



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

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Abstract. Repeated hydrographic sections provide critically needed data on and understanding of changes in basin-wide ocean CO₂ 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 CO₂ 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 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 CO₂ (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.

1 Introduction

The oceanic uptake of a fraction of the anthropogenic CO₂ (i.e. C_{ant} ; CO₂ released from humankind’s industrial and agricultural activities) has resulted in long-term changes in ocean CO₂ 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 CO₂ chemistry result in declining pH and reduced saturation states for CaCO₃ minerals (e.g. Bates et al., 2014). The average pH ($-\log_{10}[\text{H}^+]$) 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 CO₂ emission scenarios (Caldeira and Wickett, 2005; Orr, 2011; Ciais et al., 2013). The rate of change in pH is at least a hundred times faster than at any time since the last ice age (Feely et al., 2004; Raven et al., 2005), clearly outpacing natural processes in ocean chemistry that have occurred in the past due to geological processes (Raven et al., 2005). These changes

in ocean CO₂ chemistry will most likely have adverse effects on organisms, particularly calcifying ones; ecosystems (e.g. Langdon et al., 2000; Riebesell et al., 2000; Pörtner et al., 2004) and major marine biogeochemical cycles (e.g. Gehlen et al., 2011; Matear and Lenton, 2014).

The global ocean has absorbed ~ 30 % of the C_{ant} emitted to the atmosphere between 1750 and the present (Sabine et al., 2004; Khatiwala et al., 2013; DeVries, 2014; Le Quéré et al., 2015). This C_{ant} is not evenly distributed throughout the oceans (Sabine et al., 2004), but enters the interior ocean preferentially in regions of deep convective overturning and subduction (Maier-Reimer and Hasselmann, 1987; Sarmiento et al., 1992; Lazier et al., 2002). This explains why the meridional overturning circulation (MOC) makes the North Atlantic Ocean one of the most important C_{ant} sinks of the global ocean, storing 25 % of the global oceanic C_{ant} (Sabine et al., 2004; Khatiwala et al., 2013) despite being only 11 % of the global ocean volume (Eakins and Sharman, 2010). The MOC transports C_{ant} -laden surface waters from the Equator to the northern North Atlantic Ocean (e.g. Wallace, 2001; Anderson and Olsen, 2002; Olsen et al., 2006; Zunino et al., 2015), where deep water formation provides a pathway for C_{ant} into the interior ocean (Lazier et al., 2002; Pérez et al., 2008, 2013; Steinfeldt et al., 2009). Being regions close to deep water formation areas and where water mass transformation occurs (Sarafanov et al., 2012; García-Ibáñez et al., 2015), the Irminger and Iceland basins are geographically well placed to monitor temporal changes in the Atlantic MOC (Mercier et al., 2015) and to determine the rates of C_{ant} penetration to the deep ocean and its consequence for OA.

In this paper, we examine high-quality direct measurements of ocean CO₂ chemistry from twelve cruises conducted across the Irminger and Iceland basins between 1991 and 2015. Previous studies focused on C_{ant} uptake and its storage and effect on pH in the Irminger and Iceland basins (e.g. Pérez et al., 2008; Olafsson et al., 2009; Bates et al., 2012; Vázquez-Rodríguez et al., 2012b). Here we quantify the pH change for a 25-year period and identify its chemical and physical drivers by decomposing the observed pH change into five numerically estimated factors (temperature, salinity, alkalinity, anthropogenic CO₂ and non-anthropogenic CO₂), all based on direct measurements.

2 Materials and methods

2.1 Datasets

2.1.1 Cruise Information

We used data from twelve cruises along the same track across the Irminger and Iceland basins, with the cruise dates spanning 25 years (1991–2015; Table 1, Fig. 1a). The bottle data were accessed from the merged data product of the

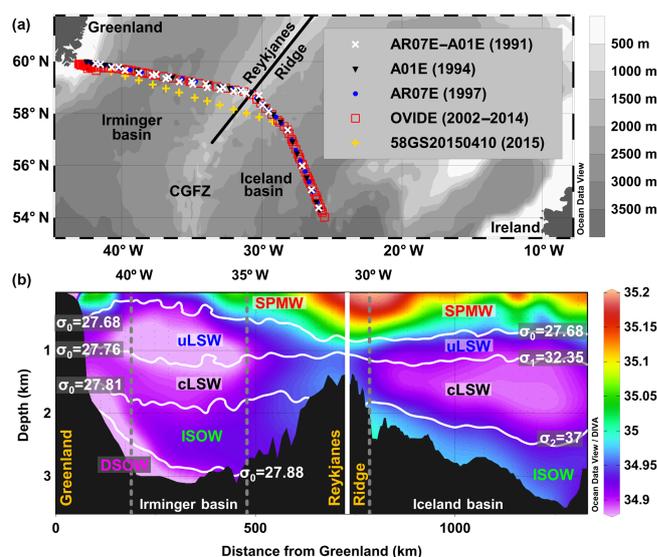


Figure 1. (a) Sampling locations of the twelve cruises used in this study (1991–2015) plotted on bathymetry (500 m intervals). The black line shows the boundary between the Irminger and the Iceland basins constituted by the Reykjanes Ridge. CGFZ stands for Charlie–Gibbs Fracture Zone. (b) Limits of the layers and basins considered in this study plotted on top of the salinity distribution for the 2004 cruise. The isopycnals delineating the layers are defined by 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 is the limit (Reykjanes Ridge) between the Irminger (left) and Iceland basins (right). The dashed vertical lines represent the longitude axis marks. The layer acronyms are Subpolar Mode Water (SPMW), upper and classical Labrador Sea Water (uLSW and cLSW, respectively), Iceland–Scotland Overflow Water (ISOW) and Denmark Strait Overflow Water (DSOW).

