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# 1 **Measuring pH in the Arctic Ocean: colorimetric method or SeaFET?**

2 Victoire Rérolle<sup>a</sup>, Diana Ruiz-Pino<sup>a</sup>, Mehrad Rafizadeh<sup>a</sup>, Socratis Loucaides<sup>b</sup>, Stathys Papadimitriou<sup>c</sup>,  
3 Matthew Mowlem<sup>b</sup>, Jianfang Chen<sup>d</sup>

4 a. Sorbonne Universités (UPMC, Univ Paris 06)-CNRS-IRD-MNHN, LOCEAN Laboratory, 75005, Paris,  
5 France

6 b. National Oceanography Centre, Southampton, SO143ZH, United Kingdom

7 c. Ocean Sciences, College of Natural Sciences, Bangor University, Menai Bridge, LL59 5AB, United  
8 Kingdom

9 d. Second institute of Oceanography, Hangzhou City, 310012, China

10 Corresponding author: [Victoire.rerolle@locean-ipsl.upmc.fr](mailto:Victoire.rerolle@locean-ipsl.upmc.fr)

11 Université Pierre & Marie Curie - boîte 100 - 4, Place Jussieu - 75252 PARIS CEDEX 05

12 Co-authors email addresses:

13 [ruizlod@locean-ipsl.upmc.fr](mailto:ruizlod@locean-ipsl.upmc.fr)

14 [Mehrad.RAFIZADEH@locean-ipsl.upmc.fr](mailto:Mehrad.RAFIZADEH@locean-ipsl.upmc.fr)

15 [s.loucaides@noc.ac.uk](mailto:s.loucaides@noc.ac.uk)

16 [s.papadimitriou@bangor.ac.uk](mailto:s.papadimitriou@bangor.ac.uk)

17 [matm@noc.ac.uk](mailto:matm@noc.ac.uk)

18 [biogeo\\_chen@hotmail.com](mailto:biogeo_chen@hotmail.com)

## 19 **Abstract**

20 The suitability of the colorimetric method in a custom-made instrumental set-up and the  
21 commercial potentiometric SeaFET® electrode sensor to measure pH in surface oceanic water in  
22 the Arctic was investigated during the Chinese Arctic Research Expedition (CHINARE) in summer  
23 2014. The instruments were set up in parallel on the on-board underway seawater supply for 65  
24 days, enabling comparison in various conditions in the Arctic Ocean from the Chukchi Sea to the  
25 ice-covered high latitudes (81°N) and the open-water North-western Pacific Ocean. Overall, the  
26 instruments yielded pH datasets of similar high quality (method uncertainty  $\leq 0.010$ ). Detailed  
27 comparison with the parallel colorimetric pH measurements indicated that the measurements with  
28 the SeaFET external electrode in the low salinity ice-covered area were problematical and that the  
29 internal reference electrode failed after almost 2 months of cruise. Reasons for discrepancies  
30 between the data from the two instruments and recommendations for the use of either instrument  
31 for pH measurements in the Arctic are discussed. Finally, the investigation yielded a reliable high-  
32 resolution pH dataset in surface waters along a transect from the Pacific to the Arctic Ocean.  
33 Large pH variations were observed in the ice-free Arctic surface waters, with pH ranging between  
34 7.98 and 8.49. The highest pH values were observed at the ice edge, whereas a relatively invariable  
35 pH ( $8.02 \pm 0.02$ ) was measured in under-ice seawater in the ice-covered Arctic Ocean. The high  
36 resolution surface seawater pH data set obtained here could be used as reference to detect the on-  
37 going acidification rate in the Pacific Arctic.

## 38 **Key words**

39 pH, Arctic Ocean, sensors, colorimetric, SeaFET, acidification

## 1. Introduction

The increasing concentration of CO<sub>2</sub> in the atmosphere has significant impacts on the global climate, which lead to dramatic environmental changes in the Arctic [IPCC, 2013]. Reduction of the Arctic sea ice cover as a result of global warming opens up new prospects in the Arctic, such as the opening of new shipping routes and resource exploitation. However, ongoing environmental changes are also likely to have a significant cost. Questions arise about how the marine carbon cycle will respond to these changes and, particularly, how the uptake and sequestration of atmospheric CO<sub>2</sub> in the Arctic Ocean will impact oceanic pH (acidification: pH decrease) via the CO<sub>2</sub>-seawater reaction system (oceanic carbonate system). The Arctic Ocean is particularly vulnerable to acidification because the large freshwater inputs from continental glacier melts transported by rivers reduce alkalinity, making it less effective at neutralizing the acidifying effect of CO<sub>2</sub> [Bates and Mathis, 2009]. Additionally, the cold temperature of the Arctic Ocean facilitates the absorption of anthropogenic CO<sub>2</sub> from the atmosphere through increased solubility. Due to the intense ventilation of its subsurface layers, the Arctic Ocean is estimated to contain nearly two times the global mean concentration of anthropogenic CO<sub>2</sub> [Tanhua *et al.*, 2009]. Important increases of anthropogenic carbon concentrations have recently been estimated in the intermediate layers of the Arctic Ocean [Ericson *et al.*, 2014], leading to a significant acidification of these water masses. In order to determine ongoing changes in the carbonate chemistry of the Arctic Ocean, it is essential to expand observational capacity.

The spatial and temporal distribution of pH and its variability remain unknown in most of the Arctic regions. Most of the existing pH data from the Arctic Ocean have been calculated from measurements of other parameters of the oceanic carbonate system, typically total dissolved inorganic carbon (DIC) and total alkalinity (TA), with the inherent errors of these calculations (e.g. [Millero *et al.*, 2002]). Generally, the Arctic Ocean remains one of the less documented oceans in terms of the regional dynamics of the carbonate system (e.g. GLODAP and SOCAT databases [Sabine *et al.*, 2005; Bakker *et al.*, 2014]). Available oceanographic data have been collected mostly in summer and across the shallow and large shelf [Bates and Mathis, 2009; Miller *et al.*, 2014]. Currently, the carbonate system parameter with the most abundant dataset is the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) as a result of the development of automated shipboard pCO<sub>2</sub> analysers running continuously on the underway water supply of scientific R/Vs, which are relatively easy to maintain [Bakker *et al.*, 2014]. The first surface oceanic pH values measured with an automated instrument along a cruise transect in the Arctic has recently been reported by Tynan *et al.* [2016] for the Fram strait region. The high resolution of the dataset allowed the investigators to demonstrate that local advection pre-determines the horizontal distribution of the carbonate system whereas biological activity enhances its high variability within water masses. Automated shipboard and in situ sensors are therefore essential to obtain continuous data with high spatial and temporal resolution in order to resolve natural variations of the carbonate system and underlying changes due to anthropogenic activities [Takeshita *et al.*, 2015].

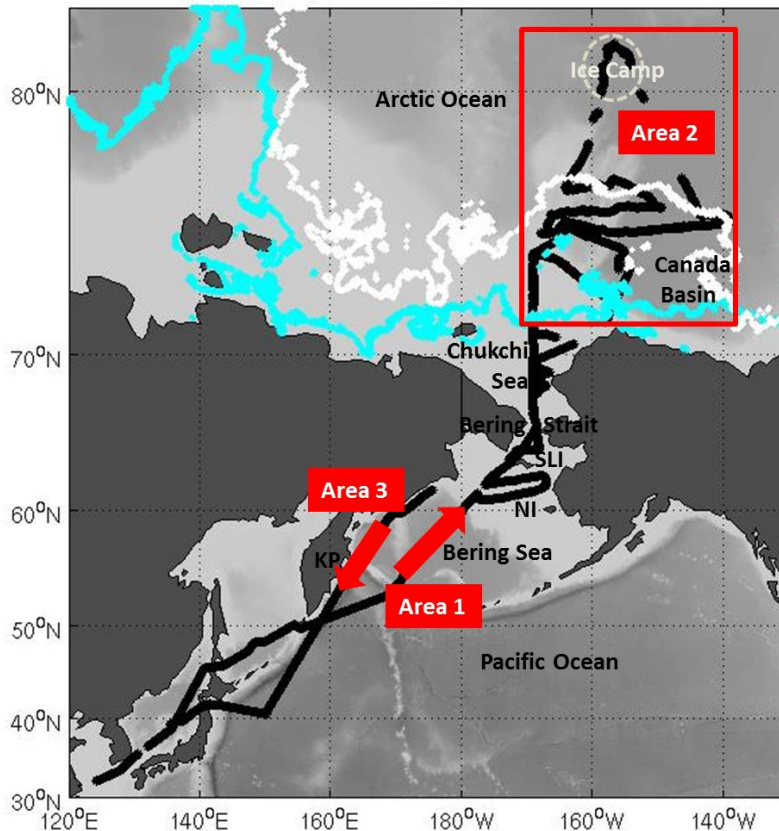
Quality pH measurements are critical for long-term ocean acidification research (precision  $\leq 0.003$  pH unit; GOA-ON report; Newton *et al.*, 2015) but challenging to obtain with an automated instrument, particularly in the Arctic Ocean where salinity and temperature can be low and surface ice (sea ice) is extensive. The challenge is not only to find pH sensors with the longevity, stability, reliability, and robustness required for deployments in the Arctic, but also the measurement method

83 must be capable of accurate pH measurement in Arctic conditions. Several automated underway pH  
84 systems have recently been developed based on the colorimetric method [Assmann *et al.*, 2011;  
85 Rérolle *et al.*, 2012]. An advantage of the colorimetric method is that the temperature and salinity  
86 dependence of the (purified) pH indicator dye *meta*-Cresol Purple (mCP) is already well-  
87 characterised in the temperature (T) and practical salinity (S) ranges  $5 \leq T \leq 35$  °C and  $20 \leq S \leq 40$   
88 [Liu *et al.*, 2011]. The colorimetric method can provide high quality data (accuracy  $\sim 0.005$  pH unit  
89 and precision  $\leq 0.0005$  pH unit, [Carter *et al.*, 2013]) in wide ranges of salinity and temperature with  
90 a negligible drift over long periods of time [Rérolle *et al.*, 2012]. However, this method has the  
91 drawback that it consumes indicator, which, as it should be purified to achieve high accuracy  
92 measurements [Yao *et al.*, 2007], is currently not easy to obtain. Additionally, colorimetric analysers  
93 are usually relatively complex, with pumps, valves, mixer, and fragile optical components which  
94 make them expensive, power hungry and potentially unreliable over long (> 6 month) deployments.  
95 An alternative method is potentiometric pH determination using either glass electrodes [Seiter and  
96 DeGrandpre, 2001] or ion-sensitive field-effect transistors (ISFET) [Shitashima *et al.*, 2002].  
97 Potentiometric sensors have the key advantages of being relatively small, not consuming reagents,  
98 and having fast response times allowing for continuous high frequency measurements. On the other  
99 hand, these sensors can drift over time and require co-localised discrete samples to correct possible  
100 calibration offset [Bresnahan *et al.*, 2014]. Potentiometric sensors can also be sensitive to salinity  
101 and temperature changes. A recently developed ISFET-based pH sensor (SeaFET®) has been  
102 demonstrated to have great stability over 9 months of deployment at surface seawater [Bresnahan  
103 *et al.*, 2014; Martz *et al.*, 2010]. The use of the SeaFET pH sensors is increasing rapidly worldwide  
104 because of its ease of use and good performance in seawater [Bresnaha *et al.*, 2014; Hofmann *et al.*,  
105 2011].

