoid the bias due to the reduced availability of cruises during the 90's with respect to the 2000's.

3 RESULTS AND DISCUSSION

3.1 Distribution of water mass properties

The Irminger and Iceland basins in the North Atlantic are characterized by warm and saline surface waters, and cold and less saline intermediate and deep waters (Fig. 2a,b). The central waters (here represented by the SPMW layer), which dominates the upper ~700 m, are warmer and saltier in the Iceland basin than in the Irminger basin, reflecting the water mass transformation that takes place along the path of the North Atlantic Current (NAC) (Brambilla and Talley, 2008). In particular, the mixing of the SPMW layer with the surrounding waters while flowing around the Reykjanes Ridge (evident in the salinity distribution; see also García-Ibáñez et al. (2015)), in conjunction with the air−sea heat loss, results in a colder and fresher SPMW layer in the Irminger basin. The uLSW and cLSW layers, below the SPMW layer, are saltier in the Iceland basin due to their mixing with the surrounding waters during their journey from their formation regions (Bersch et al., 1999; Pickart et al., 2003; García-Ibáñez et al., 2015). The ISOW layer dominates at depths beneath the cLSW layer. This layer is saltier in the Iceland basin, reflecting its circulation. ISOW comes from the Iceland–Scotland sill and flows southwards into the Iceland basin, where it mixes with the older North Atlantic Deep Water (NADW). Then, it crosses the Reykjanes Ridge through the Charlie−Gibbs Fracture Zone (Fig. 1a), where it mixes with the cLSW and DSOW, becoming fresher. In the bottom of the Irminger basin, a fifth layer is distinguished, DSOW, being the coldest and freshest layer of the section.

The general pattern of pH_{Tis} (Fig. 2c) follows by and large the distribution expected from the surface production of organic material and remineralisation at depth. Consequently, high pH values (> 8.05) are found in upper layers, while the values generally decrease with depth down to < 7.95 in the deepest layers. This overall pattern is disrupted at ~500 m in the Iceland basin by a layer with relatively low pH_{Tis} values (< 7.98), coinciding with relatively high AOU and DIC values (Fig. 2e,f). This layer could be associated with an area of slower circulation where the products of the remineralization of the organic matter accumulate. This thermocline layer could also be influenced by waters of southern origin (Sarafanov et al., 2008), which are advected into the region by the NAC, whose extension is closely related to the North Atlantic Oscillation (Desbruyères et al., 2013). The presence of this low pH layer lowers the average pH of our SPMW layer in the Iceland basin compared to the Irminger basin (Fig. 3). An opposite pattern is found in the uLSW layer. The water mass formation occurring in the Irminger basin (Pickart et al., 2003; García-Ibáñez et al., 2015; Fröb et al., 2016; Piron et al., 2016) transfers recently ventilated low DIC and high pH waters to depth, which causes the mean pH of uLSW in the Irminger basin to be higher than in the Iceland basin. Finally, the layers that contain the overflow waters have the lowest pH values. The presence of the older NADW in the ISOW layer in the Iceland basin decreases the mean pH of this layer here, making it lower than in the Irminger basin.

The upper layer waters of the section have low DIC values, which rapidly increase when increasing depth (Fig. 2f). The low DIC values in the uppermost ~200 m are a consequence of the photosynthetic activity that withdraws DIC from seawater. Below ~200 m the DIC distribution is almost homogeneous, only disrupted by relatively high values in the Iceland basin at ~500 m associated with the thermocline layer, and at the bottom, associated with the old NADW. The gradients in anthropogenic and natural components of DIC are much stronger. The C_{ant} values are high, close to saturation (approximately 80% of the C_{ant} concentration expected from a surface ocean in equilibrium with the atmospheric CO_2), near the surface and decrease with depth (Fig. 2h), because C_{ant} enters the ocean from the atmosphere. The C_{nat} distribution has an opposite pattern, with low

229 surface values and high bottom values (Fig. 2g), similar to that of the AOU distribution (Fig. 2e), since C_{nat} is

230 linked to the ventilation of water masses, i.e., respiration and renewal of the water mass.

231   The A_T distribution along the section resembles the salinity distribution, with high values associated with the

232 relatively saline central waters and relatively low and almost homogeneous values in the rest of the section (Fig.

