4   LONG-TERM TRENDS IN SURFACE OCEAN pH IN THE NORTH ATLANTIC

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12   ABSTRACT

13   Presently available direct pH measurements do not have a sufficient data density in

14   space or time in order to determine long-term trends across wider geographic regions, limiting

15   our ability to assess the magnitude and impacts of ocean acidification. We overcome this

16   limitation by using the much more frequently measured fugacity of CO_2 (fCO_2), as

17   synthesized in the SOCAT data product, from which we calculate pH using algorithms for

18   alkalinity based on temperature and salinity. The estimated pH at 25°C, i.e., $pH_{sws}^{25°C}$ has a

19   calculation error of 0.0033±0.0003, and evaluation using co-located pH observations yields a

20   RMSE of 0.010 and a non-significant bias of 0.004. The estimated $pH_{sws}^{25°C}$ is rather sensitive

21   to uncertainties and biases in fCO_2, while uncertainties in alkalinity, temperature, and salinity

22   matter much less. The high precision and low bias of the computed pH permits us to apply

23   this method to data from the North Atlantic Subpolar Gyre, for which we find a statistically

24   significant trend in surface ocean pH_{sws}^{insitu} of -0.0022±0.0004 yr^{-1} over the period 1981 to 2007.

25   This long-term trend in pH is nearly entirely driven by the long-term trend in surface ocean

26   fCO_2, while the impact of temperature is negligible. This pH trend is very close to that

27   expected based on the assumption of thermodynamic equilibrium of CO_2 between the

28   atmosphere and the surface ocean.

29

30   KEY WORDS

31   pH, ocean acidification, trend analysis, carbon cycle, North Atlantic

32

33   1. INTRODUCTION

34   Approximately 30 % of the human-induced CO_2 emissions have been taken up by the

35   ocean so far (Sabine et al., 2004; Khatiwala et al., 2013; IPCC, 2013), having led to a long-

36   term decrease in pH and in the saturation state with regard to mineral calcium carbonates – a

37   process that is commonly referred to as ocean acidification. Despite the growing recognition

38   of the potential consequences of this pH decrease on marine organisms and ecosystems (*e.g.*

39   Doney et al., 2007; Gattuso and Hansson, 2011), we know long-term trends of pH for just a

40   handful of time-series stations (*e.g.* Bates, 2007; Gonzalez-Davila et al., 2010; Santana-

41   Casiano et al., 2007; Leinweber and Gruber, 2013). The observed trends vary between 0.002

42   and 0.004 yr^{-1}, largely consistent with the expected trends based on the assumption that the

43   perturbation of the surface ocean's carbonate chemistry follows that of the CO_2 concentration

44   in the overlying atmosphere (Sarmiento and Gruber, 2006). It is not unreasonable to assume

45   that this is the case also over wider geographic regions, but no observation-based estimate of

46   such trends is currently available to test this assumption. This is mainly because surface ocean

47   pH is rarely measured directly owing to the lack of a system for continuous measurements

48   (Byrne and Co-Authors, 2010). Efforts are being made to develop and implements such

49   systems (*e.g.* Rerolle et al., 2012), but these have not been widely used yet, so the spatial

50   coverage of surface ocean pH measurements remains poor. Thus, currently the only way to

51   analyze long-term trends in pH based on observations is to calculate it using two other

52   measured ocean carbon system parameters.

53   For the first carbon system parameter, the CO_2 fugacity (fCO_2) is an ideal candidate,

54   as it has been extensively measured across all ocean basins and over several decades with

55   relatively high precision and accuracy (Byrne and Co-Authors, 2010). Furthermore the

56 Surface Ocean CO_2 Atlas (SOCAT) effort has synthesized most of these observations into a

57 comprehensive data base with more than 6.3 million measurements (Pfeil et al., 2013). For the

58 second carbon chemistry parameter we chose alkalinity, since several algorithms are available

59 to estimate this from salinity and temperature (Lee et al., 2006; Millero et al., 1998; Nondal et

60 al., 2009). Furthermore, alkalinity does not respond to the invasion of anthropogenic CO_2

61 from the atmosphere, so that its long-term trends are much smaller than those of dissolved

62 inorganic carbon (DIC). Finally, the computation of pH from fCO_2 and alkalinity has a much

63 smaller uncertainty than that from fCO_2 and DIC given typical measurement precisions for

64 these parameters (Dickson and Riley, 1978; Zeebe and Wolf-Gladrow, 2001).