106 In this study, we compare the performance of a custom-made colorimetric analyser and a SeaFET  
107 sensor during a transect in the Arctic Ocean. We assess the quality of the pH data obtainable from  
108 these pH instruments and discuss practical considerations regarding instrumentation challenges. To  
109 this end, both instruments were connected to the underway seawater supply of the *MV XueLong*  
110 during the 6<sup>th</sup> Chinese Arctic Research Expedition (CHINARE) in summer 2014. Finally, a unique  
111 high-resolution pH dataset is presented for the Pacific sector of the Arctic Ocean.

## 112 2. Materials and methods

113 The 6<sup>th</sup> Chinese Arctic Research Expedition (CHINARE) took place between the 11<sup>th</sup> of July and the  
114 23<sup>rd</sup> of September 2014 aboard the icebreaker *MV XueLong* (“Snow Dragon”). The ship visited  
115 various oceanic areas in the North Pacific, the Bering Sea, the Chukchi Sea, the Canada Basin, and  
116 the Arctic Ocean where it was stationed for an 8-day ice camp from the 18<sup>th</sup> (157.6°W;80.9°N) to the  
117 25<sup>th</sup> (156.2°W;81.1°N) of August (Figure 1).



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**Figure 1:** Map of the *MV Xue Long* transect (black dots) during the 6<sup>th</sup> Chinese Arctic Research Expedition in summer 2014. The areas of the three datasets are indicated in red, while the location of the ice camp is indicated in grey. Area1 on the outbound leg was ice-free, Area2 was ice-covered and includes the ice camp, and Area3 on the return leg was ice-free. Red arrows indicate the outbound and return legs of the transect. The blue and white dots show the sea-ice edge contours on the weeks of the 25<sup>th</sup> of July and the 3<sup>rd</sup> of September, respectively. Ice concentration data were obtained from the satellite AMSR2 database [Beitsch *et al.*, 2013] and sea-ice edge contours are defined for ice concentration between 25 and 40%. Saint Lawrence Island (SLI), Nunivak Island (NI), and Kamchatka Peninsula (KP) are also indicated for reference.

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## 2.1. Cruise Set Up

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Two pH instruments were running in parallel: a commercially available SeaFET Ocean pH sensor from Satlantic [Martz *et al.*, 2010] and a custom-made colorimetric bench-top analyser using *meta*-cresol purple indicator [Rérolle *et al.*, 2013]. The two pH instruments were set up to run continuously on the underway seawater supply (intake at ~6 m depth) in the on-board wet lab from the 14<sup>th</sup> of July in the Japan Sea until the 16<sup>th</sup> of September in the Pacific Ocean east of the Kamchatka Peninsula. The underway water flow was irregular and when it was too low to run all the instruments, only the SeaFET sensor was left on and the colorimetric analyser was switched off. As a result, the colorimetric sensors had to be stopped for 30% of the length of the cruise (see Figure 3.d for gaps in dataset). Through the entire transect, 68,313 data point were initially collected with the SeaFET instrument and 2,451 with the colorimetric sensor. After data quality control (QC), a number of data points were removed from the data set due to the low quality of either surface seawater salinity (SSS), surface seawater temperature (SST), sensors measurement temperature or high gradient salinity data. The first three days (14-16/07/2014) of SeaFET measurements were also omitted from

142 the dataset because of the discrepancy between internal and external reference data (Figure 5.a).  
143 After QC, 11 % of the SeaFET pH data and 3 % of the colorimetric pH data were removed. Finally,  
144 2,115 data points represented simultaneous (<1 min difference) measurements with the two  
145 instruments and are used here for sensor performance comparison. Cruise pH and hydrological data  
146 are shown in Figure 3. The pH is reported in the total proton scale throughout the document.

147 The SeaFET instrument is a potentiometric system based on ion-sensitive field-effect transistors  
148 (ISFET) [Martz *et al.*, 2010]. The instrument combines one Durafet pH sensor and two different  
149 reference electrodes referred to as internal reference and external reference by the manufacturer.  
150 The principle of the two reference electrodes will not be detailed here (see Martz *et al.* [2010] for  
151 further details) but the key aspect is that the external reference is sensitive to salinity and is more  
152 stable than the internal one, which is not sensitive to salinity within the typical seawater conditions  
153 (30-36) [Bresnahan *et al.*, 2014]. The two SeaFET sensing pairs (Durafet+Internal reference and  
154 Durafet+External reference electrodes) will be referred as SeaFET\_int and SeaFET\_ext. The  
155 instrument was connected to the underway seawater supply using the flow-cell provided by the  
156 manufacturer. The accuracy of the SeaFET sensor is 0.02 according to manufacturer's specifications.  
157 The instrument was set up in a continuous data recording mode using the SeaFETCom<sup>®</sup> software to  
158 log the data directly on the computer. The data were recorded using the sensor's measurement  
159 temperature (T\_SeaFET) probe and a value of 35 for salinity. The instrument was new (serial  
160 number: 106) and the calibration coefficients from the manufacturer were used (Appendix A).  
161 Measurements were made every 4 seconds.

162 The colorimetric pH measurement method is based on the use of an indicator dye (here, *m*-Cresol  
163 Purple, mCP) with an acidic (HI) and a basic (I<sup>2-</sup>) form having different colour. The indicator is added  
164 to the seawater sample and the relative amount of the two forms of the dissociated indicator,  
165 deduced from absorption measurements, indicates the pH of the solution:  $\text{pH} = \text{pK}_{\text{ind}} + \log_{10}((R-$   
166  $e_1)/(e_2-Re_3))$ , with  $R = A_1/A_2$ ,  
167  $e_1 = \epsilon_1(\text{HI}^-)/\epsilon_2(\text{HI}^-)$ ,  $e_2 = \epsilon_1(\text{I}^{2-})/\epsilon_2(\text{HI}^-)$ ,  $e_3 = \epsilon_2(\text{I}^{2-})/\epsilon_2(\text{HI}^-)$ ,  $A_1, A_2 =$  absorbance at wavelengths 1 and 2,  
168 the maxima of the indicator acid and basic forms, and  $\epsilon_i(\text{I}^{2-}), \epsilon_i(\text{HI}^-) =$  extinction coefficients at  
169 wavelength  $i$  ( $i = 1, 2$ ) of the basic (I<sup>2-</sup>) and acid (HI) forms of the dye (see Rérolle *et al.* [2012] for  
170 detailed description of the method). The colorimetric analyser used during the cruise was adapted  
171 from the microfluidic system detailed in Rérolle *et al.* [2013]. The colorimetric measurement cell was  
172 immersed in a sampling chamber to reduce warming of the sample and possible gas exchange with  
173 the atmosphere. A tungsten light source was coupled to a blue LED in order to obtain suitable light  
174 spectra for the use of purified mCP indicator. The purified mCP indicator solution was prepared in  
175 0.7 M NaCl, and the mCP calibration coefficients from Liu *et al.* (2011), valid for  $T = 5 - 35$  °C and  $S =$   
176  $20 - 40$ , were used to determine pH from absorbance measurements. The validity of extending the  
177 use of these coefficients to temperatures lower than 5 °C was evaluated by measuring the pH of a  $S$   
178  $= 35$  Tris buffer in synthetic seawater and non-equimolar Tris/Tris-H<sup>+</sup> composition (0.02 mol kg<sup>-1</sup> Tris  
179 + 0.040 mol kg<sup>-1</sup> Tris-H<sup>+</sup>) in the laboratory. This validation was performed with a pH set-up identical  
180 to the shipboard system at 0 and 25 °C. The pH of this buffer was characterized electrochemically  
181 with the Harned Cell to near its freezing point (Papadimitriou *et al.*, manuscript submitted to *Marine*  
182 *Chemistry*). Measurements were made every 6-7 minutes.

183 Discrete seawater samples for DIC and TA were collected from the underway seawater supply ( $n =$   
184 25). The samples were collected using standard protocols [A G Dickson *et al.*, 2007] in 500 mL

185 borosilicate glass bottles and poisoned with a saturated mercuric chloride solution for storage. The  
 186 samples were shipped back to the laboratory (LOCEAN, UPMC Paris) by cargo and were analysed for  
 187 DIC and TA five months after the cruise using a custom-made potentiometric method based on  
 188 *Edmond* [1970]. The accuracy of the analysis was estimated to be within  $4 \mu\text{mol kg}^{-1}$  for DIC and TA  
 189 based on analyses of certified reference material (Batch 139, Scripps Institution of Oceanography,  
 190 University of California San Diego). The pH of the discrete underway seawater samples was  
 191 calculated from the DIC and TA data using version 2.1 of CO2Sys.xls [*Pierrot et al.*, 2006] and the  
 192 carbonic acid dissociation constants of (i) *Roy et al.* [1993], defined for low temperatures, and (ii) the  
 193 re-fit of Mehrbach et al. (1973) data by *A Dickson and Millero* [1987] as recommended by *A G*  
 194 *Dickson et al.* [2007]. The boric acid dissociation constant of *Dickson* [1990a], the bisulphate ion  
 195 acidity constant of *Dickson* [1990b], and the boron-to-chlorinity ratio of *Lee et al.* [2010] were used  
 196 in the computations.

197 Continuous SST and SSS data were obtained from the Sea-Bird Electronics SBE21 ThermoSalinoGraph  
 198 (TSG) installed on the ship's underway supply. Because the two pH instruments were set up in a  
 199 different laboratory from the TSG set-up, the temperature of the seawater increased between the  
 200 TSG and the pH instruments. The measurement temperatures of the colorimetric and SeaFET®  
 201 instruments were on average  $1.2 \pm 0.5 \text{ }^\circ\text{C}$  and  $1.9 \pm 0.6 \text{ }^\circ\text{C}$  higher than SST, respectively, with larger  
 202 discrepancy at lower SST. All the pH data have therefore been corrected to in situ temperature using  
 203 the equation from Millero et al. (2007),  $\text{dpH/dT} = -0.001582$ . Low salinity values were observed  
 204 during the transect through the ice. During the ice camp phase of the study, discrete salinity  
 205 measurements ( $S_{\text{WTW}}$ ) were made with a hand-held conductivity probe (WTW ProfiLine Cond 197i,  
 206 Germany) in under-ice water sampled from 5 m depth through a hole drilled in the ice.