233 2d). The exception comes with the ISOW layer. The high A_T values found in the ISOW layer of the Iceland

234 basin are not mirrored in the salinity distribution. This reflects the influence of NADW that is traced by the

235 relatively large amounts of silicate related to the influence of the Antarctic Bottom Water, which provides high

236 A_T from dissolution of $CaCO_3$. The influence of these high A_T values is then transported by the ISOW

237 circulation to the Irminger basin.

3.2 Water mass acidification and drivers

239   Trends of pH_{Tis} in each layer and basin are presented in Table 3, in Fig. 3 and in Supplementary Fig. S1. The

240 pH_{Tis} has decreased in all layers of the Irminger and Iceland basins during the time period of more than 20 years

241 (1991–2015) that is covered by the data. The trends are stronger in the Irminger basin due to the presence of

242 younger waters. The rate of pH decline decreases with depth, except for the DSOW layer that has acidification

243 rates close to those found in the cLSW layer. This indicates that DSOW is a newly formed water mass that has

244 recently been in contact with the atmosphere. Moreover, the acidification rate in the ISOW layer in the Irminger

245 basin is relatively low, which could be related to the increasing importance of the relatively old NADW in this

246 layer, with the reduction in cLSW formation since mid-90s (Lazier et al., 2002; Yashayaev, 2007).

247   The observed rate of pH_{Tis} decrease in the SPMW layer of the Iceland basin (-0.0016 ± 0.0001 pH units·yr^{-1};

248 Table 3, Fig. 3b) is in agreement with that observed at the Iceland Sea time-series (68ºN, 12.66ºW; Olafsson et

249 al. (2009, 2010)) for the period 1983–2014 (-0.0014 ± 0.0005 pH units·yr^{-1}; Bates et al. (2014)). However, our

250 rate of pH_{Tis} decrease in the SPMW layer in the Irminger basin (-0.0018 ± 0.0001 pH units·yr^{-1}) is lower than

251 that observed in the sea surface waters of the Irminger Sea time-series (64.3ºN, 28ºW; Olafsson et al. (2010)) for

252 the period 1983–2014 (-0.0026 ± 0.0006 pH units·yr^{-1}; Bates et al. (2014)), which is exceptionally high

253 compared to the other time series summarized here. Bates et al. (2014) linked the high acidification rate found at

254 the Irminger Sea time-series to the high rate of increase in DIC (1.62 ± 0.35 µmol·kg^{-1}·yr^{-1}) observed at this site,

255 which is almost three times our rate of increase in DIC (0.64 ± 0.07 µmol·kg^{-1}·yr^{-1}, Fig. 5c). This is based on

256 data from only one site, further north than our section, and indicates that spatial variations are substantial in this

257 region. Besides, the acidification rates in the SPMW layer of both basins here reported are in agreement with the

258 rates of -0.0020 ± 0.0004 pH units·yr^{-1} determined for the North Atlantic subpolar seasonally stratified biome for

259 the period 1991-2011 (Lauvset et al., 2015). Compared to the Subtropical Atlantic time-series stations, our rates

260 in the SPMW layer of both basins are in agreement with those observed at ESTOC (29.04ºN, 15.50ºW; Santana-

261 Casiano et al. (2007), González-Dávila et al. (2010)) for the period 1995–2014 (-0.0018 ± 0.0002 pH units·yr^{-1};

262 Bates et al. (2014)) and BATS (32ºN, 64ºW; Bates et al. (2014)) for the period 1983–2014 (-0.0017 ± 0.0001 pH

263 units·yr^{-1}; Bates et al. (2014)). Compared to the Pacific Ocean, the OA rates in the Iceland and Irminger basins

264 are in agreement with those reported for the Central North Pacific based on data from the time-series station

265 HOT (22.45ºN, 158ºW; Dore et al. (2009)) for the period 1988–2014 (-0.0016 ± 0.0001 pH units·yr^{-1}; Bates et

266 al. (2014)), but are slightly higher than those determined by Wakita et al. (2013) in the winter mixed layer at the

267 Subarctic Western North Pacific (time-series stations K2 and KNOT) for the period 1997–2011 (-0.0010 ±

268   0.0004 pH units·yr⁻¹). Wakita et al. (2013) attributed the lower than expected pH trends to an increasing A_T

269   trend.