65   In order to assess the usefulness of any pH trend computed from fCO_2 and alkalinity,

66 we first determine the calculation errors and assess their sources in detail. We then test the

67 precision, accuracy, and robustness of the estimated pH against direct observations. Since

68 there are no measurements of pH and fCO_2 available in the SOCAT data base from the same

69 water sample, we use measurements of in situ pH from the CARINA data base that are

70 located reasonably close in space and time. After being convinced of the robustness of our

71 estimated pH, we use it to identify its long-term trend in the North Atlantic Subpolar Gyre,

72 and determine what drives its changes.

73   The North Atlantic Subpolar Gyre is a particularly interesting region in this regard

74 since several studies have found significant changes in the surface ocean carbon chemistry

75 (*e.g.* Corbière et al., 2007; Schuster et al., 2009; Metzl et al., 2010), but what has been driving

76 these changes and whether they are short-term variations or long-term trends are still active

77 areas of research (*e.g.* Levine et al., 2011; McGrath et al., 2012).

78

79 2. DATA AND METHODS

80   We focus our analyses on the North Atlantic Subpolar Gyre region (Fig. 1), whose

81   area is roughly equivalent to the subpolar seasonally stratified (SPSS) biome in Fay and

82   McKinley (2013) but cut off at the Greenland-Scotland Ridge. The boundaries were

83   determined using a self-organizing map method to cluster data with similar characteristics in

84   sea-surface temperature (SST), sea-surface salinity (SSS), mixed layer depth, and chlorophyll-

85   *a* (Lauvset et al., in prep).

86   The Surface Ocean CO_2 Atlas Version 1.5 (SOCATv1.5) data product (Pfeil et al.,

87   2013) represents the main source of the data. It contains quality controlled and internally

88   homogenized direct measurements of surface ocean carbon fCO_2, largely from ships of

89   opportunity, as well as the associated sea surface salinity (SSS) and sea surface temperature

90   (SST) measurements. Of the 1,071,669 fCO_2 measurements contained in the data base within

91   the North Atlantic, only 444,000 have simultaneous entries of all three parameters. These

92   observations form the basis for our analyses.

93   We estimated alkalinity using the algorithms developed by Lee et al. (2006) and

94   Nondal et al. (2009). The former was used everywhere, except for the region north of 60°N in

95   the North Atlantic, were we employed the Nondal et al. (2009) algorithms, as they were

96   specifically developed for this region. Surface ocean pH – at both *in situ* temperature and at

97   25 ℃ – was then computed using CO2SYS (Lewis and Wallace, 1998) using the measured

98   fCO_2 and the estimated alkalinity as input, and the dissociation constants from Mehrbach

99   (1973) refitted by Dickson and Millero (1987). Several other dissociation constants were

100   tried (*e.g.* Millero et al., 2002; Millero et al., 2010) but the choice of constants does not affect

101   the results presented in this paper.

102   Co-located surface alkalinity and $pH_{sws}^{25°C}$ observations (*i.e.,* shallower than 15 m)

103   available in the CARINA data product (Key et al., 2010) were used to evaluate the estimated

104   alkalinity and $pH_{sws}^{25°C}$. In CARINA, only direct measurements of $pH_{sws}^{25°C}$ were considered and

105   only those data that came from cruises for which no adjustments were made during the 2nd

106   quality control (http://carina.geomar.de/). These data have an estimated accuracy of <0.005

107   pH units (Velo et al., 2010), derived using data from below 1500 m, but we assume that this

108   holds also for the surface layer. Similarly, the alkalinity observations in CARINA have an

109   estimated accuracy of 6 μmol kg^{-1} (Velo et al., 2009). To finally identify the co-located

110   samples in the subset of the CARINA database that fulfill the above criteria, we searched for

111   pH (and alkalinity) observations that were taken in the same month and within an area of

112   1˚x1˚of any of the SOCAT fCO_2 measurements. This resulted in the identification of 66 data

113   points in the CARINA data product that could be used for the evaluation. For all these data

114   points the carbon system had been over-determined (*i.e.* more than two out of the four

115   parameters were measured) revealing an internal consistency in $pH_{sws}^{25°C}$ of ~0.0036. As

116   shown later (Sect. 3.1) this is approximately the same as our calculation error. The evaluation

117   of the estimated alkalinity and $pH_{sws}^{25°C}$ against the direct measurements was done using several

118   statistical tests (Table 1), including tests for normality, equal variance, and equal

119   mean/median (Stow et al. 2009).