Global Data Analysis Project version 2 (GLODAPv2; Olsen et al., 2016) at <http://cdiac.ornl.gov/oceans/GLODAPv2>, except for more recent data collected during the OVIDE 2012 and 2014 cruises and the 2015 cruise (58GS20150410). The data of the 1991 cruises (64TR91_1 and 06MT18_1) were merged and treated as a single cruise.

2.1.2 Ocean CO₂ chemistry measurements

The twelve cruises selected for our study have high-quality measurements of the seawater CO₂ 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 was calibrated with certified reference materials (CRMs) with an overall accuracy of $4 \mu\text{mol kg}^{-1}$. For samples without direct A_T measurements, A_T was estimated using a 3-D moving window multilinear regression algorithm (3DwMLR), using potential temperature (θ), salinity, nitrate, phosphate, silicate and

Table 1. List of hydrographic cruises used in this study (Fig. 1a). P.I. denotes principal investigator, #St the number of stations used here and “Measurements” refers to the seawater CO₂ system measurements performed during these cruises.

Cruise name	Expocode	Month yr ⁻¹	Vessel	P.I.	#St	Measurements	Reference
AR07E	64TR91_1	04–05/1991	<i>Tyro</i>	H. M. van Aken	12	DIC	Stoll et al. (1996)
A01E	06MT18_1	09/1991	<i>Meteor</i>	J. Meincke	15	A _T and DIC	Meincke and Becker (1993)
A01E	06MT30_3	11–12/1994	<i>Meteor</i>	J. Meincke	27	DIC	Koltermann et al. (1996)
AR07E	06MT39_5	08–09/1997	<i>Meteor</i>	A. Sy	32	DIC	Rhein et al. (2002)
OVIDE 2002	35TH20020610	06–07/2002	<i>Thalassa</i>	H. Mercier	38	pH and A _T	Lherminier et al. (2007)
OVIDE 2004	35TH20040604	06–07/2004	<i>Thalassa</i>	T. Huck	56	pH and A _T	Lherminier et al. (2010)
OVIDE 2006	06MM20060523	05–06/2006	<i>Maria S. Merian</i>	P. Lherminier	44	pH and A _T	Gourcuff et al. (2011)
OVIDE 2008	35TH20080610	06–07/2008	<i>Thalassa</i>	H. Mercier	45	pH and A _T	Mercier et al. (2015)
OVIDE 2010	35TH20100610	06/2010	<i>Thalassa</i>	T. Huck; H. Mercier	46	pH and A _T	Mercier et al. (2015)
CATARINA*	29AH20120623	06–07/2012	<i>Sarmiento de Gamboa</i>	A. F. Ríos	44	pH and A _T	This work
GEOVIDE*	35PQ20140517	05–06/2014	<i>Pourquoi Pas?</i>	G. Sarthou	31	pH and A _T	This work
58GS20150410	58GS20150410	04–05/2015	<i>G.O. Sars</i>	A. Olsen	10	A _T and DIC	Fröb et al. (2016)

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

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 calibrated with CRMs, achieving an overall accuracy of 2 μmol kg⁻¹. For the cruises for which direct DIC measurements had not been performed, it was computed from A_T and pH using the thermodynamic equations of the seawater CO₂ system (Dickson et al., 2007) and the CO₂ dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987). These calculated DIC values have an associated uncertainty of 4 μmol 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, pH was computed from A_T and DIC using the thermodynamic equations of the seawater CO₂ system (Dickson et al., 2007) and the CO₂ 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 μmol 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 μmol 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_{T_{is}}).

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:

$$C_{\text{ant}} = \text{DIC}_{\text{meas}} - \Delta C_{\text{bio}} - \text{DIC}_{\text{preind}} - \Delta C_{\text{diseq}}, \quad (1)$$

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}). 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 empirical parameterisation of the preformed A_T (A_T⁰) for the computation of the calcium carbonate dissolution and of the ΔC_{diseq} term (Vázquez-Rodríguez et al., 2012a). The A_T⁰ is based on the concept of potential alkalinity (PA_T = A_T + NO₃ + PO₄) and is defined as A_T⁰ = PA_T – (NO₃⁰ + PO₄⁰) (Vázquez-Rodríguez et al., 2012a), where NO₃⁰ and PO₄⁰ are the preformed nitrate and phosphate concentrations, respectively. NO₃⁰ and PO₄⁰ are determined as NO₃⁰ = NO₃ – AOU / R_{ON} and PO₄⁰ = PO₄ – AOU / R_{OP}. In the former equations AOU (apparent oxygen utilisation) is the difference between the saturated concentrations of oxygen calculated using the equations of Benson and Krause (1984) and the measured con-

centrations of oxygen, while R_{ON} and R_{OP} are the Redfield ratios proposed by Broecker (1974).

The φC_T^0 method presents two main advantages relative to the previous method proposed by Gruber et al. (1996). First, the spatiotemporal variability of A_T^0 is taken into account. And second, the parameterisations of A_T^0 and ΔC_{diseq} are determined using the subsurface layer as a reference (Vázquez-Rodríguez et al., 2012a), where the age of the water parcel, and therefore its C_{ant} concentration, is estimated using CFC measurements (Waugh et al., 2006). The overall uncertainty of the φC_T^0 method has been estimated at $5.2 \mu\text{mol kg}^{-1}$ (Pérez et al., 2008; Vázquez-Rodríguez, 2009a).