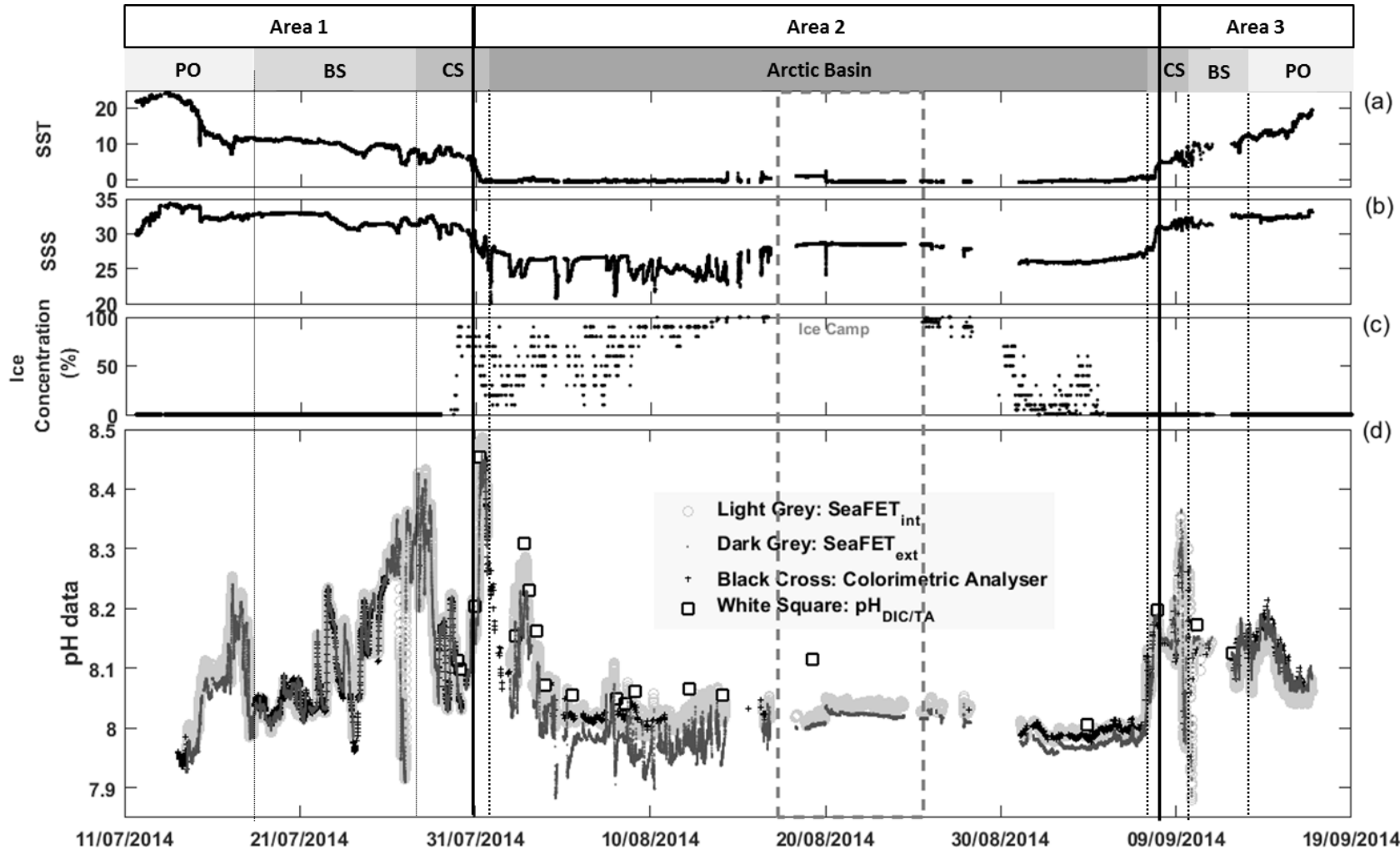
## 207 2.2. Data analysis

### 208 2.2.1. Geographic grouping of pH measurements

209 The data were split in three sub-sets corresponding to measurements taken in the ice-free Area1 on  
 210 the outbound leg of the cruise, the ice-covered Area2, and the ice-free Area3 on the return cruise leg  
 211 (Figure 2). Area2 also comprises data collected in the low salinity ( $\text{SSS} < 30$ ) and cold temperature  
 212 ( $\text{SST} < 6 \text{ }^\circ\text{C}$ ) open surface water off the edge of the ice-covered area. Definition of the areas covered  
 213 by the three datasets was done using temperature and salinity criteria as detailed in Table 1 and  
 214 shown in Figures 1 and 2. The SST was about  $20 \text{ }^\circ\text{C}$  at the start and end of the transect in the Pacific  
 215 Ocean and decreased to  $-0.9 \text{ }^\circ\text{C}$  in the ice-covered Arctic Ocean (Figure 2.a). Following a similar  
 216 pattern, the salinity ranged between 30 and 35 in the Pacific Ocean and an average 26 in the Arctic  
 217 Ocean (Figure 2.b).

218 Table 1: Geographic and hydrological characteristics of the Areas defined to study the pH datasets  
 219 from CHINARE 2014.

Dataset	Start date	End date	Start GPS location	End GPS location	SSS	SST
Area1 (outbound leg)	14/07/14 02h00	30/07/14 17h33	40.37N 136.81E	71.00N -167.69E	29.36-34.31	4.17 to 24.30
Area2 (ice-covered leg)	30/07 17h34	07/09 19h47	71.01N -167.71E	72.53N -168.98E	19.89-30.46	-0.87 to 6.12
Area3 (return leg)	07/09/14 19h48	16/09/14 05h38	72.53N -168.98E	42.36N 151.42E	30.10-33.32	2.80 to 19.48



220  
 221 **Figure 2:** In situ seawater surface temperature (a), salinity (b), ice concentration (c), and pH (total proton scale) (d) during the CHINARE2014 research cruise.  
 222 Light grey circles represent pH data from SeaFET<sub>int</sub>, dark grey dots pH data from SeaFET<sub>ext</sub>, black crosses indicate the colorimetric pH data, and open  
 223 squares the pH calculated from discrete DIC and TA analyses using the carbonic acid constants from Roy *et al.* [1993]. Data corresponding to Area1 (ice-free  
 224 outbound), Area2 (Arctic ice-covered), and Area3 (ice-free return leg) are delimited with the vertical solid lines and the ice camp with the vertical dotted  
 225 lines. The Pacific Ocean (PO), Bering Strait (BS), Chukchi Sea (CS), and Arctic Basin areas are also indicated.



### 2.2.2. Measurement precision and uncertainty

The short term precision of the instruments was estimated at nine CTD stations where the ship was stationary for at least 1 hour. Given the various frequencies of the instruments, precision was estimated by both the standard deviation of the data obtained in 1 hour of measurement and the standard deviation of 10 consecutive measurements. Results were similar for both methods and only results from consecutive measurements are discussed.

To estimate the uncertainty in the salinity data, a comparison was made between underway salinity ( $S_{UW}$ ) and surface CTD data collected with a Sea-Bird Electronics SBE-19 ( $S_{CTD}$ ). The impact of this uncertainty on colorimetric and SeaFET\_ext pH datasets was estimated by comparing pH colorimetric and SeaFET\_ext obtained with  $S_{UW}$  and then pH colorimetric and SeaFET\_ext obtained with  $S_{UW} + S_{uncertainty}$ .

The uncertainty of the colorimetric pH dataset is evaluated as the square root of the sum of squares of the estimated uncertainty of the method and uncertainties due to errors in the measurement temperature and salinity. The uncertainty of the method was estimated as the square root of the sum of squares of the discrepancy between the certified and measured pH of the Tris buffer and the uncertainty in the Tris buffer characterisation (0.004 pH unit; Papadimitriou et al., submitted to Marine Chemistry). The colorimetric measurement temperature uncertainty (0.5 °C) was estimated from the standard deviation amongst the three thermistors immersed in the colorimetric chamber.

The uncertainty in the comparison between calculated pH from DIC and TA and colorimetric pH was calculated as the square root of the sum of squares of the estimated uncertainties due to lack of synchronicity between the discrete and continuous pH sampling, discrete sample handling and storage, and computational errors due to uncertainty in the thermodynamic constants of the marine carbonate system and uncertainty in DIC, TA and colorimetric pH measurements. These calculations are detailed in Appendix C.

### 2.2.3. Quantitative comparison of pH datasets

The agreement between the colorimetric, SeaFET\_int and SeaFET\_ext data sets (Figure 3) was evaluated using Pearson's correlation coefficient ( $r$ ), mean and standard deviation of residuals (MR and SR), and the root mean square error (RMSE) of the linear fit. Data sets are considered to compare well when  $r > 0.9$ , with MR and SR  $\leq 0.01$  pH unit. The correlation between each pair of pH dataset was computed using a multiple linear regression in Matlab (function *regress*) [Chatterjee and Hadi, 1986].

Factors that may give rise to data discrepancies between the sensors were investigated by Pearson's correlation between pH residuals and other measured environmental parameters (pH datasets, SSS, SST, T\_SeaFET, T\_colorimetric and date), as well as inter-correlation between these parameters. A stepwise regression (*stepwisefit*) resulted in keeping the parameters *pH datasets*, *SSS*, and *SST* to determine the factors influencing distribution variability of pH residuals along the cruise transect [Draper and Smith, 1998]:  $pH\_residuals = x_{pH\_SeaFET} \cdot pH\_SeaFET + x_{SSS} \cdot SSS + x_{SST} \cdot SST$ , with  $x_{parameter}$  = regression coefficient for each parameter. The percent relative contribution from each parameter to the pH dataset discrepancy was calculated as follows:  $RMSE \cdot x_{parameter} / \text{sum}(x_{parameters})$ . All parameters were standardized (centred to 0 and variance scaled to 1) before performing the multi-linear regressions:  $p_{standardized} = (p_i - p_{mean}) / \sigma_p$ , where  $p$  = parameter and  $\sigma_p$  = parameter standard deviation.

267 **2.2.4. Final pH dataset**

268 A final data set (pH\_final) was obtained by combining the data from SeaFET\_int sensor in Area1 and  
269 Area2 with the data from SeaFET\_ext sensor in Area3. Data from the colorimetric sensor were used  
270 to fill gaps in the dataset, consisting mostly of 259 data points over ten hours on the 14<sup>th</sup> of July and  
271 over seven hours on the 17<sup>th</sup> of July.

272 **3. Results and Discussion**

273 Surface seawater temperature, salinity, pH and ice concentration datasets collected during CHINARE  
274 2014 are presented Figure 2.