120   Commonly error propagation calculations are made by linearizing non-linear functions

121   using a Taylor series expansion, but since the pH calculation from fCO_2 and alkalinity is a

122   series of non-linear equations, this method significantly underestimates the total error. We

123   have therefore determined the calculation error of $pH_{sws}^{25°C}$ using the full carbon chemistry

124   equations in CO2SYS. In eight different calculations we calculated $pH_{sws}^{25°C}$ for

125   alkalinity$\pm\sigma_{alk}$, $fCO_2\pm\sigma_{fCO2}$, SST$\pm\sigma_{SST}$, and SSS$\pm\sigma_{SSS}$ separately. The total error was then

126   computed by summing the square of the error introduced by the uncertainty in each of the

127   four parameters. σ_{alk} is the root mean square deviation or standard error of calculation

128   published with the different algorithms (Lee et al., 2006; Nondal et al., 2009), ranging from

129   6.4–9.7 μmol kg^{-1}; σ_{fCO2} is the measurement error of 2 μatm; σ_{SST} is the instrument

130   uncertainty of 0.001 ºC; and σ_{SSS} is the instrument uncertainty of 0.01. σ_{fCO2}, σ_{SST}, and σ_{SSS}

131   were taken from the meta-data available with the SOCATv1.5 data product. A σ_{SST} of only

132   0.001 ºC in SST is very low so the effect on the total error of increasing this to 0.1 ºC has also

133   been calculated. The RMSE of our calculated alkalinity compared to measured alkalinity is

134   8.1μmol kg^{-1} (Table 2), which is in the middle of the range of published uncertainties. We

135   take this to indicate that using the root mean square deviation as a measure of uncertainty in

136   the estimated alkalinity is robust. We limited the error analysis to that of pH on the seawater

137   scale at a constant temperature of 25˚C ($pH_{sws}^{25°C}$) as all the observations available for

138   validation are also $pH_{sws}^{25°C}$.

139   For the trend analysis, pH at *in situ* temperatures (pH_{sws}^{insitu}) was calculated, so that the

140   potential influence of changes in SST is included. The long-term trend in the estimated

141   pH_{sws}^{insitu} was determined using an ordinary least squares (OLS) linear regression, after first

142   deseasonalizing the data following the method of Takahashi et al. (2009). To test the

143   robustness of this method, we determined the trend also from the linear portion of a fit that

144   contains a harmonic plus a linear trend following the method of Fay and McKinley (2013).

145   Specifically, we fitted a function of the form y=a+b*x+c*cos(2πx+d), where x is the decimal

146   year minus the initial year, and where b is the parameter of interest, *i.e.*, the long-term rate of

147   change.

148

149   3. RESULTS AND DISCUSSION

150   *3.1 Calculation error*

151   The mean calculation error of our estimated $pH_{sws}^{25°C}$ in the North Atlantic of

152   0.0033±0.0003 is somewhat larger, but comparable to the value of 0.0021 calculated by Zeebe

153   and Wolf-Gladrow (2001) for the same parameter pair. For comparison, the calculation error

154   for $pH_{sws}^{25°C}$ estimated using observations of alkalinity and DIC from the CARINA data product

155   is considerably larger, i.e., 0.0073±0.0015, confirming our choice of the fCO_2-alkalinity pair

156   as the better choice for computing pH. Our calculation error of pH is about three times larger

157   than the estimated precision of pH measured directly using the spectrophotometric method

158   (*e.g.* (Rerolle et al., 2012)). Our calculation error is, however, relatively small compared to the

159   long-term trend of mean surface ocean pH of ~0.002 yr^{-1}, *i.e.*, after two years, the change

160   exceeds the calculation uncertainty.

161   The calculation error is dominated by the uncertainty in fCO_2 while the error due to

162   uncertainties in SST and SSS are negligibly small (Fig. 2). For SST this is largely due to the

163   assumed small instrument uncertainty. If we increased the uncertainty for SST to 0.1 ˚C, the

164   error due SST in $pH_{sws}^{25°C}$ would increase to that due to the uncertainty in alkalinity (not

165   shown), while the overall calculation error increases only marginally to 0.0037±0.0003. The

166   direct error introduced by SSS is very small (~0.00007, Fig. 2), however, correct SSS values

167   are vital in order to calculate unbiased alkalinity and therefore important also in the pH

168   calculation.

169

170   *3.2 Evaluation using observed pH*

171   Before testing our computed pH with the 66 co-located CARINA measurements, we

172   need to ensure that the two data sets have measured the same water masses. To this end, we

173   first check the consistency of the SST, SSS, and alkalinity data. The strong correlation with a

174   slope of very nearly one between the temperature and salinity data in the SOCATv1.5 and

175   CARINA data products (Fig. 3) show that we are indeed comparing the same water masses

176   and conditions, despite our generous definition of "co-location", *i.e.*, that the samples have

177   been taken within the same month and within a 1°x1° square. A more thorough statistical

178   comparison also shows that these data compare well (Table 2). It needs to be noted that while

179   there is a bias (*i.e.* a difference in the median values) these are not statistically significant

180   differences given the range and variability in the data. These differences are still of interest to

181   this analysis as it points to how variability in the data affects the final results, and by what

182   means. Analyzing these differences also allows us to ensure that errors are not accumulated

183   in the two-step calculation of pH.