2.1.4 Trend uncertainty

The uncertainties and reproducibilities of the analysis and calculation methods were determined from the deep waters sampled at the Iberian Abyssal Plain during the seven repetitions of the OVIDE line, since these waters are expected to be in near steady state. The standard deviations of those samples for each cruise (Table 2) were taken as an estimate of the uncertainty at each cruise. The uncertainties of the AOU, A_T and $\text{pH}_{T_{is}}$ for the seven cruises were similar. The standard deviations of C_{ant} ($1.2\text{--}1.6 \mu\text{mol kg}^{-1}$) and $\text{pH}_{T_{is}}$ ($0.002\text{--}0.003$ pH units) for each of the seven cruises are lower than the inherent uncertainty of the φC_T^0 estimates ($5.2 \mu\text{mol kg}^{-1}$) and the accuracy of the spectrophotometric pH measurements (0.0055 pH units), which provides confidence that these data are suitable for trend determination. The standard deviations of the C_{ant} estimates are rather similar to those from other regions where C_{ant} has been compared across many cruises (i.e. $2.4 \mu\text{mol kg}^{-1}$ in the South Atlantic Ocean, Ríos et al. (2003); $2.7 \mu\text{mol kg}^{-1}$ in the equatorial Atlantic Ocean, 24° N, Guallart et al. (2015); and $2.7 \mu\text{mol kg}^{-1}$ reported from a transect along the western boundary of the Atlantic Ocean from 50° S to 36° N, Ríos et al., 2015). The standard deviations of the mean values of the Iberian Abyssal Plain samples across all (last row of Table 2) were taken as an estimate of the reproducibility of the methodologies. The high reproducibility of the pH measurements, at an order of magnitude higher than the uncertainty (0.0055 pH units, Carter et al., 2013), is suggestive of high quality data. Using these standard deviations for the seven cruises, and taking into account the 25 years considered in this study, the threshold of detectability of pH trends at 95 % of confidence is 0.00012 pH units yr^{-1} , which renders confidence to the estimated trends.

2.2 Water mass characterisation

Changes in ocean CO_2 chemistry were determined for the main water masses in the Irminger and Iceland basins. These are (1) Subpolar Mode Water (SPMW), (2) upper and classical Labrador Sea Water (uLSW and cLSW, respectively), (3) Iceland–Scotland Overflow Water (ISOW) and (4) Den-

mark Strait Overflow Water (DSOW; Fig. 1b). The layers defining the water masses were delimited using potential density following Azetsu-Scott et al. (2003), Kieke et al. (2007), Pérez et al. (2008) and Yashayaev et al. (2008). The advantage of working in layers is the relatively low variability of the physical and chemical properties within the layers, 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 $\text{pH}_{T_{is}}$, which is pressure sensitive and for which we needed to define a unique reference pressure to remove pressure effects due to varying sampling strategies. $\text{pH}_{T_{is}}$ 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 interannual trends, only samples with pressure ≥ 75 dbar were considered. The 75 dbar level was determined by the depth of the seasonal nutrients draw-down along the section. The average values of the variables for each layer and their standard deviations can be found in the Supplement (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. 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, which is taken into account by the relationship proposed by Uppström (1974).

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

$$\left(\frac{d\text{pH}_{T_{is}}}{dt}\right)_{\text{total}} = \frac{\partial \text{pH}_{T_{is}}}{\partial T_{is}} \frac{dT_{is}}{dt} + \frac{\partial \text{pH}_{T_{is}}}{\partial S} \frac{dS}{dt} + \frac{\partial \text{pH}_{T_{is}}}{\partial A_T} \frac{dA_T}{dt} + \frac{\partial \text{pH}_{T_{is}}}{\partial \text{DIC}} \left(\frac{dC_{ant}}{dt} + \frac{dC_{nat}}{dt}\right). \quad (2)$$

To estimate $\frac{\partial \text{pH}_{T_{is}}}{\partial \text{var}}$ (where “var” refers to each of the drivers: T_{is} , S , A_T and DIC) we calculated a $\text{pH}_{T_{is}}$ for each layer and

Table 2. Mean values of pressure (in dbar), potential temperature (θ , in $^{\circ}\text{C}$), salinity, apparent oxygen utilisation (AOU, in $\mu\text{mol kg}^{-1}$), total alkalinity (A_{T} , in $\mu\text{mol kg}^{-1}$), anthropogenic CO_2 (C_{ant} , in $\mu\text{mol kg}^{-1}$) and pH at total scale and in situ conditions of temperature and pressure ($\text{pH}_{\text{T}_{\text{is}}}$) for the bottom waters of the Iberian Abyssal Plain sampled during the seven OVIDE cruises. “ N ” represents the number of data considered in each cruise and “ \pm ” the standard deviation. The last row represents the intercruise standard deviation of the mean values.

Year (N)	Pressure	θ	Salinity	AOU	A_{T}	C_{ant}	$\text{pH}_{\text{T}_{\text{is}}}$
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

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 the sensitivity of $\text{pH}_{\text{T}_{\text{is}}}$ to changes in C_{ant} is the same as the sensitivity to changes in C_{nat} since both are DIC; therefore only $\frac{\partial \text{pH}_{\text{T}_{\text{is}}}}{\partial \text{DIC}}$ is necessary. To estimate each $\frac{d\text{var}}{dt}$ term we performed a linear regression between var and time for each layer.

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

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 1990s compared to the 2000s.

3 Results and discussion

3.1 Distribution of water mass properties

The Irminger and Iceland basins in the North Atlantic are characterised by warm and saline surface waters as well as 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. At the bottom of the Irminger basin a fifth layer, DSOW, being the coldest and freshest layer of the section, is distinguished.