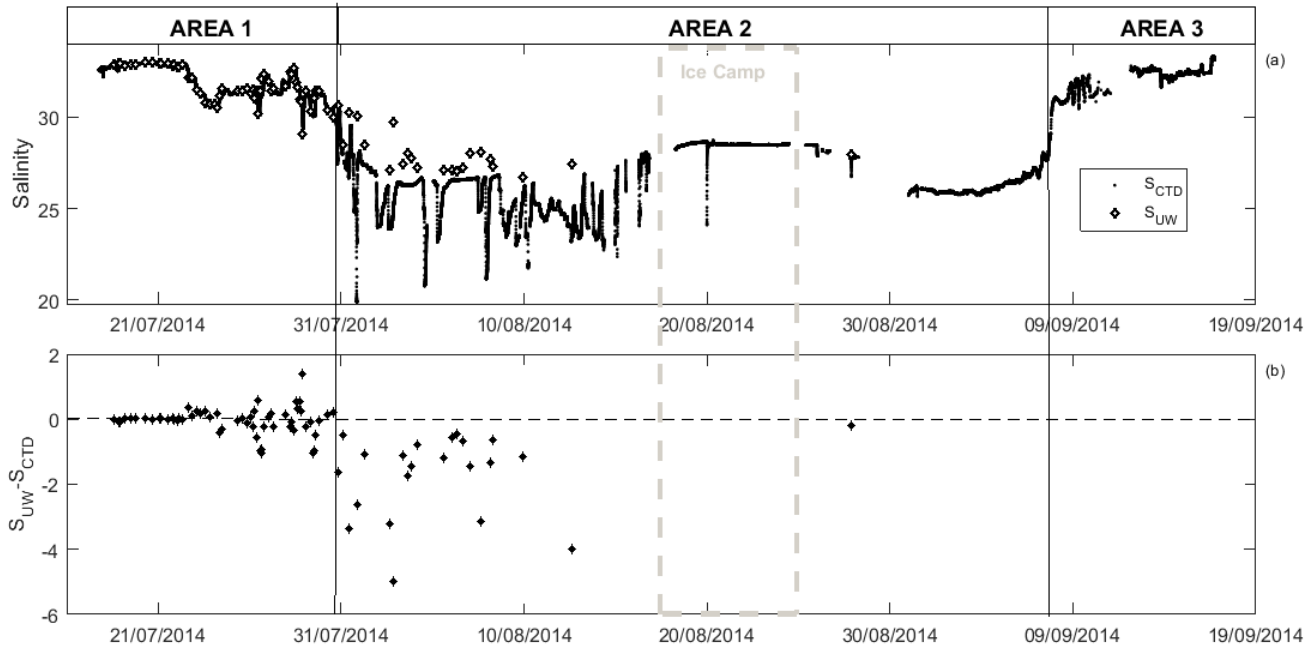
275 **3.1. Measurement precision and uncertainty: results**

276 Short term precision of the two SeaFET electrodes and the colorimetric analyser was 0.0005 and  
277 0.0010, respectively (n = 10, see 2.2.2. Measurements precision and uncertainty).

278 **3.1.1. Salinity observations: uncertainty in the iced-covered region and its**  
279 **contribution to pH uncertainty**

280 During transit in the ice-covered Area2,  $S_{UW}$  was between 0.02 to 4.00 units lower than  $S_{CTD}$   
281 ( $S_{uncertainty}=S_{UW} - S_{CTD} = -1.8 \pm 1.3$ , n = 24, Figure 3). No such discrepancy was observed with the  
282 temperature sensor (Appendix B). The conductivity sensor does not appear to have drifted during  
283 the cruise because  $S_{UW}$  compared well in areas visited both on the outbound and on the return legs  
284 of the cruise. Additionally, there was good agreement between  $S_{UW} = 28.49 \pm 0.02$  (n = 5735) during  
285 the 8-day long stationary ice-camp phase and  $S_{WTW} = 28.2 \pm 0.2$  (n = 3) measured with the hand-held  
286 salinometer in under-ice seawater. A small part of the salinity discrepancy during transit in Area2  
287 may be due to sampling mismatch between the underway inlet and the CTD cast as observed in the  
288 outbound ice-free Area1, where  $S_{UW} - S_{CTD} = -0.04 \pm 0.41$  (n = 59). However, the comparatively larger  
289 discrepancy between the two salinity datasets in Area2 indicates additional contributing factors,  
290 such as potentially problematical measurements with the underway salinometer due to ice  
291 fragments or air bubbles, or both, pumped in the underway supply during transit through the ice-  
292 covered region. Due to the unaccounted-for discrepancy between  $S_{UW}$  and  $S_{CTD}$  in the ice-covered  
293 Area2 stated above, the corresponding uncertainty in pH\_SeaFET\_ext and pH\_colorimetric was  
294 estimated by comparing the pH data processed using  $S_{UW}$  and  $S_{UW}+1.8$ . In this comparison,  
295 pH\_colorimetric( $S_{UW}+1.8$ ) was found to be  $0.002 \pm 0.001$  pH unit lower than pH\_colorimetric( $S_{UW}$ ). In  
296 contrast, pH\_SeaFET\_ext( $S_{UW}+1.8$ ) was found to be  $0.027 \pm 0.005$  pH unit higher than  
297 pH\_SeaFET\_ext( $S_{UW}$ ). Because the pH\_colorimetric data from Area2 are less susceptible to  
298 uncertainty in salinity, they are considered to be more reliable than the pH\_SeaFET\_ext data. The  
299 pH\_SeaFET\_int is not considered to be sensitive to salinity within the salinity range encountered in  
300 this study and, so, will not be affected by the salinity uncertainty during transit in this region of the  
301 Arctic Ocean.

302



303  
 304 **Figure 3:** Comparison of underway salinity ( $S_{UW}$ ) data with salinity data from surface CTD casts ( $S_{CTD}$ ).  
 305 a)  $S_{UW}$  is shown in black dots and  $S_{CTD}$  in white diamonds. b) Salinity residuals ( $S_{UW}-S_{CTD}$ ). Data  
 306 corresponding to Area1 (ice-free outbound), Area2 (Arctic, ice-covered), and Area3 (ice-free return  
 307 leg) are delimited by the vertical solid lines and the ice camp by the vertical dotted lines.

### 308 3.1.2. Comparison between measured and calculated pH data

309 Similar trends were observed between the measured pH and the pH calculated from discrete DIC  
 310 and TA data (Figure 2d). However, a discrepancy of  $0.034 \pm 0.036$  pH unit was obtained between  
 311 measured and calculated pH using carbonic acid constants from Roy et al. [1993] ( $0.045 \pm 0.035$  with  
 312 constants from Mehrbach et al. [1973] refitted by A Dickson and Millero [1987]). This discrepancy is  
 313 likely due to lack of synchronicity between the discrete and continuous pH sampling, discrete sample  
 314 handling and storage, and computational errors due to uncertainty in the thermodynamic constants  
 315 of the marine carbonate system. The overall uncertainty in the comparison between calculated pH  
 316 from DIC and TA and colorimetric pH was estimated to be 0.041 pH unit (see Materials and methods  
 317 section and Appendix C for calculation details). This is the same order of magnitude as the observed  
 318 discrepancy between measured and calculated pH.

### 319 3.1.3. Colorimetric measurement uncertainty

320 The discrepancy of our measured buffer pH from the electrochemical value was between 0.001 pH  
 321 unit at 25 °C and 0.005 pH unit at 0°C (see Materials and methods section). An error of 0.006 pH unit  
 322 is obtained from the maximum discrepancy between the certified and measured Tris buffer pH  
 323 (0.005 pH unit) and the uncertainty in the Tris buffer characterisation (0.004 pH unit; *Papadimitriou*  
 324 *et al.*, submitted to *Marine Chemistry*). The error due to the salinity uncertainty is estimated to be  
 325 within 0.002 pH unit (see section 3.1.1.), while the error due to the colorimetric measurement  
 326 temperature uncertainty is 0.002 pH unit. The combined measurement uncertainty is thus computed  
 327 to be 0.007 pH unit, and, based on this, the colorimetric dataset (pH\_colorimetric) from the entire  
 328 cruise is considered of good quality and will be used as reference data to study pH\_SeaFET data  
 329 quality.

330 **3.2. Comparison of pH sensors**

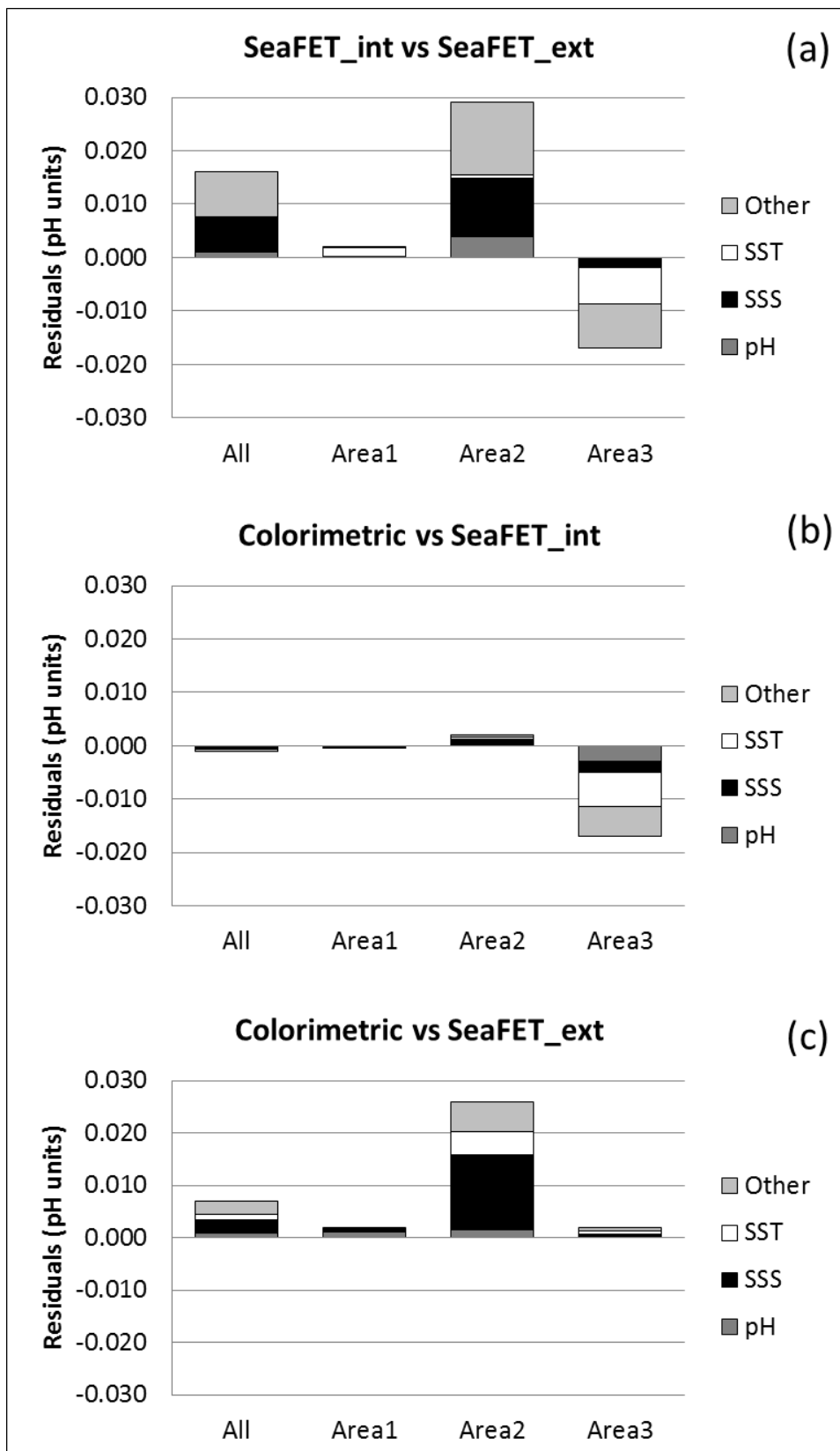
331 The results from the statistical comparison of the sensor data are presented in Table 2 and Figure 4.  
 332 The coefficients from the multi-linear regression are detailed in Appendix D. The correlation  
 333 between the data from both sensors was high ( $r > 0.9$ ) but significant discrepancies with mean  
 334 residuals (MR) higher than 0.010 pH unit were observed in some areas. The highest MR was found  
 335 between pH\_SeaFET\_int and pH\_SeaFET\_ext ( $MR_{All\_SeaFET} = 0.016 \pm 0.022$  pH unit, Table 2). The two  
 336 sensors compared well in open ocean water (Area1) with residuals  $pH\_SeaFET\_int -$   
 337  $pH\_SeaFET\_ext = 0.002 \pm 0.005$  but the comparison worsened with residuals about an order of  
 338 magnitude higher in Area2 (positive residuals) and Area3 (negative residuals). Data from SeaFET\_int  
 339 compared well with the colorimetric data from open ocean water in Area1 and the ice-covered  
 340 Area2, with residuals between  $0.000 \pm 0.007$  and  $0.002 \pm 0.011$  pH unit. In Area3, the SeaFET\_int  
 341 data differed from the colorimetric data, with similar discrepancies to those observed between  
 342 SeaFET\_int and SeaFET\_ext. Finally, the data from SeaFET\_ext compared well with the colorimetric  
 343 data in the open water regions in Area1 and Area3 (absolute residuals  $\leq 0.002 \pm 0.016$ ) whereas  
 344 large discrepancies were observed in the ice-covered Area2 (residuals =  $-0.026 \pm 0.016$ ). Reasons for  
 345 these discrepancies will be discussed in 3.4. SeaFET sensor performance.