270   To infer the causes of the acidification trends reported here, we decomposed the pH trends into their individual

271   components as described in Sect. 2.2. The values of each term of $\frac{\partial pH_{Tis}}{\partial var}$ and $\frac{dvar}{dt}$ (where 'var' refers to each of

272   the drivers) described in Sect. 2.2 can be found in the Supplementary Table S2 and in Figs. 4-6, respectively.

273   The results of solving Eq. (2) are presented in Table 3. The sum of the pH changes caused by the individual

274   drivers (i.e., $\left(\frac{dpH_{Tis}}{dt}\right)_{total}$) matches the observed pH trends ($\left(\frac{dpH_{Tis}}{dt}\right)_{obs}$), which renders confidence to the

275   method.

276   The temperature changes (Fig. 4a,b) have generally resulted in small to negligible pH declines (Table 3).

277   Specifically, warming corresponds to a pH decrease of at least 0.0002 pH units·yr⁻¹ in the SPMW layer of the

278   Iceland basin and in the LSW and DSOW layers of the Irminger basin, while the effect of temperature changes

279   on pH in the other layers is negligible. Temperature driven pH change is larger in the LSW layers in the Irminger

280   than in the Iceland basin. In the case of the uLSW layer, this is possibly explained by the deep convection

281   occurring in the Irminger basin (Pickart et al., 2003; García-Ibáñez et al., 2015; Fröb et al., 2016; Piron et al.,

282   2016). In the case of the cLSW layer, the higher pH changes driven by temperature changes in the Irminger basin

283   could be explained by the rapid advection of this water mass from the Labrador Sea to this basin (Yashayaev et

284   al., 2007). Temperature driven pH change in the DSOW layer could be related to the entrainment of LSW into

285   DSOW that takes place downstream of the Greenland-Iceland sills (Read, 2000; Yashayaev and Dickson, 2008).

286   The temperature effect on pH evaluated here is thermodynamic. The same applies to the salinity effect, which

287   however is small to negligible, reflecting that salinity changes in the region (Fig. 4c,d) are insufficiently large to

288   significantly change pH.

289   Overall, the A_T has increased in the Irminger and Iceland basins (Fig. 5a,b), corresponding to increasing pH

290   (Table 3), which counteracts the acidification from the CO_2 absorption. The contribution from A_T to reduce

291   ocean acidification is significant in all the layers, except for uLSW of the Iceland basin (where the trend in A_T is

292   decreasing, but not significant; Fig. 5b). The similar behaviour of the salinity and A_T trends over time may

293   indicate that the changes in A_T are mainly driven by changes in salinity. The A_T increasing trends observed in the

294   SPMW layer could be related to the increasing presence of waters of subtropical origin (with higher A_T) as the

295   subpolar gyre was shrinking from the mid-90s and into the 2000s (e.g., Flatau et al., 2003; Häkkinen and Rhines,

296   2004; Böning et al., 2006). In the case of the LSW layers, the increase in A_T can be explained by the mid-90s

297   cessation of the cLSW formation (Lazier et al., 2002; Yashayaev, 2007), with the consequent salinization (and

298   increase in A_T) of this water mass. The signal of the cLSW salinization was then transmitted to the overflow

299   layers due to the entrainment events (Sarafanov et al., 2010).

300   The DIC increase (Fig. 5c,d) is the main cause of the observed pH decreases (Table 3), and corresponds to pH

301   drops between -0.00099 ± 0.00014 pH units·yr⁻¹ and -0.00205 ± 0.00011 pH units·yr⁻¹. The waters in both the

302   Irminger and Iceland basins gained DIC in response to the increase in atmospheric CO_2; the convection

303   processes occurring in the former basin (Pickart et al., 2003; Thierry et al., 2008; de Boisséson et al., 2010;

304   García-Ibáñez et al., 2015; Fröb et al., 2016; Piron et al., 2016) and in the surrounding ones (i.e., Labrador and

305   Nordic Seas) provide an important pathway for DIC to pass from the surface mixed layer to the intermediate and

306   deep layers. The effect of the DIC increase on pH is generally dominated by the anthropogenic component