184   The mean difference between the two sources of temperature is -0.012±0.3 ºC, thus

185   reflecting no systematic offset (Table 2). In contrast, there is a difference in salinity between

186   the two data sets, with CARINA salinity being higher by 0.14±0.10 relative to SOCAT

187   salinity. Salinity is a secondary parameter in the SOCAT data product since it does not affect

188   fCO_2 greatly, while salinity is a primary parameter in the CARINA data product. So the mean

189   difference between the data products is likely due to lesser instrument calibration and quality

190   control on the salinity data in SOCAT, but it could also be an artifact of the relatively few

191   data points used for validation. The difference between the two sources of salinity is not

192   statistically significant, but it leads to a mean alkalinity difference which disappears when the

193   salinity difference is corrected before calculation of alkalinity (Table 2).

194   The mean $pH_{sws}^{25°C}$ difference between the two data sets amounts to 0.0040±0.0022,

195   with SOCAT suggesting more alkaline conditions than CARINA, but this difference is not

196   statistically significant. The mean salinity-induced offset of alkalinity is not the cause, as this

197   difference increases to 0.0046±0.0098 when the salinity difference is removed before

198   calculation. As this pH difference is equivalent to a 2.9±1.6 µatm difference in fCO_2 and the

199   measurement uncertainty of fCO_2 is ±2 µatm, it is instead more likely that differences in fCO_2

200   are the most likely cause of difference in $pH_{sws}^{25°C}$. This is supported by the calculation error in

201   the estimated $pH_{sws}^{25°C}$ being most sensitive to fCO_2. However, there are no independent

202   observations of fCO_2 available to test this.

203   In addition to the correlation analysis and statistical evaluation a Brown-Forsythe's

204   test for equal variance and a Mann-Whitney U test for equal medians (Table 1) confirm that

205   there is no statistically significant difference in the distribution, variance, and median of the

206   estimated $pH_{sws}^{25°C}$ compared to the available $pH_{sws}^{25°C}$ observations in CARINA. We are thus

207   confident that the SOCATv1.5 data compare well to the CARINA data and that any

208   differences that exist in the temperatures and salinities do not significantly affect the pH

209   calculation.

210

211   *3.3 Decadal change and variability*

212   The ordinary least squares regression analysis of the three decades of data reveal

213   substantial long-term trends in surface ocean pH in the North Atlantic Subpolar Gyre. A

214   linear regression of the deseasonalized pH_{sws}^{insitu} data over the three decades shows a

215   statistically significant trend (with a 95% confidence interval) of -0.0022±0.0004 yr^{-1}, with a

216   standard error of 0.0002 and an r^2 of 0.61 (Fig. 4a). The trend in $pH_{sws}^{25°C}$ is very similar,

217   permitting us to focus on the biologically and biogeochemically more relevant pH_{sws}^{insitu}.

218   This trend is only moderately sensitive to the fact that the data density is much smaller

219   in the 1980s (Fig. 1) when there are only two years of data. Excluding the 1980s from the

220   regression the trend becomes -0.0027±0.0006 yr^{-1} and the r^2 decrease (Fig. 4a). However,

221   within the confidence intervals these two trends are not significantly different from each

222   other. This is consistent with the findings in McKinley et al. (2011), where their 1993-2005

223   trend in fCO$_2$ is larger than their 1981-2009 trend, but with a difference that is not statistically

224   significant. The trend is also not impacted by possible inhomogeneities in the data, as the

225   three decades of data have distributions with similar variances and similar spatial

226   distributions. Finally, the trend is also robust with regard to the method to determine it. The

227   long-term trend found by the second trend determination method, i.e., where we fitted the data

228   by a function containing a harmonic and a linear trend part, turns out to not be significantly

229   different from the one found using the OLS regression method.

230   Our pH_{sws}^{insitu} trend in the subpolar North Atlantic is of the same magnitude as the trends

231   of -0.0017±0.0003 yr^{-1} and -0.0017±0.0005 yr^{-1} found at the BATS and ESTOC time series

232   (Bates, 2007; Gonzalez-Davila et al., 2010; Santana-Casiano et al., 2007), and the ~-0.002 yr^{-1}

233   (0.038-0.0041 over 19 years) found by McGrath et al. (2012) in the Rockall Trough. Similar

234   rates of pH change have also been observed in the Pacific Ocean (*e.g.* Byrne et al., 2010).