346  
 347 Figure 4 shows that a large part of the residuals between the two SeaFET datasets and between  
 348 SeaFET\_ext and the colorimetric analyser is due to the salinity distribution in the entire transect and  
 349 in Area2. In contrast, in Area3, temperature seems to be the predominant factor in explaining the  
 350 residuals between the two SeaFET datasets and between SeaFET\_int and the colorimetric dataset,  
 351 which in fact was probably to be due to a fault in the internal electrode (see 3.4.2 drift of the  
 352 internal electrode).

353 **Table 2:** Comparison between the underway data from the colorimetric and SeaFET sensors, divided  
 354 into three datasets (Area1, Area2 and Area3: for definitions, see section *Materials and methods*):  $r$  =  
 355 Pearson’s correlation coefficient, MR = mean standard deviation of residuals, and SR = standard  
 356 deviation of residuals. Datasets where comparison is good (mean residuals  $\leq 0.010$ ) are highlighted  
 357 in bold.

Sensors Y vs X	Dataset	Correlation	Residuals (X-Y)		NB Points
		$r$	MR	SR	
SeaFET_ext vs SeaFET_int	All	0.994	0.016	0.022	60787
	<b>Area1</b>	<b>0.997</b>	<b>0.002</b>	<b>0.005</b>	16877
	Area2	0.998	0.029	0.018	36333
	Area3	0.928	-0.017	0.004	7577
Colorimetricvs SeaFET_int	All	0.989	-0.001	0.010	2110
	<b>Area1</b>	<b>0.997</b>	<b>0.000</b>	<b>0.007</b>	1495
	<b>Area2</b>	<b>0.991</b>	<b>0.002</b>	<b>0.011</b>	459
	Area3	0.952	-0.017	0.020	156
Colorimetricvs SeaFET_ext	All	0.977	-0.007	0.014	2110
	<b>Area1</b>	<b>0.999</b>	<b>-0.002</b>	<b>0.006</b>	1495
	Area2	0.972	-0.026	0.016	459
	<b>Area3</b>	<b>0.997</b>	<b>-0.002</b>	<b>0.016</b>	156

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**Figure 4:** Results of the multi-linear regression analysis using pH<sub>SeaFET</sub>, SSS, and SST to explain residuals between pH datasets. Underway data are divided into three datasets (Area1, Area2, and Area3; see section *Materials and methods*). (a) Residuals = pH<sub>SeaFET\_int</sub> – pH<sub>SeaFET\_ext</sub>. (b) Residuals = pH<sub>colorimetric</sub> – pH<sub>SeaFET\_int</sub>. (c) Residuals = pH<sub>colorimetric</sub> – pH<sub>SeaFET\_ext</sub>.

### 364           **3.3.    Colorimetric analyser: Performance at near-zero temperatures**

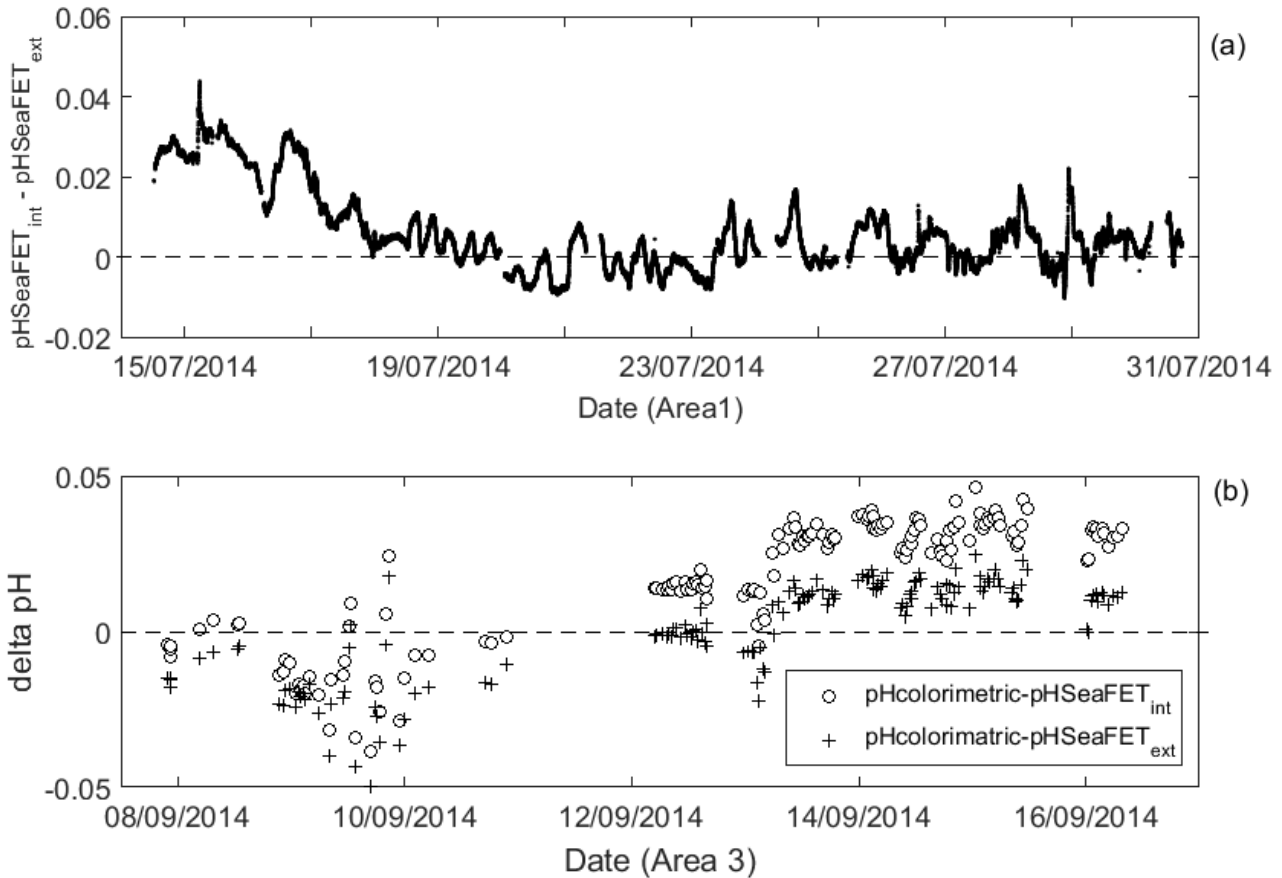
365    The colorimetric method can be used at temperatures down to  $-1.8\text{ }^{\circ}\text{C}$  without any further  
366    adaptation as long as a good mixing between the indicator and the seawater is ensured (solution  
367    viscosity will increase at low measurement temperature). However, the mCP has only been  
368    characterised above  $5\text{ }^{\circ}\text{C}$  by *Liu et al.* [2011] and care should be taken when using equations outside  
369    their definition range. In this case, the extinction coefficients and dissociation constants ( $\text{pK}_a'$ ) have  
370    been shown to be close to linear with temperature [*DeGrandpre et al.*, 2014; *Liu et al.*, 2011] and  
371    extending equations to lower temperatures may lead to negligible errors. This assumption is  
372    supported by comparison with equations from *DeGrandpre et al.* [2014] defined for a temperature  
373    down to  $0\text{ }^{\circ}\text{C}$  showing a discrepancy lower than 0.010 in  $\text{pK}_a'$  at  $0\text{ }^{\circ}\text{C}$ . During this investigation, the  
374    SSS remained within the range of the *Liu et al.* [2011] mCP characterisation. As an additional check,  
375    the performance of the custom-made colorimetric set-up used in this investigation was evaluated  
376    with a Tris buffer solution prior to the cruise with good agreement (see section 3.1.3.), which  
377    indicates that the *Liu et al.* (2011) indicator calibration coefficients are suitable for the minimum  
378    measurement temperature in this study ( $0.36\text{ }^{\circ}\text{C}$ ). Until relevant buffer data become available,  
379    extrapolation to below-zero temperatures of the existing oceanographic equations is not  
380    recommended because the indicator parameters behaviour close to the freezing point of seawater is  
381    unknown.

382    Although the colorimetric method can be easily extended *a priori* to operate at near-zero  
383    temperatures, deploying an in situ colorimetric pH instrument is not straightforward. First, in situ  
384    colorimetric systems typically use LEDs as light source with wavelengths known to shift at low  
385    temperature [Chhajed et al., 2005]. So, even if an LED were centred on the desired wavelength at  $20$   
386     $^{\circ}\text{C}$ , it may be several nanometres away at  $0\text{ }^{\circ}\text{C}$ . It is then required to check the calibration not only of  
387    the pH indicator dye, but also the entire sensor at the temperature range of deployment. Second, a  
388    colorimetric analyser requires a pumping system and valves to control the indicator and sample  
389    flows. Power settings to activate the different components of an autonomous instrument are usually  
390    optimised in order to minimise the power requirement and may not be the same for temperatures  
391    typical of the temperate and tropical oceanic waters and for temperatures near or below zero as in  
392    Arctic waters. For example, the power requirements of each component, particularly pumps and  
393    valves, may vary with temperature. Battery output will also decrease at low temperature.  
394    Instrument settings must then be optimised depending on the deployment conditions. It is therefore  
395    highly recommended to check with the manufacturer that the sensor has been calibrated and set up  
396    for the intended deployment conditions.