307   (Table 3). The exception comes with the cLSW layer of the Irminger basin, where the natural component

resulting from the aging of the layer dominates. In general, the Irminger basin layers have higher C_{ant} increase rates than the Iceland basin layers (Fig. 6a,b), and therefore larger pH declines, presumably a result of convection in the Irminger basin itself and advection of newly ventilated waters from the Labrador Sea. The highest C_{ant} increase rates are found in the SPMW layer, owing to its direct contact with the atmosphere, and result in the strongest rates of pH decrease. In the Irminger basin, the rise in C_{ant} levels of the SPMW layer correspond to about 87% of the rate expected from a surface ocean maintaining its degree of saturation with the atmospheric CO_2 rise (computed using as reference the globally averaged marine surface annual mean pCO_2 data from the NOAA, ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2_annmean_gl.txt), while in the Iceland basin, this rate is about 73% of the expected rate. The lower fraction in the Iceland basin compared to the Irminger basin is a consequence of the inclusion of the aforementioned poorly ventilated thermocline waters in our SPMW layer (Fig. 2e,h). Note than none of the C_{ant} trends of the SPMW layers correspond to 100% of the rate expected from assuming saturation with the atmospheric CO_2 rise. This can be explained by the fact that surface waters CO_2 concentration rise lags that of the atmosphere by between two to five years in this region (Biastoch et al., 2007; Jones et al., 2014). We also note that the temperature and A_T changes impact the pH of the SPMW layer, decreasing and increasing it, respectively. This could indicate the increasing presence of warmer and more saline (with higher A_T) waters of subtropical origin, which, because A_T effects dominate (as stated before, the effect of salinity change on pH is negligible), in a net sense partially counteracts the effects of increasing DIC values. Overall this change can be explained as the result of the contraction of the subpolar gyre that took place since mid-90s (e.g., Flatau et al., 2003; Häkkinen and Rhines, 2004; Böning et al., 2006). Wakita et al. (2013) also found lower than expected acidification rates in the surface waters of the Pacific Ocean, which they explained as being the consequence of increasing A_T. Finally, the strong influence of anthropogenic component on the pH decrease of the DSOW layer stands out, and is the main agent of the pH decline in this layer.

The pH changes related to C_{nat} changes (Fig. 6c,d) can be interpreted as changes related to ventilation of water masses and water mass changes (with different A_T and DIC). Stronger pH decreases related to C_{nat} changes indicate lack of ventilation and accumulation of DIC from remineralised organic material. This is clearly the case for the cLSW layer, where the observed pH decrease is caused by a combination of the effects of C_{ant} and C_{nat} (Table 3). The greater influence of C_{nat} in the cLSW layer is the result of the aging of this water mass after its last formation event, in the mid-90s (e.g., Lazier et al., 2002; Azetsu-Scott et al., 2003; Kieke et al., 2007; Yashayaev, 2007). Similar effect of the C_{nat} changes on pH is observed in the overflow layers of the Irminger basin, which are influenced by the mixing with cLSW (García-Ibáñez et al., 2015). Finally, there is a contrast between the C_{nat} influence on the pH of the uLSW layer in both basins. The inter-annual variability of the uLSW properties attenuates due to mixing over the length and timescales of the transit from the Labrador Sea (Cunningham and Haine, 1995; Paillet et al., 1998), which causes the inter-annual variability in the C_{nat} values of the uLSW layer in the Iceland basin to be smoother than in the Irminger basin (Fig. 6c,d). Therefore, the lower inter-annual variability in the C_{nat} values of the uLSW layer in the Iceland basin promotes better detectability of the ventilation of the uLSW layer, whose effects offset up to 60% the effects of acidification on the uLSW layer of the Iceland basin.

Vázquez-Rodríguez et al. (2012b) have previously studied the pH changes in the different water masses of the Irminger and Iceland basins. These authors carried out a pH normalization to avoid potential biases due to different ventilation stages and rates of each layer, from the different spatial coverage of the evaluated cruises.

348 The normalized pH values (pH$_N$) for each layer were obtained using multiple linear regressions between the

349 observed mean pH$_{SWS25}$ (pH at seawater scale and 25ºC) and the observed mean values of θ, salinity, silicate and

350 AOU, referred to the mean climatological values of θ, salinity, silicate and AOU compiled in WOA05

351 (http://www.nodc.noaa.gov/OC5/WOA05/pr_woa05.html). This normalization, combined with the different

352 temporal coverage (1981–2008), causes the rates reported by Vazquez-Rodriguez et al. (2012b) differ from those

353 obtained in the present work. The pH$_N$ trends reported for the SPMW and uLSW layers of the Irminger basin and