235   This confirms model predictions and theoretical considerations that suggest very little spatial

236   variability in the ocean acidification induced trend in surface ocean pH (*e.g.* IPCC, 2013).

237   An OLS regression of the underlying drivers of pH, *i.e.*, fCO_2, alkalinity, SSS and SST

238   reveals that the long-term trend in pH_{sws}^{insitu} between 1981 and 2007 in the subpolar North

239   Atlantic is almost entirely driven by the long-term trend in surface ocean fCO_2 of 2.0±0.38

240   µatm yr^{-1} (Fig. 5). This is because there is no statistically significant trend in either alkalinity,

241   SSS, or SST between 1981 and 2007 in our data set. The rate of increase in surface ocean

242   fCO_2 of 2.0 µatm yr^{-1} is slightly larger, but not significantly different from that of atmospheric

243   fCO_2 over this period, consistent with the expectation that the surface ocean has remained in

244   thermodynamic equilibrium with the atmospheric perturbation. Our findings for fCO_2 are also

245   consistent with those of Fay and McKinley (2013) for their spatially more extensive North

246   Atlantic Subpolar seasonally stratified biome, as they also identified no significant trend in

247   the air-sea difference of fCO_2. Finally, our findings that trends in pH are largely being driven

248   by changes in surface water chemistry support the results of McGrath et al. (2012) from the

249   Rockall Trough, where they also primarily linked the decrease in pH to the observed increase

250   in dissolved inorganic carbon driven by uptake of CO_2 from the atmosphere.

251

252   4. CONCLUSIONS

253   With atmospheric CO_2 bound to increase further, surface ocean acidification is

254   virtually certain to aggravate. It is important to have a good knowledge of the present trends

255   in the most important ocean acidification relevant parameters, such as pH, so as to be able to

256   put future trends into the right context. However, until direct pH measurements have a good

257   enough data density for long-term trend analysis, other data sources must be used. Here we

258   have shown that the SOCAT data product can be used to estimate $pH_{sws}^{25°C}$ with a calculation

259   error of 0.0033±0.0003. This confirms previous findings that the fCO_2 and alkalinity

260   parameter pair is the more precise and thus the better choice for computing pH – compared to

261   *e.g.* alkalinity and dissolved inorganic carbon pair – even though alkalinity has to be

262   estimated using empirical algorithms based on temperature and salinity. The difference in the

263   calculated $pH_{sws}^{25°C}$ to the co-located measurements from CARINA is not caused by the

264   systematic differences in salinity and alkalinity, but is most likely due to the strong sensitivity

265   of $pH_{sws}^{25°C}$ to both the uncertainty and the variance in fCO_2. Since our calculation error is

266   smaller than the expected trend in surface ocean pH over most of the ocean over two years,

267   we conclude that our $pH_{sws}^{25°C}$ estimates are suitable for long-term regression analysis. We

268   identify a trend of -0.0022±0.0004 yr^{-1} between 1981 and 2007 in the North Atlantic Subpolar

269   Gyre, which is of the same magnitude as the trend at BATS and ESTOC (-

270   0.0017±0.0003/0.0005 yr^{-1}) and in the Rockall Trough (-0.002 yr^{-1}). This is an important first

271   step in assessing global ocean acidification over the past few decades. Future efforts need to

272   ensure adequate sampling of pH and other parameters of interest for ocean acidification such

273   that solid records of these parameters are in place and can be used to assess the causes and

274   consequences of future biogeochemical and ecological changes.

275

276   5. ACKNOWLEDGEMENTS

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282   6. REFERENCES

283 Bates, N.R., 2007. Interannual variability of the oceanic CO2 sink in the subtropical gyre of
284   the North Atlantic Ocean over the last 2 decades. Journal of Geophysical Research-
285   Oceans, 112(C9): 26.

286 Brown, M.B. and Forsythe, A.B., 1974. Robust Tests for Equality of Variances. Journal of the
287   American Statistical Association, 69(346): 364-367.

288 Byrne, R., Co-Authors, 2010. Sensors and Systems for In Situ Observations of Marine Carbon
289   Dioxide System Variables, in: Hall, J., Harrison, D.E., Stammer, D. (Eds.),
290   Proceedings of OceanObs'09: Sustained Ocean Observations and Information for
291   Society. ESA Publication WPP-306, Venice, Italy.

292 Byrne, R.H., Mecking, S., Feely, R.A., Liu, X., 2010. Direct observations of basin-wide
293   acidification of the North Pacific Ocean. Geophysical Research Letters 37.