The general pattern of $\text{pH}_{\text{T}_{\text{is}}}$ (Fig. 2c) by and large follows 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 $\text{pH}_{\text{T}_{\text{is}}}$ 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 remineralisation 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, which has an extension that 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). The 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

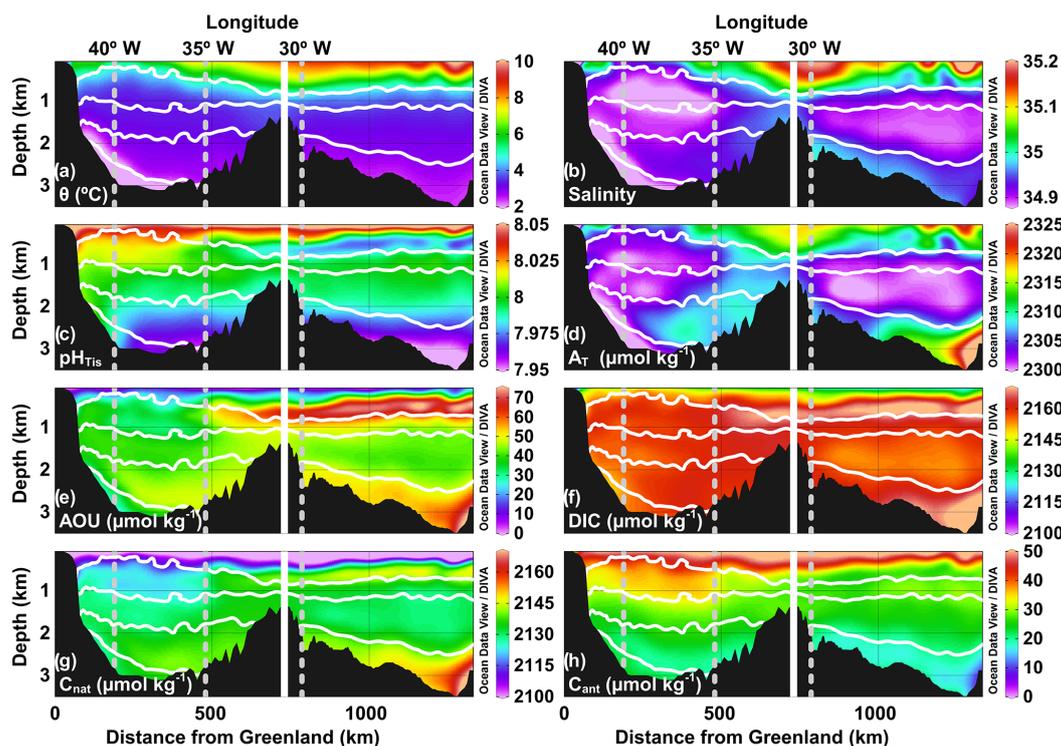


Figure 2. Distributions along the cruise track from Greenland (left) to the Iceland basin (right) over the study period (1991–2015) for (a) potential temperature (θ , in $^{\circ}\text{C}$), (b) salinity, (c) pH at total scale and in situ conditions (pH_{Tis}), (d) total alkalinity (A_{T} , in $\mu\text{mol kg}^{-1}$), (e) apparent oxygen utilisation (AOU, in $\mu\text{mol kg}^{-1}$), (f) total dissolved inorganic carbon (DIC; in $\mu\text{mol kg}^{-1}$), (g) natural DIC (C_{nat} , in $\mu\text{mol kg}^{-1}$) and (h) anthropogenic CO_2 (C_{ant} , in $\mu\text{mol kg}^{-1}$) for the 2004 cruise. The dashed vertical lines represent the longitude axis marks, and isopycnals delineating the layers are shown as white lines.

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 surface values and high bottom values (Fig. 2g), similar to that of the AOU distribution (Fig. 2e), since C_{nat} is linked to the ventilation of water masses, i.e. respiration and renewal of the water mass.

The A_{T} distribution along the section resembles the salinity distribution, with high values associated with the relatively saline central waters and relatively low and almost homogeneous values in the rest of the section (Fig. 2d). The exception comes with the ISOW layer. The high A_{T} values found in the ISOW layer of the Iceland basin are not mirrored in the salinity distribution. This reflects the influence of NADW that is traced by the relatively large amounts of silicate related to the influence of the Antarctic Bottom Water, which provides high A_{T} from dissolution of CaCO_3 . The influence of these high A_{T} values is then transported by the ISOW circulation to the Irminger basin.

3.2 Water mass acidification and drivers

Trends of pH_{Tis} in each layer and basin are presented in Table 3, in Fig. 3 and in Supplement Fig. S1. The pH_{Tis} has decreased in all layers of the Irminger and Iceland basins during a time period of more than 20 years (1991–2015) that is covered by the data. The trends are stronger in the Irminger basin due to the presence of younger waters. The rate of pH decline decreases with depth, except for the DSOW layer that has acidification rates close to those found in the cLSW layer. This indicates that DSOW is a newly formed water mass that

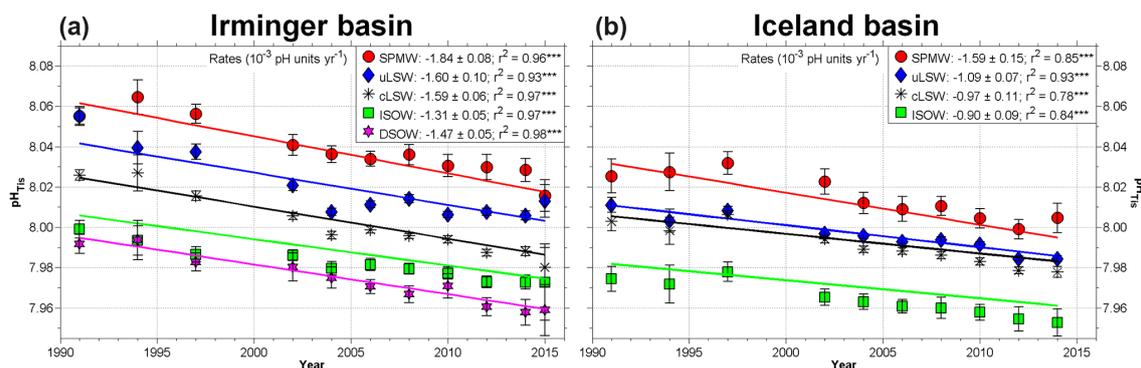


Figure 3. Temporal evolution of average pH at total scale and in situ conditions of temperature and pressure (pH_{Tis}) in the main water masses of the Irminger (a) and Iceland (b) basins between 1991 and 2015. Each point represents the average pH_{Tis} of a particular layer (SPMW (red dots), uLSW (blue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

has recently been in contact with the atmosphere. Moreover, the acidification rate in the ISOW layer in the Irminger basin is relatively low, which could be related to the increasing importance of the relatively old NADW in this layer, with the reduction in cLSW formation since the mid-90s (Lazier et al., 2002; Yashayaev, 2007).