354 for the ISOW layer of the Iceland basin are very similar to our pH$_{Tis}$ trends for these layers. However, the pH$_N$

355 trends reported by Vazquez-Rodriguez et al. (2012b) for the cLSW layer in both basins and for the ISOW layer

356 in the Irminger basin are significantly different from our pH$_{Tis}$ trends for these layers, but are very similar to pH

357 changes derived from C$_{ant}$ changes ($\frac{\partial pH_{Tis}}{\partial DIC}\frac{dC_{ant}}{dt}$ in Table 3). In the case of the DSOW layer, the pH$_N$ trend is also

358 in agreement with $\frac{\partial pH_{Tis}}{\partial DIC}\frac{dC_{ant}}{dt}$ trends. This suggests that the normalization carried out by Vazquez-Rodriguez et

359 al. (2012b) could remove some of the impact of the natural component (represented here by C$_{nat}$) over pH

360 changes, essentially due to the use of AOU in the normalization.

4 CONCLUSIONS

362 The progressive acidification of the North Atlantic waters has been assessed from direct observations obtained

363 over the last 25 years (1991–2015), with the greatest pH decreases observed in surface and intermediate waters.

364 From the study of the main drivers of the observed pH changes we conclude that the observed pH decreases are

365 mainly a consequence of the oceanic C$_{ant}$ uptake. In addition we find that they have been partially offset by A$_T$

366 increases. Thus, while the C$_{ant}$ concentration of the upper layer roughly keeps up with that expected from rising

367 atmospheric CO$_2$, the pH decreases at a lower rate than expected from C$_{ant}$ increase. The increasing arrival of

368 saline and alkaline subtropical waters transported by the NAC to the study region related to the contraction of the

369 subpolar gyre since mid-90's buffers the acidification caused by the C$_{ant}$ increase in the upper layer. The

370 acidification rates in intermediate waters are similar to those in the surface waters, and are caused by a

371 combination of anthropogenic and non-anthropogenic components. The acidification of cLSW due to the C$_{ant}$

372 uptake is reinforced by the aging of this water mass from the end of the 1990s onwards. The pH of the deep

373 waters of the Irminger basin, DSOW, has clearly decreased in response to anthropogenic forcing. We also infer

374 that water mass warming contributes between 2 and 25% to the pH decrease of the upper and intermediate

375 waters of the Irminger basin, and 10% to the pH decrease of the upper waters of the Iceland basin.

Author Contributions

377 All authors contributed extensively to the work presented in this paper. M.I.G.-I., A.F.R., H.M., A.O. and

378 F.F.P. designed the research. M.I.G.-I., P.Z., F.F, L.I.C., A.F.R., H.M., A.O. and F.F.P. analysed the physical

379 and chemical data. M.I.G.-I. and P.Z. developed the code for processing the data. M.I.G.-I. and F.F.P.

380 determined the anthropogenic CO$_2$ concentrations, average layer properties and rates, and estimated the

381 uncertainties. M.I.G.-I. wrote the manuscript and prepared all figures, with contributions from all co-authors.

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662 **Table 1: List of hydrographic cruises used in this study (Fig. 1a). P.I. denotes principal investigator, #St the number of**
663 **stations used here, and 'Measurements' refers to the seawater CO_2 system measurements performed during these**
664 **cruises.**

Cruise Name	Expocode	Month/Year	Vessel	P.I.	#St	Measurements	Reference
AR07E	64TR91_1	04–05/1991	*Tyro*	H.M. van Aken	12	DIC	Stoll et al. (1996)
A01E	06MT18_1	09/1991	*Meteor*	J. Meincke	15	A_T and DIC	Meincke and Becker (1993)
A01E	06MT30_3	11–12/1994	*Meteor*	J. Meincke	27	DIC	Koltermann et al. (1996)
AR07E	06MT39_5	08–09/1997	*Meteor*	A. Sy	32	DIC	Rhein et al. (2002)
OVIDE 2002	35TH20020610	06–07/2002	*Thalassa*	H. Mercier	38	pH and A_T	Lherminier et al. (2007)
OVIDE 2004	35TH20040604	06–07/2004	*Thalassa*	T. Huck	56	pH and A_T	Lherminier et al. (2010)
OVIDE 2006	06MM20060523	05–06/2006	*Maria S. Merian*	P. Lherminier	44	pH and A_T	Gourcuff et al. (2011)
OVIDE 2008	35TH20080610	06–07/2008	*Thalassa*	H. Mercier	45	pH and A_T	Mercier et al. (2015)
OVIDE 2010	35TH20100610	06/2010	*Thalassa*	T. Huck; H. Mercier	46	pH and A_T	Mercier et al. (2015)
CATARINA[a]	29AH20120623	06–07/2012	*Sarmiento de Gamboa*	A.F. Ríos	44	pH and A_T	This work
GEOVIDE[a]	35PQ20140517	05–06/2014	*Pourquoi Pas?*	G. Sarthou	31	pH and A_T	This work
58GS20150410	58GS20150410	04-05/2015	*G.O. Sars*	A. Olsen	10	A_T and DIC	Fröb et al. (2016)