### 397           **3.4.    SeaFET sensor performance**

#### 398           **3.4.1.    Conditioning of the electrode**

399    The SeaFET instrument requires time for warming up and conditioning of the electrodes [*Bresnahan*  
400    *et al.*, 2014], which can vary with instrument and, particularly, deployment conditions. Our SeaFET  
401    instrument required three days to stabilize based on the difference between  $\text{pH\_SeaFET\_int}$  and  
402     $\text{pH\_SeaFET\_ext}$  converging to zero after three days of deployment (Figure 6a). To reduce this  
403    instrument conditioning time requirement, it is recommended to power the sensor and to store it in  
404    natural seawater for about a week prior to deployment [*Bresnahan et al.*, 2014].



406 **Figure 5:** (a) Evidence for electrode conditioning time requirement: the difference between  
 407 pH\_SeaFET\_int and pH\_SeaFET\_ext overtime in Area1; (b) Evidence for internal reference drift: the  
 408 difference between pH\_colorimetric and pH\_SeaFET\_int/ext overtime in Area3.

### 409 3.4.2. Drift of the internal electrode

410 Based on the residuals relative to both SeaFET\_ext and colorimetric pH measurements of about  
 411 0.017 pH unit, the SeaFET\_int did not perform well in Area3 (Figures 4b and 5b) despite similar  
 412 measurement temperature and salinity conditions as in Area1 (Figure 2 and Table 1). The SeaFET\_int  
 413 data quality appears to worsen over time with the discrepancy between SeaFET\_int and SeaFET\_ext  
 414 increasing from 0.010 to more than 0.020 pH unit in a week (from the 8<sup>th</sup> to the 16<sup>th</sup> of August,  
 415 Figure 5b). A similar sensor drift has been observed by *Bresnahan et al.* [2014] and was attributed to  
 416 deterioration of the internal reference electrode. The SeaFET used in our study was an early version  
 417 of SeaFET instruments fitted with an internal electrode probably prone to early deterioration and  
 418 drift (Van Dommelen, Satlantic, pers. comm.).

### 419 3.4.3. Performance in open ocean conditions and at low measurement temperatures

420 Good comparison with residuals lower than 0.010 pH unit (Table 2 and Figure 4) between either  
 421 pH\_SeaFET\_int or pH\_SeaFET\_ext and pH\_colorimetric in Area1 shows that SeaFET\_int and  
 422 SeaFET\_ext sensors performed well in open ocean conditions ( $29 < S < 34$  and  $4 < T < 25$  °C). Indeed,  
 423 the pH discrepancy (within 0.007 pH unit) was within the colorimetric measurement uncertainty.  
 424 The reliability of the SeaFET measurements was therefore better than 0.010 pH unit without the  
 425 need to apply a correction using a discrete in situ sample after deployment as recommended in  
 426 *Bresnahan et al.* [2014]. The SeaFET instrument was operated at measurement temperatures down  
 427 to 1.0 °C with a mean  $T_{\text{SeaFET}} = 1.9 \pm 0.8$  °C in Area2. Contrary to salinity, low measurement

428 temperatures do not seem to affect the quality of the SeaFET sensor data (Area2 in Figure 4b and  
429 4c). According to SeaFET User Manual, the instrument operating measurement temperature range is  
430 down to 0 °C, which would prevent deploying the sensor in situ in several areas of the Arctic where  
431 below-zero temperatures occur, although several users have reported such use without issue (IOCCP  
432 Sensors summer course participants) but this still requires further investigations.

#### 433 **3.4.4. Low salinity data quality and the external reference sensor**

434 The estimated uncertainty in pH\_SeaFET\_ext in Area2 due to salinity uncertainty (0.027 pH unit, see  
435 section 3.1.1.) is of the same order of magnitude as the mean discrepancy observed between  
436 pH\_SeaFET\_ext and the two other pH datasets (Table 2). It is therefore likely that the poor quality of  
437 the salinity data in Area2 mostly explains the poor comparison between pH\_SeaFET\_ext and the  
438 other two pH datasets of this study. Takeshita et al. (2014) showed that the external reference  
439 electrode (Cl-ISE) had a near-Nernstian behaviour to the chloride ion activity between salinity 20 and  
440 35. It is therefore expected that the SeaFET\_ext sensor should perform well with the range of salinity  
441 met in the ice-covered, low salinity regions of the Arctic ocean provided that the Cl<sup>-</sup> to Br<sup>-</sup> ratio is  
442 similar to that in the open ocean areas. However, during the ice-camp phase of this study, when S<sub>UW</sub>  
443 was reliable and stable around 28.5 for 8 days, a mean discrepancy of 0.015 ±0.004 pH unit (n =  
444 5677) was still observed between the pH\_SeaFET\_int and pH\_SeaFET\_ext data sets. We do not  
445 anticipate sea ice formation and decay to alter the chloride ion composition in Arctic oceanic waters  
446 but, until further tests are conducted along these lines, the reason for this discrepancy remains  
447 unidentified.

#### 448 **3.5. Choice of sensor**

449 The comparison with the bench-top colorimetric analyser showed that high quality pH data could be  
450 obtained by the ISFET with the internal reference electrode whereas the external reference  
451 electrode did not perform well in the ice-covered area. The quality of the data from both internal  
452 and external reference electrodes did not appear to be affected by the low measurement  
453 temperature to 1 °C in the Arctic region. The SeaFET instrument can therefore be used to measure  
454 pH in the Arctic but it is advisable to use the internal electrode data in ice-melt low salinity  
455 conditions. Long term stability of the instrument in such environment also requires further  
456 investigation.

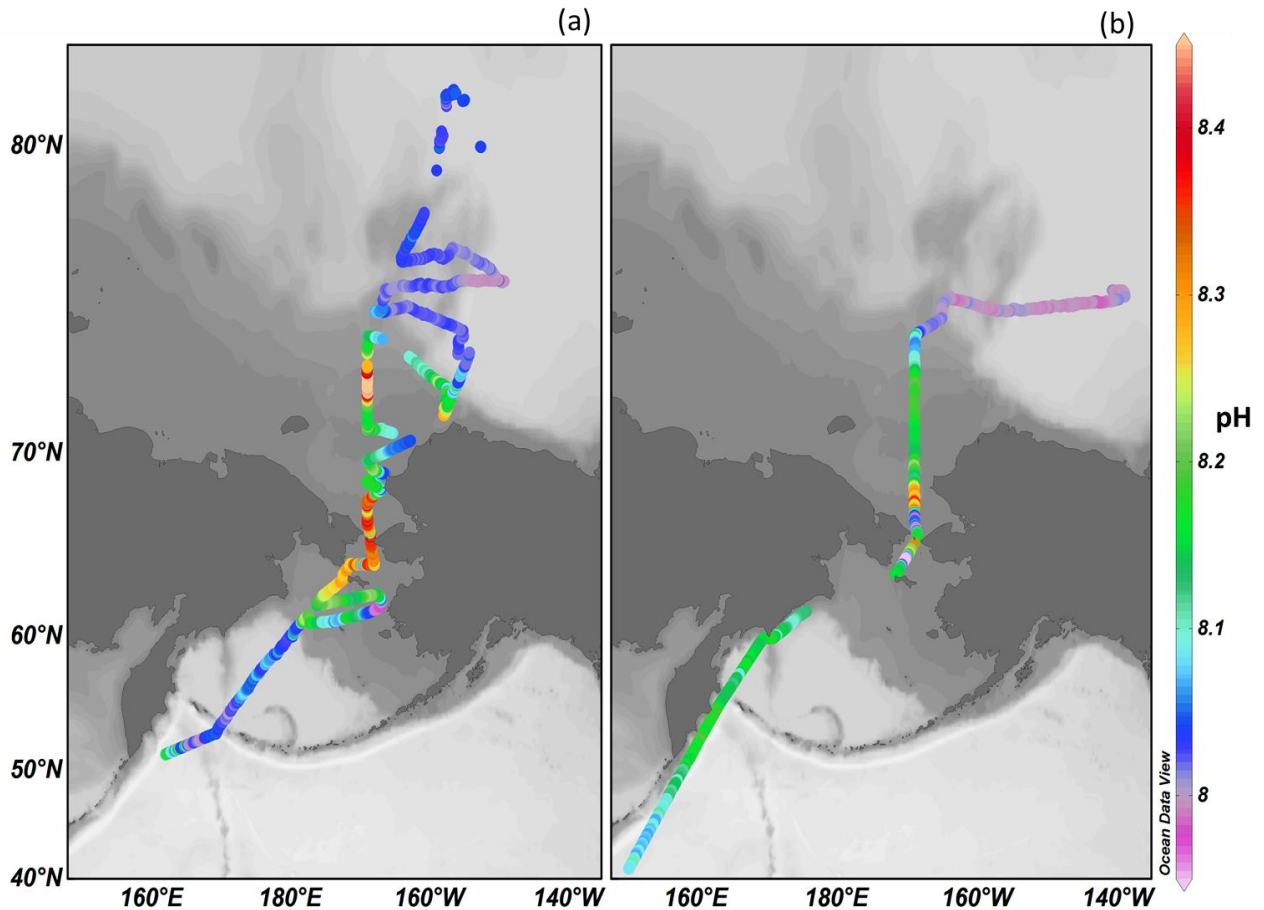
457 The choice of instrument will ultimately depend on the user constraints and deployment conditions.  
458 **The colorimetric method presents the key advantage that the instrument calibration can be tested in**  
459 **the laboratory without need for an in situ re-calibration**, but regular checks with discrete samples or  
460 Tris buffer measurement are always advisable during deployment. Also, the colorimetric  
461 measurements are reproducible in the long term [Byrne et al., 2010]. Although difficult and  
462 expensive to obtain, the purified mCP indicator dye has been carefully characterized in the open  
463 ocean temperature and salinity range and can be reasonably extended to 0 °C. However,  
464 colorimetric instruments require valves and pumps which can be problematic and make these  
465 instruments often less reliable at low temperature. On the other hand, the SeaFET instrument has  
466 been shown to provide high quality measurements even at low temperature and the simpler  
467 instrumentation make it currently more amenable to in situ deployments at low temperature.  
468 However, when using the SeaFET instrument, it is strongly recommended to use regularly an  
469 independent procedure, such as discrete colorimetric pH data, or calculated pH from DIC/TA data, to  
470 re-calibrate SeaFET at in situ conditions and monitor sensor drift (see [Bresnahan et al., 2014] for



471 detailed in situ calibration procedure). This is particularly critical for long term deployments. Finally,  
472 independent of the choice of sensor, it is recommended to check with the manufacturer that the  
473 instrument is calibrated and set up for the expected deployment conditions.

### 474 3.6. A new Arctic pH data set

475 Figure 6 presents the geographic distribution of surface pH<sub>final</sub> along the outbound and return legs  
476 of our transect in the investigated regions of the North Pacific and Arctic oceans. The overall  
477 uncertainty of this dataset is estimated to be within 0.01 pH unit. This dataset can be used for  
478 marine carbonate chemistry studies and long-term ocean acidification monitoring.