The observed rate of pH_{Tis} decrease in the SPMW layer of the Iceland basin (-0.0016 ± 0.0001 pH units yr^{-1} ; Table 3, Fig. 3b) is in agreement with that observed at the Iceland Sea time series (68°N , 12.66°W ; Olafsson et al., 2009, 2010) for the period 1983–2014 (-0.0014 ± 0.0005 pH units yr^{-1} ; Bates et al., 2014). However, our rate of pH_{Tis} decrease in the SPMW layer in the Irminger basin (-0.0018 ± 0.0001 pH units yr^{-1}) is lower than that observed in the sea surface waters of the Irminger Sea time series (64.3°N , 28°W ; Olafsson et al., 2010) for the period 1983–2014 (-0.0026 ± 0.0006 pH units yr^{-1} ; Bates et al., 2014), which is exceptionally high compared to the other time series summarised here. Bates et al. (2014) linked the high acidification rate found at the Irminger Sea time series to the high rate of increase in DIC ($1.62 \pm 0.35 \mu\text{mol kg}^{-1} \text{yr}^{-1}$) observed at this site, which is almost three times our rate of increase in DIC ($0.64 \pm 0.07 \mu\text{mol kg}^{-1} \text{yr}^{-1}$, Fig. 5c). This is based on data from only one site, further north than our section, and indicates that spatial variations are substantial in this region. Besides, the acidification rates in the SPMW layer of both basins reported here are in agreement with the rates of -0.0020 ± 0.0004 pH units yr^{-1} determined for the North Atlantic subpolar seasonally stratified biome for the period 1991–2011 (Lauvset et al., 2015). Compared to the subtropical Atlantic time series stations, our rates in the SPMW layer of both basins are in agreement with those observed at ESTOC (European Station for Time se-

ries in the ocean) (29.04°N , 15.50°W ; Santana-Casiano et al., 2007; González-Dávila et al., 2010) for the period 1995–2014 (-0.0018 ± 0.0002 pH units yr^{-1} ; Bates et al., 2014) and BATS (Bermuda Atlantic Time-series Study) (32°N , 64°W ; Bates et al., 2014) for the period 1983–2014 (-0.0017 ± 0.0001 pH units yr^{-1} ; Bates et al., 2014). Compared to the Pacific Ocean, the OA rates in the Iceland and Irminger basins are in agreement with those reported for the central North Pacific based on data from the time series station HOT (Hawaii Ocean Time-series) (22.45°N , 158°W ; Dore et al., 2009) for the period 1988–2014 (-0.0016 ± 0.0001 pH units yr^{-1} ; Bates et al., 2014), but are slightly higher than those determined by Wakita et al. (2013) in the winter mixed layer at the subarctic western North Pacific (time series stations K2 and KNOT) for the period 1997–2011 (-0.0010 ± 0.0004 pH units yr^{-1}). Wakita et al. (2013) attributed the lower-than-expected pH trends to an increasing A_{T} trend.

To infer the causes of the acidification trends reported here, we decomposed the pH trends into their individual components as described in Sect. 2.2. The values of each term, $\frac{\partial \text{pH}_{\text{Tis}}}{\partial \text{var}}$ and $\frac{d\text{var}}{dt}$ (where “var” refers to each of the drivers), described in Sect. 2.2 can be found in the Supplement in Table S2 and Figs. 4–6, respectively. The results of solving Eq. (2) are presented in Table 3. The sum of the pH changes caused by the individual drivers, i.e. $\left(\frac{d\text{pH}_{\text{Tis}}}{dt}\right)_{\text{total}}$ matches the observed pH trends $\left(\left(\frac{d\text{pH}_{\text{Tis}}}{dt}\right)_{\text{obs}}\right)$, which renders confidence to the method.

The temperature changes (Fig. 4a, b) have generally resulted in small-to-negligible pH declines (Table 3). Specifically, warming corresponds to a pH decrease of at least 0.0002 pH units yr^{-1} in the SPMW layer of the Iceland basin