665 [a]Both CATARINA (http://catarina.iim.csic.es/en) and GEOVIDE (http://www.geovide.obs-vlfr.fr) cruises contain the OVIDE section
666 (http://www.umr-lops.fr/Projets/Projets-actifs/OVIDE), and in the study are referred to as OVIDE 2012 and 2014, respectively.

Year (N)	Pressure	θ	Salinity	AOU	A$_T$	C$_{ant}$	pH$_{Tis}$
2002 (144)	4205	2.182 ± 0.080	34.913 ± 0.008	86.1 ± 2.0	2351 ± 3	6.4 ± 1.3	8. 013 ± 0.003
2004 (158)	4263	2.162 ± 0.075	34.908 ± 0.007	87.1 ± 1.4	2352 ± 3	6.2 ± 1.2	8.013 ± 0.003
2006 (132)	4252	2.170 ± 0.082	34.913 ± 0.008	85.4 ± 1.6	2350 ± 3	6.2 ± 1.3	8.014 ± 0.003
2008 (125)	4206	2.179 ± 0.075	34.911 ± 0.007	84.9 ± 1.8	2353 ± 4	7.0 ± 1.6	8.016 ± 0.003
2010 (131)	4312	2.163 ± 0.077	34.908 ± 0.008	85.9 ± 1.6	2351 ± 3	7.0 ± 1.2	8.013 ± 0.002
2012 (102)	4397	2.149 ± 0.077	34.909 ± 0.008	87.9 ± 1.6	2352 ± 3	5.1 ± 1.2	8.015 ± 0.002
2014 (54)	4441	2.141 ± 0.069	34.904 ± 0.007	87.4 ± 1.36	2353 ± 3	5.5 ± 1.5	8.016 ± 0.003
		0.015	0.003	1.1	1.1	0.7	0.0015

672

Table 3: Observed temporal changes of pH at total scale and in situ conditions (in situ temperature and pressure; $\left(\frac{dpH_{Tis}}{dt}\right)_{obs}$) for the main water masses in the Irminger and Iceland basins for the period 1991–2015. pH changes caused by the main drivers (in situ temperature, T_{is}; salinity, S; total alkalinity, A_T; total dissolved inorganic carbon, DIC; the latter decomposed into its anthropogenic and natural components, C_{ant} and C_{nat}, respectively) are also shown, as well as the pH changes determined as the sum of the pH changes caused by the individual drivers ($\left(\frac{dpH_{Tis}}{dt}\right)_{total}$). All the trends are calculated based on the annually interpolated values and are in 10^{-3} pH units·yr^{-1}. Values in parenthesis are the percentages of the observed pH change explained by each one of its drivers. Consult Fig. 1 for water mass acronyms.