294 Corbière, A., Metzl, N., Reverdin, G., Brunet, C., Takahashi, T., 2007. Interannual and
295   decadal variability of the oceanic carbon sink in the North Atlantic subpolar gyre.
296   Tellus 59B, 168-178.

297 Dickson, A.G., Riley, J.P., 1978. Effect of Analytical Error on Evaluation of Components of
298   Aquatic Carbon-Dioxide System. Marine Chemistry 6, 77-85.

299 Dickson, A.G., Millero, F.J., 1987. A comparison of the equilibrium-constants for the
300   dissociation of carbonic-acid in seawater media. Deep-Sea Research Part a-
301   Oceanographic Research Papers 34, 1733-1743.

302 Dickson, A.G., Sabine, C. and Christian, J.R. (Editors), 2007. Guide to best practices for
303   ocean CO2 measurements. PICES Special Publication 3, 191 pp pp.

304 Doney, S.C. et al., 2007. Impact of anthropogenic atmospheric nitrogen and sulfur deposition
305   on ocean acidification and the inorganic carbon system. Proceedings of the National
306   Academy of Sciences of the United States of America, 104(37): 14580-14585.

307 Fay, A.R. and McKinley, G.A., 2013. Global trends in surface oceanpCO2from in situ data.
308   Global Biogeochemical Cycles, 27(2): 541-557.

309 Gattuso, J.-P. and Hansson, L., 2011. Ocean acidification. Oxford University Press.

310   Gonzalez-Davila, M., Santana-Casiano, J.M., Rueda, M.J. and Llinas, O., 2010. The water
311   column distribution of carbonate system variables at the ESTOC site from 1995 to
312   2004. Biogeosciences, 7(10): 3067-3081.

313   Gruber, N. et al., 2009. Oceanic sources, sinks, and transport of atmospheric CO2. Global
314   Biogeochemical Cycles, 23(GB1005).

315   IPCC, 2013. Climate Change 2013: The Physical Science Basis.

316   Jarque, C.M. and Bera, A.K., 1980. Efficient tests for normality, homoscedasticity and serial
317   independence of regression residuals. Economics Letters, 6(3): 255-259.

318   Key, R.M. et al., 2010. The CARINA data synthesis project: introduction and overview. Earth
319   Syst. Sci. Data, 2: 105-121.

320   Khatiwala, S. et al., 2013. Global ocean storage of anthropogenic carbon. Biogeosciences,
321   10(4): 2169-2191.

322   Kruskal, W.H. and Wallis, W.A., 1952. Use of ranks in one-criterion variance analysis.
323   Journal of the American Statistical Association, 47(260): 583-621.

324   Lauvset, S.K., Gruber, N., Landschützer, P. and Olsen, A., in prep. Global long-term trend
325   and variability in surface ocean pH.

326   Leinweber, A., and N. Gruber, Variability and trends of ocean acidification in the Southern
327   California Current System: A time series from Santa Monica Bay, Journal of
328   Geophysical Research, 118, doi:10.1002/jgrc, 2013

329   Le Quéré, C. et al., 2013. The global carbon budget 1959–2011 Earth Syst. Sci. Data, 5: 165-
330   185.

331   Lee, K. et al., 2006. Global relationships of total alkalinity with salinity and temperature in
332   surface waters of the world's oceans. Geophysical Research Letters, 33(19): L19605.

333   Levine, N.M. et al., 2011. The impact of the North Atlantic Oscillation on the uptake and
334   accumulation of anthropogenic CO2 by North Atlantic Ocean mode waters. Global
335   Biogeochem. Cycles, 25(3): GB3022.

336   Lewis, E. and Wallace, D.W.R., 1998. Program developed for CO2 system calculations,
337   ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge
338   National Laboratory, U.S. Department of Energy.

339   McGrath, T., Kivimae, C., Tanhua, T., Cave, R.R. and McGovern, E., 2012. Inorganic carbon
340   and pH levels in the Rockall Trough 1991-2010. Deep-Sea Research Part I-
341   Oceanographic Research Papers, 68(0): 79-91.

342   McKinley, G.A., Fay, A.R., Takahashi, T. and Metzl, N., 2011. Convergence of atmospheric
343   and North Atlantic carbon dioxide trends on multidecadal timescales. Nature
344   Geoscience, 4(9): 606-610.

345 Mehrbach, C., Culberso.Ch, Hawley, J.E., Pytkowic.Rm, 1973. Measurement of apparent
346   dissociation-constants of carbonic-acid in seawater at atmospheric-pressure.
347   Limnology and Oceanography 18, 897-907.