479 **Figure 6:** Surface pH data collected during CHINARE 2014. (a) Surface pH data collected from the 17<sup>th</sup>  
480 of July until the 28<sup>th</sup> of August. (b) Surface pH data collected from the 31<sup>st</sup> of August until the 16<sup>th</sup> of  
481 September.  
482

483 Our finalized pH data set shows large pH variations in the explored Arctic regions across the shelves  
484 in ice-free and ice-covered surface seawater. Hot spots with a pH increase of up to 0.40 pH unit  
485 relative to the other regions of the transect were seen in the Bering Strait and the Chukchi Sea  
486 (Figure 6). In contrast, the pH remained relatively stable in under-ice seawater well into the sea ice  
487 zone, within 0.02 pH unit from a mean value of 8.02, which is comparable to the reported pH = 8.0 in  
488 the ice-covered Fram Strait by *Tynan et al.*, [2016]. Also, in a similar pattern to that reported in the  
489 Fram Strait (pH maximum = 8.5; *Tynan et al.*, [2016]), the highest pH values observed here  
490 (maximum = 8.49) were measured at the ice edge on the 31<sup>st</sup> of July at 73.00 °N and 168.97 °W,  
491 where, as evidenced by the brown aggregates observed in the water, we probably encountered a  
492 large diatom bloom. On the return leg of the transect, when we transited the same area, the pH was

493 8.18, which is 0.3 pH unit lower than a month before during the putative diatom bloom. This pH  
494 change is in the same order of magnitude as the estimated 0.25 pH change in the course of an ice-  
495 edge bloom in the Fram Strait by Tynan et al. [2016]. High pH values (up to 8.41) were also  
496 measured in the Bering Strait on the way north. The lowest pH values (7.93) was measured in the  
497 Bering Strait north of Saint Lawrence Island (SLI, Figure 1) at 64.36 °N and 169.45 °W where colder (-  
498 2 °C) and more saline waters (+1 practical salinity unit compared to surrounding waters) were locally  
499 encountered probably due to upwelled water as evidenced by the well-mixed water column. Low pH  
500 values (down to 7.96 pH units) were also measured close to the Alaskan coast at 61.70 °N and  
501 167.65 °W north of Nunivak Island (NI, Figure 1). This low pH area maybe be due to the plume of the  
502 Yukon river water discharge as evidenced by fresher water ( $S = 30.4$ ) compared to surrounding water  
503 ( $S > 30.8$ ). Lower aragonite saturation state has also been observed in the area in 2012 [Mathis et al.,  
504 2015], which would imply low pH values for these water masses.

#### 505 **4. Conclusion**

506 A SeaFET pH sensor and a bench-top colorimetric pH analyser comparison was performed in surface  
507 Arctic and North Pacific waters in boreal summer 2014. The comparison allowed testing of the  
508 increasingly common SeaFET pH sensor for use in Arctic conditions, where the highest and fastest  
509 anthropogenic acidification is expected. The two instruments were used successfully to measure low  
510 temperature seawater pH in the Arctic Ocean, provided that the SeaFET internal reference dataset  
511 was used in the low salinity ice-covered area instead of the SeaFET external reference dataset. The  
512 SeaFET instrument presents the advantage of being simple to use, while the lack of mechanical  
513 components make it more reliable than current colorimetric instruments in low temperature  
514 conditions. However, for long term deployment without access to the instrument for recalibration, a  
515 colorimetric analyser would be favoured. Further development is still required for pH measurements  
516 in below-zero temperature hypo-saline and hyper-saline polar waters. Finally, a unique high  
517 resolution (15 measurement minute<sup>-1</sup>) and high quality surface water pH dataset (uncertainty  
518  $\leq 0.010$  and precision  $\leq 0.001$  pH unit) was obtained using the two instruments in different oceanic  
519 water masses in open water in the North Pacific, Bering Sea, and Chukchi Sea, as well as in the ice-  
520 covered region of the Arctic Ocean. Large pH variations were observed on the Arctic shelves, with pH  
521 (total proton scale) ranging between 7.98 and 8.49 whereas the under-ice seawater pH was  
522 relatively stable at  $8.02 \pm 0.02$ . The large spatial and seasonal pH variability observed here is not yet  
523 described by climatological models in the Arctic Oceans. As a result of this and the rigorous data  
524 quality assessment, we propose this novel and reliably measured pH data for use as reference to  
525 detect the on-going acidification rate in the Arctic. This highlights the pressing need for more  
526 extensive measurements in space and time in order to understand the dynamics of the carbonate  
527 system in the Arctic Ocean in the face of ongoing atmospheric CO<sub>2</sub> changes.

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542 References

543

544 Assmann, S., C. Frank, and A. Koertzing (2011), Spectrophotometric high-precision seawater pH  
545 determination for use in underway measuring systems, *Ocean Sci.*, 7(5), 597-607.

546 Bakker, D., S. Hankin, A. Olsen, B. Pfeil, K. Smith, S. Alin, C. Cosca, B. Hales, S. Harasawa, and A. Kozyr  
547 (2014), An update to the Surface Ocean CO<sub>2</sub> Atlas (SOCAT version 2), *Earth*.

548 Bates, N., and J. Mathis (2009), The Arctic Ocean marine carbon cycle: evaluation of air-sea CO<sub>2</sub>  
549 exchanges, ocean acidification impacts and potential feedbacks, *Biogeosciences*, 6(11), 2433-2459.

550 Beitsch, A., L. Kaleschke, and S. Kern (2013), AMSR2 ASI 3.125 km Sea Ice Concentration Data, V0.1,  
551 edited by U. o. H. Institute of Oceanography, Germany, digital media (<ftp-projects.zmaw.de/seaice/>).

552 Bresnahan Jr, P. J., T. R. Martz, Y. Takeshita, K. S. Johnson, and M. LaShomb (2014), Best practices for  
553 autonomous measurement of seawater pH with the Honeywell Durafet, *Methods in Oceanography*,  
554 9(0), 44-60.

555 Byrne, R. H., S. Mecking, R.A. Feely, and X. Liu (2010), Direct observations of basin-wide acidification  
556 of the North Pacific Ocean, *Geophys. Res. Lett.*, 37.

557 Carter, B., J. Radich, H. Doyle, and A. Dickson (2013), An automated system for spectrophotometric  
558 seawater pH measurements, *Limnol. Oceanogr. Methods*, 11(1), 16-27.

559 Chatterjee, S., and A. S. Hadi (1986), Influential Observations, High Leverage Points, and Outliers in  
560 Linear Regression, *Statistical Science*, 1, 379-416.

561 Chhajer, S., Y. Xi, Y.-L. Li, Th. Gessmann and E. F. Schubert (2005), Influence of junction temperature  
562 on chromaticity and color-rendering properties of trichromatic white-light sources based on light-  
563 emitting diodes, *Journal of Applied Physics*, 97, 054506 .

564 DeGrandpre, M. D., R. S. Spaulding, J. O. Newton, E. J. Jaqueth, S. E. Hamblock, A. A. Umansky, and K.  
565 E. Harris (2014), Considerations for the measurement of spectrophotometric pH for ocean  
566 acidification and other studies, *Limnol. Oceanogr. Methods*, 12(12), 830-839.

567 Dickson, A., and F. Millero (1987), A comparison of the equilibrium constants for the dissociation of  
568 carbonic acid in seawater media, *Deep Sea Res. (A Oceanogr. Res. Pap)*, 34(10), 1733-1743.

569 Dickson, A. G. (1990a), Thermodynamics of the dissociation of boric acid in synthetic seawater from  
570 273.15 to 318.15 K, *Deep Sea Res. (A Oceanogr. Res. Pap)*, 37(5), 755-766.

571 Dickson, A. G. (1990b), Standard potential of the reaction:  $\text{AgCl(s)} + 12\text{H}_2\text{(g)} = \text{Ag(s)} + \text{HCl(aq)}$ , and  
572 and the standard acidity constant of the ion  $\text{HSO}_4^-$  in synthetic sea water from 273.15 to 318.15 K,  
573 *The Journal of Chemical Thermodynamics*, 22(2), 113-127.

574 Dickson, A. G., C. L. Sabine, and J. R. Christian (2007), Guide to best practices for ocean CO<sub>2</sub>  
575 measurements, *PICES special publication*, 3.

576 Draper, N. R., and H. Smith (1998), *Applied Regression Analysis*, Hoboken, NJ: Wiley-Interscience,  
577 307-312.

578 Edmond, J. M. (1970), High precision determination of titration alkalinity and total carbon dioxide  
579 content of sea water by potentiometric titration, paper presented at Deep Sea Research and  
580 Oceanographic Abstracts, Elsevier.

581 Ericson, Y., A. Ulfso, S. van Heuven, G. Kattner, and L. G. Anderson (2014), Increasing carbon  
582 inventory of the intermediate layers of the Arctic Ocean, *Journal of Geophysical Research: Oceans*,  
583 119(4), 2312-2326.

584 Hofmann, G. E., et al. (2011), High-Frequency Dynamics of Ocean pH: A Multi-Ecosystem  
585 Comparison, *Plos One*, 6(12).

586 IPCC(2013), Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the  
587 Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-  
588 K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley(eds.)].  
589 Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

590 Lee, K., T.-W. Kim, R. H. Byrne, F. J. Millero, R. A. Feely, and Y.-M. Liu (2010), The universal ratio of  
591 boron to chlorinity for the North Pacific and North Atlantic oceans, *Geochim. Cosmochim. Acta*,  
592 74(6), 1801-1811.

593 Liu, X., M. C. Patsavas, and R. H. Byrne (2011), Purification and Characterization of meta-Cresol  
594 Purple for Spectrophotometric Seawater pH Measurements, *Environ. Sci. Technol.*, 4862–4868.

595 Martz, T. R., J. G. Connery, and K. S. Johnson (2010), Testing the Honeywell Durafet for seawater pH  
596 applications, *Limnol. Oceanogr. Methods*, 8, 172-184.

597 Mehrbach, C., C. H. Culberson, J. E. Hawley, and R. M. Pytkowicz (1973), Measurement of the  
598 apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol.*  
599 *Oceanogr.*, 897-907.

600 Miller, L. A., Macdonald, R. W., McLaughlin F., Mucci, A., Yamamoto-Kawai, M., Giesbrecht, K. E.,  
601 Williams, W. L. (2014). Changes in the marine carbonate system of the western Arctic: patterns in a  
602 rescued dataset. *Polar Research* 33, 20577, doi:10.3402/polar.v343.20577.

603 Millero, F. J., D. Pierrot, K. Lee, R. Wanninkhof, R. Feely, C. L. Sabine, R. M. Key, and T. Takahashi  
604 (2002), Dissociation constants for carbonic acid determined from field measurements, *Deep Sea Res.*  
605 *(I Oceanogr. Res. Pap.)*, 49(10), 1705-1723.

606 Newton, J.A., R. A. Feely, E. B. Jewett, P. Williamson and J. Mathis (2015), Global Ocean Acidification  
607 Observing Network: Requirements and Governance Plan. 2<sup>nd</sup> Edition, GOA-ON.

608 Papadimitriou, S., S. Loucaides, V. Rérolle, E. Achterberg, A. G. Dickson, M. Mowlem, H. Kennedy  
609 (submitted), The measurement of pH in saline and hypersaline media at sub-zero temperatures:  
610 Characterization of Tris buffers, *Mar. Chem.*

611 Pierrot, D., E. Lewis, and D. W. R. Wallace (2006), MS Excel Program Developed for CO<sub>2</sub> System  
612 Calculations. ORNL/CDIAC-105a. Carbon Dioxide Information Analysis Center, edited by U. S. D. o. E.  
613 Oak Ridge National Laboratory, Oak Ridge, Tennessee.