Basin	Water mass	$\left(\frac{dpH_{Tis}}{dt}\right)_{obs}$	$\frac{\partial pH_{Tis}}{\partial T_{is}}\frac{dT_{is}}{dt}$	$\frac{\partial pH_{Tis}}{\partial S}\frac{dS}{dt}$	$\frac{\partial pH_{Tis}}{\partial A_T}\frac{dA_T}{dt}$	$\frac{\partial pH_{Tis}}{\partial DIC}\frac{dDIC}{dt}$	$\frac{\partial pH_{Tis}}{\partial DIC}\frac{dC_{ant}}{dt}$	$\frac{\partial pH_{Tis}}{\partial DIC}\frac{dC_{nat}}{dt}$	$\left(\frac{dpH_{Tis}}{dt}\right)_{total}$
Irminger	SPMW	-1.84 ± 0.08	-0.04 ± 0.08 (2)	-0.021 ± 0.008 (1)	0.26 ± 0.07 (-14)	-2.05 ± 0.11 (111)	-2.21 ± 0.14 (120)	0.16 ± 0.10 (-9)	-1.85 ± 0.15 (100.5)
	uLSW	-1.60 ± 0.10	-0.23 ± 0.03 (14)	-0.016 ± 0.002 (1)	0.25 ± 0.03 (-16)	-1.61 ± 0.08 (101)	-1.83 ± 0.16 (114)	0.22 ± 0.21 (-14)	-1.61 ± 0.09 (100.6)
	cLSW	-1.59 ± 0.06	-0.40 ± 0.03 (25)	-0.040 ± 0.003 (3)	0.70 ± 0.05 (-44)	-1.85 ± 0.07 (116)	-0.55 ± 0.07 (34)	-1.31 ± 0.09 (82)	-1.60 ± 0.09 (100.3)
	ISOW	-1.31 ± 0.05	-0.09 ± 0.02 (7)	-0.009 ± 0.003 (1)	0.29 ± 0.06 (-22)	-1.50 ± 0.07 (115)	-0.99 ± 0.07 (76)	-0.50 ± 0.09 (39)	-1.31 ± 0.09 (100.1)
	DSOW	-1.47 ± 0.05	-0.16 ± 0.05 (11)	-0.015 ± 0.003 (1)	0.55 ± 0.07 (-37)	-1.85 ± 0.08 (126)	-1.27 ± 0.09 (87)	-0.58 ± 0.09 (39)	-1.48 ± 0.12 (100.6)
Iceland	SPMW	-1.59 ± 0.15	-0.16 ± 0.13 (10)	-0.016 ± 0.011 (1)	0.17 ± 0.12 (-11)	-1.60 ± 0.17 (101)	-1.54 ± 0.13 (97)	-0.06 ± 0.08 (4)	-1.60 ± 0.24 (100.9)
	uLSW	-1.09 ± 0.07	0.02 ± 0.02 (-2)	0.003 ± 0.002 (0)	-0.10 ± 0.07 (9)	-1.03 ± 0.06 (95)	-1.68 ± 0.15 (154)	0.65 ± 0.11 (-60)	-1.10 ± 0.10 (101.0)
	cLSW	-0.97 ± 0.11	-0.06 ± 0.02 (6)	-0.007 ± 0.002 (1)	0.18 ± 0.09 (-18)	-1.09 ± 0.14 (112)	-0.98 ± 0.08 (100)	-0.12 ± 0.11 (12)	-0.98 ± 0.17 (101.0)
	ISOW	-0.90 ± 0.09	-0.03 ± 0.01 (4)	-0.003 ± 0.001 (0)	0.11 ± 0.10 (-12)	-0.99 ± 0.14 (110)	-0.95 ± 0.08 (105)	-0.04 ± 0.11 (5)	-0.91 ± 0.18 (101.6)

21

682 **Figure 1: (a) Sampling locations of the twelve cruises used in this study (1991−2015) plotted on bathymetry (500 m**
683 **intervals). The black line shows the boundary between the Irminger and the Iceland basins constituted by the**
684 **Reykjanes Ridge. CGFZ = Charlie−Gibbs Fracture Zone. (b) Limits of the layers and basins considered in this study**
685 **plotted on top of the salinity distribution for the 2004 cruise. The isopycnals delineating the layers are defined by**
686 **potential density (referenced to 0 dbar, σ_0; 1000 dbar, σ_1; and 2000 dbar, σ_2; all in kg·m^{-3}), and the vertical white line**
687 **is the limit (Reykjanes Ridge) between the Irminger (left) and Iceland basins (right). The dashed vertical lines**
688 **represent the Longitude axis marks. The layer acronyms are Subpolar Mode Water (SPMW), upper and classical**
689 **Labrador Sea Water (uLSW and cLSW, respectively), Iceland−Scotland Overflow Water (ISOW) and Denmark**
690 **Strait Overflow Water (DSOW).**