348 Metzl, N., Corbière, A., Reverdin, G., Lenton, A., Takahashi, T., Olsen, A., Johannessen, T.,
349   Pierrot, D., Wanninkhof, R., Ólafsdóttir, S.R., Olafsson, J., Ramonet, M., 2010.
350   Recent acceleration of the sea surface fCO_2 growth rate in the North Atlantic subpolar
351   gyre (1993–2008) revealed by winter observations. Global Biogeochemical Cycles 24
352   (GB4004).

353 Millero, F.J., Lee, K. and Roche, M., 1998. Distribution of alkalinity in the surface waters of
354   the major oceans. Marine Chemistry, 60: 111-130.

355 Millero, F.J., Pierrot, D., Lee, K., Wanninkhof, R., Feely, R., Sabine, C.L., Key, R.M.,
356   Takahashi, T., 2002. Dissociation constants for carbonic acid determined from field
357   measurements. Deep-Sea Research Part I-Oceanographic Research Papers 49, 1705-
358   1723.

359 Millero, F.J., Magdalena Santana-Casiano, J., Gonzalez-Davila, M., 2010. The Formation of
360   Cu(II) Complexes with Carbonate and Bicarbonate Ions in NaClO4 Solutions. Journal
361   of Solution Chemistry 39, 543-558.

362 Nondal, G., Bellerby, R.G.J., Olsen, A., Johannessen, T. and Olafsson, J., 2009. Optimal
363   evaluation of the surface ocean CO2 system in the northern North Atlantic using data
364   from voluntary observing ships. Limnology and Oceanography-Methods, 7: 109-118.

365 Pfeil, B. et al., 2013. A uniform, quality controlled Surface Ocean CO2 Atlas (SOCAT). Earth
366   Syst. Sci. Data, 5(1): 125-143.

367 Rerolle, V.M.C. et al., 2012. Seawater-pH measurements for ocean-acidification observations.
368   Trac-Trends in Analytical Chemistry, 40: 146-157.

369 Santana-Casiano, J.M., Gonzalez-Davila, M., Rueda, M.J., Llinas, O. and Gonzalez-Davila,
370   E.F., 2007. The interannual variability of oceanic CO2 parameters in the northeast
371   Atlantic subtropical gyre at the ESTOC site. Global Biogeochemical Cycles, 21(1): 16.

372 Sarmiento, J.L. and Gruber, N., 2006. Ocean biogeochemical dynamics. Princeton University
373   Press, Princeton, N.J., XII, 503 s.

374 Schuster, U., Watson, A.J., Bates, N.R., Corbière, A., Gonzalez-Davila, M., Metzl, N.,
375   Pierrot, D., Santana-Casiano, M., 2009. Trends in North Atlantic sea-surface fCO2
376   from 1990 to 2006. Deep-Sea Research Part II - Topical Studies in Oceanography 56
377   (8-10), 620-629.

378 Stow, C.A. et al., 2009. Skill assessment for coupled biological/physical models of marine
379   systems. Journal of Marine Systems, 76(1-2): 4-15.

380 Takahashi, T. et al., 2009. Climatological mean and decadal change in surface ocean pCO2,
381   and net sea-air CO2 flux over the global oceans. Deep-Sea Research Part II - Topical
382   Studies in Oceanography, 56(8-10): 554-577.

383 Velo, A., Perez, F.F., Brown, P., Tanhua, T., Schuster, U., Key, R.M., 2009. CARINA
384   alkalinity data in the Atlantic Ocean. Earth System Science Data 1, 45-61.

385 Velo, A. et al., 2010. CARINA data synthesis project: pH data scale unification and cruise
386   adjustments. Earth System Science Data, 2: 133-155.

387 Wilcoxon, F., 1945. Individual Comparisons by Ranking Methods. Biometrics Bulletin, 1(6):
388   80-83.

389 Zeebe, R., E. and Wolf-Gladrow, D., 2001. CO2 in seawater, equilibrium, kinetics, isotopes,
390   65. Elsevier, Amsterdam, PAYS-BAS, XIII, 346 pp.