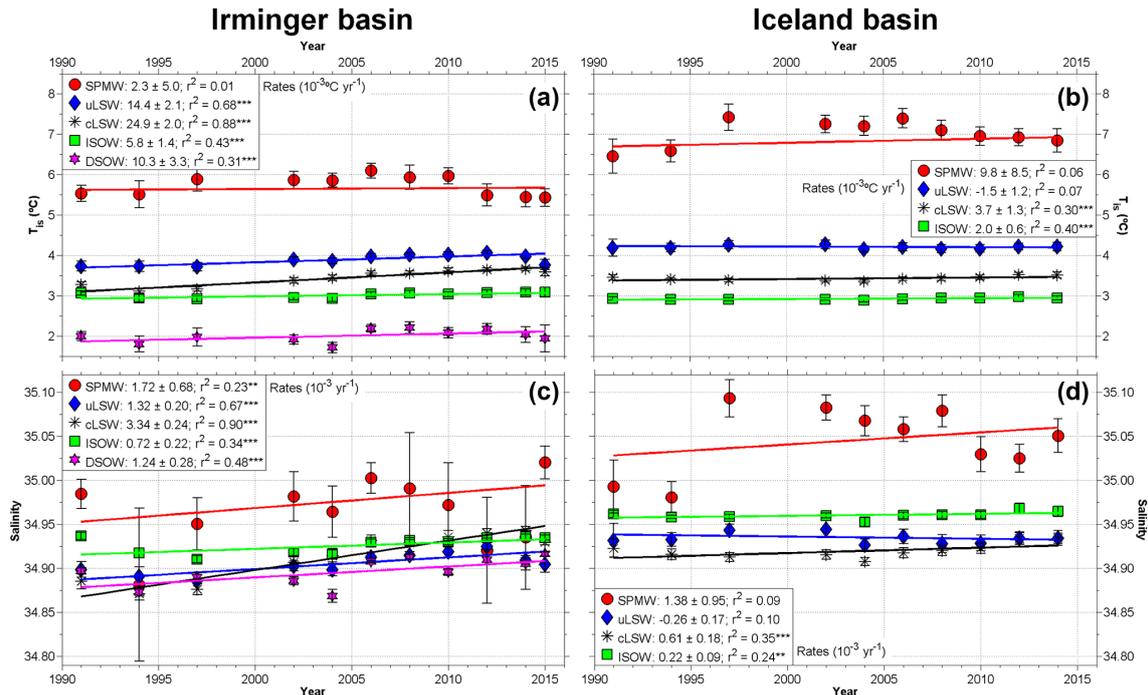


Figure 4. Temporal evolution between 1991 and 2015 of average (a, b) in situ temperature (T_{is} , in °C) and (c, d) salinity in the main water masses of the Irminger (a, c) and Iceland (b, d) basins. Each point represents the average property of a particular layer (SPMW (red dots), uLSW (blue diamonds),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

and in the LSW and DSOW layers of the Irminger basin, while the effect of temperature changes on pH in the other layers is negligible. Temperature-driven pH change is larger in the LSW layers in the Irminger than in the Iceland basin. In the case of the uLSW layer, this is possibly explained by the deep convection occurring in the Irminger basin (Pickart et al., 2003; García-Ibáñez et al., 2015; Fröb et al., 2016; Piron et al., 2016). In the case of the cLSW layer, the higher pH changes driven by temperature changes in the Irminger basin could be explained by the rapid advection of the water mass from the Labrador Sea to this basin (Yashayaev et al., 2007). Temperature driven pH change in the DSOW layer could be related to the entrainment of LSW into DSOW that takes place downstream of the Greenland–Iceland sills (Read, 2000; Yashayaev and Dickson, 2008). The temperature effect on pH evaluated here is thermodynamic. The same applies to the salinity effect, which however is small to negligible, reflecting how salinity changes in the region (Fig. 4c, d) are insufficiently large to significantly change pH.

Overall, the A_T has increased in the Irminger and Iceland basins (Fig. 5a, b), corresponding to increasing pH (Table 3), which counteracts the acidification from the CO_2 absorption. The contribution from A_T to reduce ocean acidification is significant in all layers except for uLSW of the Iceland basin

(where the trend in A_T is decreasing, but not significant; Fig. 5b). The similar behaviour of the salinity and A_T trends over time may indicate that the changes in A_T are mainly driven by changes in salinity. The A_T increasing trends observed in the SPMW layer could be related to the increasing presence of waters of subtropical origin (with higher A_T) as the subpolar gyre was shrinking from the mid-90s into the 2000s (e.g. Flatau et al., 2003; Häkkinen and Rhines, 2004; Böning et al., 2006). In the case of the LSW layers, the increase in A_T can be explained by the mid-90s cessation of the cLSW formation (Lazier et al., 2002; Yashayaev, 2007), with the consequent salinisation (and increase in A_T) of this water mass. The signal of the cLSW salinisation was then transmitted to the overflow layers due to the entrainment events (Sarafanov et al., 2010).

The DIC increase (Fig. 5c, d) is the main cause of the observed pH decreases (Table 3) and corresponds to pH drops between -0.00099 ± 0.00014 and -0.00205 ± 0.00011 pH units yr^{-1} . The waters in both the Irminger and Iceland basins gained DIC in response to the increase in atmospheric CO_2 ; the convection processes occurring in the former basin (Pickart et al., 2003; Thierry et al., 2008; de Boissésou et al., 2010; García-Ibáñez et al., 2015; Fröb et al., 2016; Piron et al., 2016) and in the sur-