691 **Figure 2: Distributions along the cruise track, from Greenland (left) to the Iceland basin (right) over study period**
692 **(1991−2015), for: (a) potential temperature (θ, in ºC), (b) salinity, (c) pH at total scale and in situ conditions (pHTis),**
693 **(d) total alkalinity (AT, in µmol·kg^{-1}), (e) apparent oxygen utilization (AOU, in µmol·kg^{-1}), (f) total dissolved inorganic**
694 **carbon (DIC; in µmol·kg^{-1}), (g) natural DIC (Cnat, in µmol·kg^{-1}) and (h) anthropogenic CO_2 (Cant, in µmol·kg^{-1}) for**
695 **the 2004 cruise. The dashed vertical lines represent the Longitude axis marks, and isopycnals delineating the layers**
696 **are shown as white lines.**

697 **Figure 3: Temporal evolution of average pH at total scale and in situ conditions of temperature and pressure (pH$_{Tis}$)**
698 **in the main water masses of the Irminger (a) and Iceland (b) basins, between 1991 and 2015. Each point represents the**
699 **average pH$_{Tis}$ of a particular layer (SPMW (red dots), uLSW (blue diamonds), cLSW (black asterisks), ISOW (green**
700 **squares) and DSOW (magenta stars)) at the time of each cruise (Table S1). The error bars are two times the error of**
701 **the mean (2σ = 2x(Standard Deviation)/$\sqrt{N}$, where 'N' is the number of samples of each layer). The legends also give**
702 **the trends (in 10^{-3} pH units·yr^{-1}) ± standard error of the estimate and the correlation coefficients (r^2), resulting from**
703 **the annually interpolated values. *** denotes that the trend is statistically significant at the 99% level (p-value < 0.01).**
704 **Consult Fig. 1 for layer acronyms.**

705 **Figure 4: Temporal evolution between 1991 and 2015 of average (a and b) in situ temperature (T$_{is}$, in ºC) and (c and**
706 **d) salinity in the main water masses of the Irminger (a and c) and Iceland (b and d) basins. Each point represents the**
707 **average property of a particular layer (SPMW (red dots), uLSW (blue diamonds), cLSW (black asterisks), ISOW**
708 **(green squares) and DSOW (magenta stars)) at the time of each cruise (Table S1). The error bars are 2σ. The legends**
709 **also give the trends (in 10^{-3} units·yr^{-1}) ± standard error of the estimate and the correlation coefficients (r^2), resulting**
710 **from the annually interpolated values. ** denotes that the trend is statistically significant at the at the 95% level (p-**
711 **value < 0.05), and *** at 99% level (p-value < 0.01). Consult Fig. 1 for layer acronyms.**

712 **Figure 5: Temporal evolution between 1991 and 2015 of average (a and b) total alkalinity (A$_T$, in µmol·kg^{-1}) and (c**
713 **and d) total dissolved inorganic carbon (DIC, in µmol·kg^{-1}) in the main water masses of the Irminger (a and c) and**
714 **Iceland (b and d) basins. Each point represents the average property of a particular layer (SPMW (red dots), uLSW**
715 **(blue diamonds), cLSW (black asterisks), ISOW (green squares) and DSOW (magenta stars)) at the time of each**
716 **cruise (Table S1). The error bars are 2σ. The legends also give the trends (in µmol·kg^{-1}·yr^{-1}) ± standard error of the**
717 **estimate and the correlation coefficients (r^2), resulting from the annually interpolated values. * denotes that the trend**
718 **is statistically significant at 90% level (p-value < 0.1), and *** at the 99% level (p-value < 0.01). Consult Fig. 1 for**
719 **layer acronyms.**

720 **Figure 6: Temporal evolution between 1991 and 2015 of average (a and b) anthropogenic CO_2 (C$_{ant}$, in µmol·kg^{-1}) and**
721 **(c and d) natural DIC (C$_{nat}$ = DIC - C$_{ant}$, in µmol·kg^{-1}) values in the main water masses of the Irminger (a and c) and**
722 **Iceland (b and d) basins. Each point represents the average property of a particular layer (SPMW (red dots), uLSW**
723 **(blue diamonds), cLSW (black asterisks), ISOW (green squares) and DSOW (magenta stars)) at the time of each**
724 **cruise (Table S1). The error bars are 2σ. The legends also give the trends (in µmol·kg^{-1}·yr^{-1}) ± standard error of the**
725 **estimate and the correlation coefficients (r^2), resulting from the annually interpolated values. *** denotes that the**
726 **trend is statistically significant at the 99% level (p-value < 0.01). Consult Fig. 1 for layer acronyms.**