391

392 FIGURES AND TABLES

393 **Figure 1. Map of the North Atlantic showing Subpolar Gyre region for which the regression analysis was**
394 **performed. The black dots show data in the 1980s, the blue dots show data in the 1990s, and the red dots**
395 **show data in the 2000s.**
396

397 **Figure 2. Figure showing the median of the total calculation error for pH, the error in pH due to**
398 **uncertainty in alkalinity, the error in pH due to uncertainty in fCO_2, the error in pH due to uncertainty in**
399 **SST, and the error in pH due to uncertainty in SSS. The total calculation error for pH is the squared sum**
400 **of the individual errors. The box shows the mean and the upper and lower quartile of the data, the gray**
401 **points are outliers (defined as data outside of $\pm 2.7\sigma$).**
402

403 **Figure 3. Evaluation of SOCAT derived estimates with measurements from CARINA. Shown are the**
404 **correlation of (a) SST which has a slope of 0.98 and an r^2 of 0.99, (b) SSS which has a slope of 0.92 and an**
405 **r^2 of 0.97, (c) pH which has a slope of 0.96 and an r^2 of 0.98, and (d) alkalinity which has a slope of 0.87**
406 **and an r^2 of 0.98. For all variables SOCAT-derived estimates on the y-axis and the CARINA**
407 **measurements on the x-axis. Monthly averages for the same year in $1°\text{x}1°$ grids are compared. The black**
408 **points show data that have not been corrected for the salinity bias and the gray plusses show data after**
409 **the bias has been corrected for. Note that for pH removing the salinity bias does not change the data so**
410 **there are no gray plusses. The solid black line is the 1:1 line. See Table 2 for further statistics comparing**
411 **the SOCAT-derived estimates with the CARINA measurements.**
412

413 **Figure 4a. Timeseries of surface ocean (a) pH_{sws}^{insitu} and (b) $pH_{sws}^{25°C}$ in the North Atlantic Subpolar Gyre.**
414 **The grey dots are the measured data and the black circles are the monthly deseasonalized data. The**
415 **ordinary least squares (OLS) linear regression line for the full period (1981-2007) is shown as a solid black**
416 **line and its equation is given in black. The dashed line shows the OLS linear regression line for the period**
417 **1990-2007 with its equation in grey. F and p-value are the F-statistic and its p-value respectively. For**
418 **details on the deseasonalization and the regression method see Sect. 2.**
419

420 **Figure 5. Timeseries of (a) SST, (b) alkalinity, and (c) fCO_2 in the North Atlantic Subpolar Gyre. The**
421 **grey dots are the measured data and the black circles are the monthly deseasonalized data. The OLS**
422 **linear regression line for the full period (1981-2007) is shown as a solid black line while the dashed line**
423 **shows the OLS linear regression for the 1990-2007 period. For fCO_2 the regression equation is given in**
424 **black for the full period and in grey for the shorter period. SST and alkalinity does not have a significant**
425 **trend so no equation is given. F and p-value are the F-statistic and its p-value respectively. For details on**
426 **the deseasonalization and the regression method see Sect. 2.**
427

428 **Table 1. Names and descriptions of the statistical tests used. For all these tests the null hypothesis is**
429 **rejected if the resulting p-value is less than 0.05.**

Name of test	Null hypothesis	Alternative hypothesis	Usage	Reference

Jarque-Bera	Data are normally distributed	Data are not normally distributed		(Jarque and Bera, 1980)
Brown-Forsythe[a]	$\sigma^2_1=\sigma^2_2=\sigma^2_n$	At least one σ^2 is different		(Brown and Forsythe, 1974)
Mann-Whitney[b]	$\eta_1=\eta_2=\eta_n$	At least one η is different	Use when the variances are equal	(Wilcoxon, 1945)
Kruskal-Wallis[b]	$\eta_1=\eta_2=\eta_n$	At least one η is different	Use when variances are *not* equal	(Kruskal and Wallis, 1952)

430 [a] σ^2 is the variance
431 [b] η is the median

432

433 **Table 2. Table showing the statistical comparison observations and estimates. All statistical tests used in**
434 **this study are fully explained in (Stow et al., 2009), and the reader is referred there for details.**

Name of test	pH	Calculated alkalinity	Alkalinity calculated without the SSS bias	SST	SSS
Model efficiency	0.98	0.93	0.97	1.00	0.92
Cost function	0.021	0.072	0.036	0.0034	0.076
Bias	0.0040	-5.5	0.45	-0.012	-0.14
Absolute average error	0.0081	6.5	4.4	0.20	0.15
Correlation coefficient (r)	0.99	0.98	0.99	0.99	0.99
RMSE	0.010	8.1	5.7	0.30	0.18

435
436

$pH_{1981-2007} = -0.0022*year + 12.50$, $r^2 = 0.61$, F = 107.24, p-value = 1.3e-15

$pH_{1990-2007} = -0.0027*year + 13.43$, $r^2 = 0.57$, F = 83.28, p-value = 3.4e-13

$fCO_2^{1981-2007} = 2.0*year + -3679, r^2 = 0.62, F = 110.82, p\text{-value} = 5.4e{-}16$

$fCO_2^{1990-2007} = 2.5*year + -4573, r^2 = 0.58, F = 89.08, p\text{-value} = 8.4e{-}14$