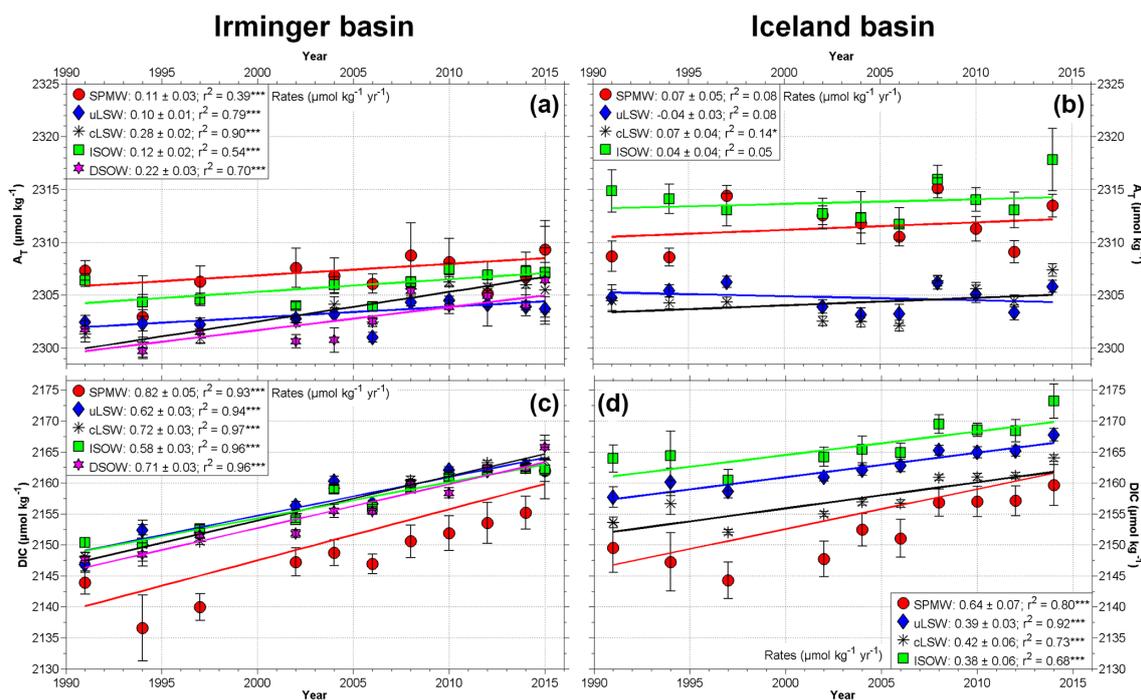


Figure 5. Temporal evolution between 1991 and 2015 of average (a, b) total alkalinity (A_T , in $\mu\text{mol kg}^{-1}$) and (c, d) total dissolved inorganic carbon (DIC, in $\mu\text{mol kg}^{-1}$) in the main water masses of the Irminger (a, c) and Iceland (b, d) basins. Each point represents the average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

rounding ones (i.e. Labrador and Nordic seas) provide an important pathway for DIC to pass from the surface mixed layer to the intermediate and deep layers. The effect of the DIC increase on pH is generally dominated by the anthropogenic component (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 layers, owing to their 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 the globally averaged marine surface annual mean $p\text{CO}_2$ data from the NOAA as a reference, 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 that 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 water CO_2 concentration rise lags behind that of the atmosphere by between two and 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 that the increasing presence of warmer and more saline (with higher A_T) waters of subtropical origin partially counteracts the effects of increasing DIC values, because A_T effects dominate (as stated before, the effect of salinity change on pH is negligible). Overall this change can be explained as the result of the contraction of the subpolar gyre that took place since the 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 the 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).

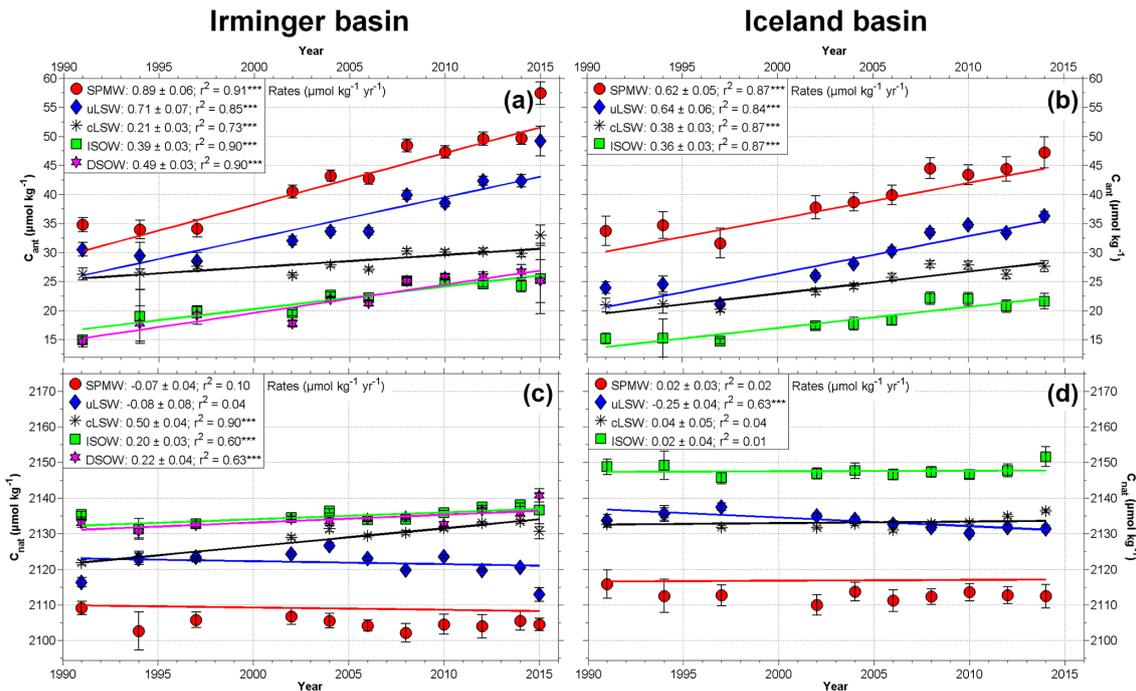


Figure 6. Temporal evolution between 1991 and 2015 of average (a, b) anthropogenic CO_2 (C_{ant} , in $\mu\text{mol kg}^{-1}$) and (c, d) natural DIC ($C_{\text{nat}} = \text{DIC} - C_{\text{ant}}$, in $\mu\text{mol kg}^{-1}$) values in the main water masses of the Irminger (a, c) and Iceland (b, d)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

Stronger pH decreases related to C_{nat} changes indicate a 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). A similar effect of 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 interannual 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 interannual 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 interannual variability in the C_{nat} values of the uLSW layer in the Iceland basin promotes better detectability of the ventilation of the uLSW layer, resulting in an offset up to 60 % of the effects of acidification on the uLSW layer of the Iceland basin.