614 Rérolle, V. M. C., C. F. A. Floquet, M. C. Mowlem, D. P. Connelly, E. P. Achterberg, and R. R. G. J.  
615 Bellerby (2012), Seawater-pH measurements for ocean-acidification observations, *TrAC, Trends Anal.*  
616 *Chem.*, 40(0), 146-157.

617 Rérolle, V. M. C., C. F. A. Floquet, A. J. K. Harris, M. C. Mowlem, R. R. G. J. Bellerby, and E. P.  
618 Achterberg (2013), Development of a colorimetric microfluidic pH sensor for autonomous seawater  
619 measurements, *Anal. Chim. Acta*, 786(0), 124-131.

620 Roy, R. N., L. N. Roy, K. M. Vogel, C. Porter-Moore, T. Pearson, C. E. Good, F. J. Millero, and D. M.  
621 Campbell (1993), The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and  
622 temperatures 0 to 45 C, *Mar. Chem.*, 44(2), 249-267.

623 Sabine, C., R. M. Key, A. Kozyr, R. A. Feely, R. Wanninkhof, F. J. Millero, TH. Peng, J. L. Bullister, and  
624 K. Lee (2005), Global ocean data analysis project (GLODAP): results and data, ORNL/CDIAC-145,  
625 NDP-083. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory,  
626 U.S. Department of Energy, Oak Ridge, Tennessee, 110 pp.

627 Seiter, J., and M. DeGrandpre (2001), Redundant chemical sensors for calibration-impossible  
628 applications, *Talanta*, 54(1), 99-106.

629 Shitashima, K., M. Kyo, Y. Koike, and H. Henmi (2002), Development of in situ pH sensor using ISFET,  
630 IEEE.

631 Takeshita, Y., T. Martz, K. S. Johnson and A. G. Dickson (2014), Characterization of an Ion sensitive  
632 Field Effect Transistor and Chloride Ion Selective Electrodes for pH Measurements in Seawater,  
633 *Analytical Chemistry*, 86, 11189-11195.

634 Takeshita, Y., C. Frieder, T. Martz, J. Ballard, R. Feely, S. Kram, S. Nam, M. Navarro, N. Price, and J.  
635 Smith (2015), Including high frequency variability in coastal ocean acidification projections,  
636 *Biogeosci. Disc.*, 12(9).

637 Tanhua, T., E. P. Jones, E. Jeansson, S. Jutterström, W. M. Smethie, D. W. R. Wallace, and L. G.  
638 Anderson (2009), Ventilation of the Arctic Ocean: Mean ages and inventories of anthropogenic CO<sub>2</sub>  
639 and CFC-11, *Journal of Geophysical Research: Oceans*, *114*(C1), C01002.  
640 Yao, W., X. Liu, and R. H. Byrne (2007), Impurities in indicators used for spectrophotometric  
641 seawater pH measurements: Assessment and remedies, *Mar. Chem.*, *107*(2), 167-172.  
642 Tynan, E., J. S. Clarke, M. P. Humphreys, M. Ribas-Ribas, M. Esposito, V. M. C. **Rerolle**, S. Thorpe, T.  
643 Tyrrell, E. P. Achterberg (2016), Physical and biogeochemical controls on the variability in surface pH  
644 and calcium carbonate saturation states in the Atlantic sectors of the Arctic and Southern Oceans,  
645 *Deep-Sea Res. Part II*.

646

647 **Appendix**

648 **Appendix A: SeaFET instrument calibration coefficients from the manufacturer**

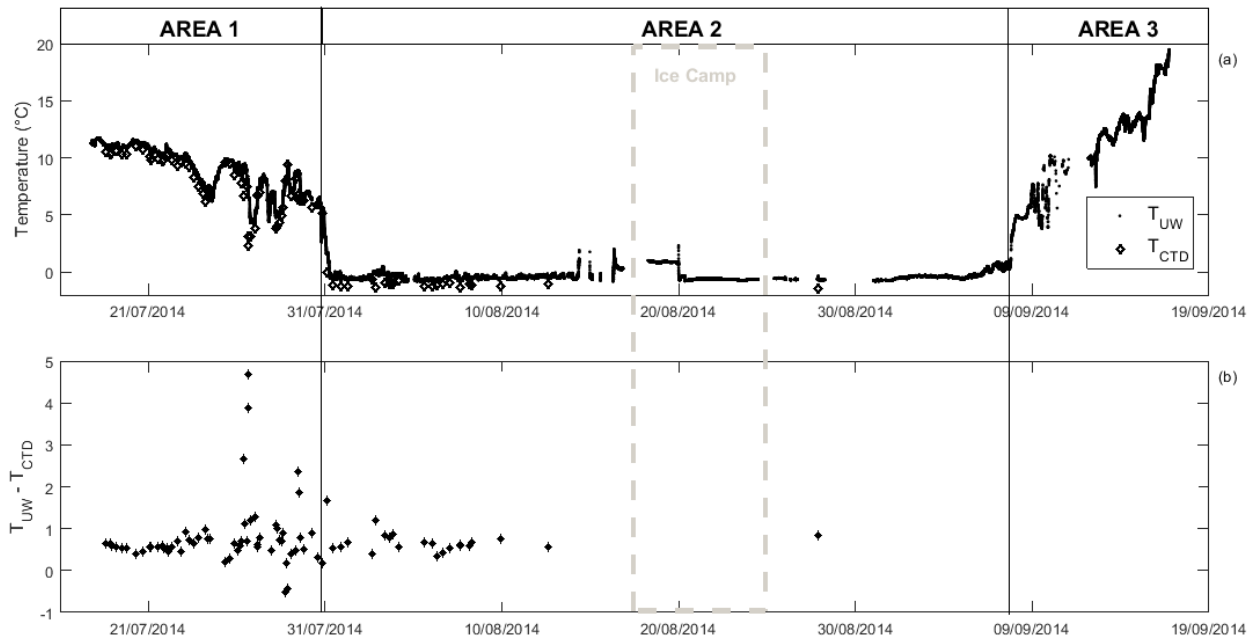
649

FILE-VERSION	3.0.0
APP-VERSION	SeaFETCom 1.1.2_149
INSTR-PACKAGE	SFET_0106_001.xml SeaFET0106 1.0 2014-01-08-0400 22489
TIME-STAMP	2014-07-14T21:33:03+0200
FW-VERSION	SeaFET v3.4.1
SERIAL-NUMBER	106
CAL_PHINT_OFFSET_COEFF	-6.13E-02
CAL_PHINT_SLOPE_COEFF	-1.10E-03
CAL_PHEXT_OFFSET_COEFF	-1.08E+00
CAL_PHEXT_SLOPE_COEFF	-1.05E-03

650

651 **Appendix B: Comparison of underway temperature ( $T_{UW}$ ) data with temperature data**  
652 **from surface CTD casts ( $T_{CTD}$ ).**

653 a)  $T_{UW}$  is shown in closed circles and  $T_{CTD}$  in open diamonds. b) Temperature residuals ( $T_{UW}-T_{CTD}$ ).  
654 Data corresponding to Area1 (ice-free outbound), Area2 (Arctic ice-covered), and Area3 (ice-free  
655 return) are delimited with the vertical solid lines and the ice camp with the vertical dotted lines.



656  
657

658 **Appendix C: Estimation of pH uncertainty in comparison between measured and**  
659 **calculated pH**

660 1. DIC/TA uncertainty:

- 661 ○ DIC/TA measurement accuracy:  $4 \mu\text{mol kg}^{-1}$
- 662 ○ Error due to sample handling and storage (average of standard deviation between
- 663 replicates values):  $3 \mu\text{mol kg}^{-1}$

664 ➤ Uncertainty in DIC/TA:  $\sqrt{4^2 + 3^2} = 5 \mu\text{mol kg}^{-1}$

665 **pH uncertainty due to uncertainty in DIC/TA = 0.021 pH unit.** pH uncertainty was estimated  
666 by computing pH with  $\text{DIC} \pm 5 \mu\text{mol kg}^{-1}$  and/or  $\text{TA} \pm 5 \mu\text{mol kg}^{-1}$  and calculating the standard  
667 deviation of the pH values obtained.

668 2. **pH uncertainty due to sample and sensor data mismatch = 0.001 pH unit.** Estimated from  
669 standard deviation of five minutes of pH measurement.

670 3. **pH colorimetric method uncertainty = 0.007 pH unit.**(see paragraph 3.4.2 for estimation  
671 details).

672 4. Temperature uncertainty:

- 673 ○ Uncertainty in temperature =  $0.04 \text{ }^\circ\text{C}$ .
- 674 ○ Seawater pH sensitivity to temperature =  $0.015 \text{ pH degC}^{-1}$ .

675 **pH uncertainty due to temperature uncertainty = 0.001 pH unit.**

676 5. **pH uncertainty due to uncertainty in thermodynamics constants = 0.035 pH unit.**  
677 Uncertainty estimated from standard deviation of pH values obtained using various  
678 combinations of thermodynamics constants (7 combinations).

679 ➔ **Overall pH uncertainty in calculated and colorimetric pH datasets comparison =**

680  $\sqrt{0.021^2 + 2 \times 0.001^2 + 0.007^2 + 0.035^2} = \underline{\underline{0.041 \text{ pH unit}}}$ .

681



**Appendix D: Results of the multi-linear regressions between pH dataset residuals and pH\_SeaFET, SSS and SST (all the parameters are standardised).**

RMSE is the Root Mean Squared Error.  $x_{pH}$ ,  $x_{SSS}$  and  $x_{SST}$  are the coefficients resulting from the correlation:  $pH\_residuals = x_{pH} \cdot pH\_SeaFET + x_{SSS} \cdot SSS + x_{SST} \cdot SST$ . The percentage columns indicate how much of the pH dataset residuals are explained by each parameter.

Sensors	Dataset	RMSE	$x_{pH}$	$x_{SSS}$	$x_{SST}$	fstat	% pH	% SSS	% SST
SeaFEText vs SeaFETint	All	0,47	0,14	-0,97	0,04	70801	6	40	2
	Area1	0,94	0,00	-0,05	-0,30	1060	0	13	78
	Area2	0,53	0,30	-0,84	-0,05	30517	14	38	2
	Area3	0,51	-0,02	-0,20	-0,74	7215	1	11	39
Colorimetric vs SeaFETint	All	0,66	0,30	1,21	-0,47	923	10	40	16
	Area1	0,90	0,59	-0,24	0,21	121	51	21	18
	Area2	0,78	0,00	0,89	0,18	146	0	64	13
	Area3	0,67	0,22	-0,17	-0,49	63	17	13	38
Colorimetric vs SeaFEText	All	0,64	0,37	1,15	-0,47	1000	12	37	15
	Area1	0,88	0,65	-0,23	0,21	141	53	19	17
	Area2	0,78	0,08	0,75	0,23	101	6	55	17
	Area3	0,68	0,20	-0,18	-0,51	62	16	14	39