Vázquez-Rodríguez et al. (2012b) previously studied the pH changes in the different water masses of the Irminger and Iceland basins. These authors carried out a pH normalisation to avoid potential biases due to different ventilation stages and rates of each layer from the different spatial coverage of the evaluated cruises. The normalised pH values (pH_N) for each layer were obtained using multiple linear regressions between the observed mean pH_{SWs25} (pH at seawater scale and 25°C) and the observed mean values of θ , salinity, silicate and AOU, referring to the mean climatological values of θ , salinity, silicate and AOU compiled in WOA05 (http://www.nodc.noaa.gov/OC5/WOA05/pr_woa05.html). This normalisation, combined with the different temporal coverage (1981–2008), causes the rates reported by Vázquez-Rodríguez et al. (2012b) to differ from those obtained in the present work. The pH_N trends reported for the SPMW and uLSW layers of the Irminger basin and for the ISOW layer of the Iceland basin are very similar to our pH_{Tis} trends for these layers. However, the pH_N trends reported by Vázquez-Rodríguez et al. (2012b) for the cLSW layer in both basins and for the ISOW layer in the Irminger basin are significantly different from our pH_{Tis} trends for these layers, but are very similar to pH changes derived from C_{ant} changes: $\frac{\partial \text{pH}_{\text{Tis}}}{\partial \text{DIC}} \frac{dC_{\text{ant}}}{dt}$ (Table 3). In the case of the DSW

Table 3. Observed temporal changes of pH at total scale and in situ temperature and pressure conditions: $\left(\frac{dpH_{T_{15}}}{dt}\right)^{obs}$ 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_{15} ; salinity, S ; 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 $\left(\frac{dpH_{T_{15}}}{dt}\right)^{total}$. 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.

	$\left(\frac{dpH_{T_{15}}}{dt}\right)^{obs}$	$\frac{\partial pH_{T_{15}}}{\partial T_{15}} \frac{dT_{15}}{dt}$	$\frac{\partial pH_{T_{15}}}{\partial S} \frac{dS}{dt}$	$\frac{\partial pH_{T_{15}}}{\partial A_T} \frac{dA_T}{dt}$	$\frac{\partial pH_{T_{15}}}{\partial DIC} \frac{dDIC}{dt}$	$\frac{\partial pH_{T_{15}}}{\partial DIC} \frac{dC_{ant}}{dt}$	$\frac{\partial pH_{T_{15}}}{\partial DIC} \frac{dC_{nat}}{dt}$	$\left(\frac{dpH_{T_{15}}}{dt}\right)^{total}$
Irminger	SPMW	-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	-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	-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	-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	-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	-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	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	-0.06 ± 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	-0.03 ± 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)

layer, the pH_N trend is also in agreement with $\frac{\partial pH_{T_{15}}}{\partial DIC} \frac{dC_{ant}}{dt}$ trends. This suggests that the normalisation carried out by Vázquez-Rodríguez et al. (2012b) could remove some of the impact of the natural component (represented here by C_{nat}) over pH changes, essentially due to the use of AOU in the normalisation.

4 Conclusions

The progressive acidification of the North Atlantic waters has been assessed from direct observations obtained over the last 25 years (1991–2015), with the greatest pH decreases observed in surface and intermediate waters. From the study of the main drivers of the observed pH changes we conclude that the observed pH decreases are mainly a consequence of the oceanic C_{ant} uptake. In addition we find that they have been partially offset by A_T increases. Thus, while the C_{ant} concentration of the upper layer roughly keeps up with the concentration expected from rising atmospheric CO_2 , the pH decreases at a lower rate than expected from C_{ant} increase. The increasing arrival of saline and alkaline subtropical waters transported by the NAC to the study region, related to the contraction of the subpolar gyre since the mid-90s, buffers the acidification caused by the C_{ant} increase in the upper layer. The acidification rates in intermediate waters are similar to those in the surface waters and are caused by a combination of anthropogenic and non-anthropogenic components. The acidification of cLSW due to the C_{ant} uptake is reinforced by the aging of this water mass from the end of the 1990s onwards. The pH of the deep waters of the Irminger basin, DSOW, has clearly decreased in response to anthropogenic forcing. We also infer that water mass warming contributes between 2 and 25 % to the pH decrease of the upper and intermediate waters of the Irminger basin, and 10 % to the pH decrease of the upper waters of the Iceland basin.

5 Data availability

OVIDE 2012 data was accessed from the Cli-var & Carbon Hydrographic Data Office (CCHDO; <http://cchdo.ucsd.edu/cruise/29AH20120622>), and OVIDE 2014 data is publicly available at http://www.obs-vlfr.fr/proof/ftpfree/geovide/ALKALINITY_PH/. The data from the 58GS20150410 cruise is unpublished and can be obtained per request to Are Olsen (are.olsen@gfi.uib.no). They have not yet been made public in order to protect the interest of a PhD student who relies heavily on them for her work. It is our intention to release them when that has been completed, in 2017.

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Author contributions. All authors contributed extensively to the work presented in this paper. Maribel I. García-Ibáñez, Aida F. Ríos, Herlé Mercier, Are Olsen and Fiz F. Pérez designed the research. Maribel I. García-Ibáñez, Patricia Zunino, Friederike Fröb, Lidia I. Carracedo, Aida F. Ríos, Herlé Mercier, Are Olsen and Fiz F. Pérez analysed the physical and chemical data. Maribel I. García-Ibáñez and Patricia Zunino developed the code for processing the data. Maribel I. García-Ibáñez and Fiz F. Pérez determined the anthropogenic CO₂ concentrations, average layer properties and rates, and estimated the uncertainties. Maribel I. García-Ibáñez wrote the manuscript and prepared all figures, with contributions from all co-authors.

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