



Report on product related to net community production and the biological carbon pump

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EXECUTIVE SUMMARY

Based on our findings in the subpolar North Atlantic, float-based pH measurements are currently not capable of systematically reaching a quality that yields observation-based surface ocean DIC data at the required accuracies of the “weather” ($\pm 10 \mu\text{mol kg}^{-1}$) or “climate” goals ($\pm 2 \mu\text{mol kg}^{-1}$) as defined by the ocean carbon community. While the situation in the study region may be more challenging than in other regions of the world ocean and therefore does not necessarily reflect the overall status of float-based pH measurements, this study highlights the crucial need to reduce float-pH uncertainties to derive DIC quantities. Indeed, dissolved inorganic carbon content estimates derived from float-based pH measurement can be considered as a pertinent approach to quantify the net amount of carbon removed from the atmosphere via the biological pump (Net Community Production; NCP). The results illustrate, however, the uncertainty and lack of objective criteria associated with the choice of the reference method for the delayed-mode pH correction (CANYON-B or LIR) as well the reference depth for this correction. This results in potentially significant but typically unknown uncertainty associated with the resulting accuracy of fully corrected delayed mode pH data.

Given a typical seasonal cycle of DIC of 5-20 $\mu\text{mol kg}^{-1}$ in the most of the surface ocean (Keppler et al., 2020), it is unclear how useful float-based DIC values at “weather goal” quality are. Currently, the achievement of more accurate DIC values from float pH is limited mostly though by the uncertainty of TA that is needed in calculation procedure. Even “climate goal” pH quality would therefore not yield “climate goal” DIC. The evidence provided here is, however, that float-based pH can have biases in excess of the “weather goal” accuracy of 0.01 in pH that would cause DIC to also miss “weather goal” quality. This points at the need of an additional reference point, ideally at the surface where the resulting DIC data are of highest importance for the quantification of net community production.

We argue that dedicated crossover analyses with carbon measurements by the “ship-of-opportunity” network (SOCONET/ICOS) could be employed in assessing and perhaps systematically correcting float-based pH measurements at the surface. Our regional focus and limited dataset limits the statistical significance of our findings but may nevertheless show a way forward. We propose that the scientific community explores this in a systematic way.

Clearly, float-based pH measurements provide wonderful perspectives and a completely new approach to carbon observations in the global ocean. As is typical for novel sensor technology and was also experienced for float-based oxygen observations, it is long way, however, from having a suitable sensor to delivering routine quality-assured data. The combination of BGC-Argo and ICOS, as explored further in the H2020 project GEORGE, holds great potential to i) enhance data quality and ii) reduce the bias in derived estimates of sea-air CO_2 fluxes (Denvil-Sommer et al., 2021).

Disclaimer:

This document represents the situation described in D4.7 which – at the time of data evaluation and writing of the report – was primarily based on data from 2021. We have updated the analysis with 2022 data. Unfortunately, all pH sensors of the 5 pH/O₂ floats deployed in 2021 are affected by the manufacturing problem that leads to deteriorated data quality and early sensor failure. This has both reduced the amount and compromised the quality of the data from the 5 floats. The results shown in D4.7, D4.8 and D4.9 are therefore based largely on 3 earlier pH/O₂ floats with much higher data quality.

However, as some pH floats and Ship-of-Opportunity line (SOOP) are still in operation more data are coming in and the database is growing daily. This will allow us to improve the statistics of our analyses and hence the robustness of the results. Therefore the results presented here are based on the *status quo* and are not necessarily the final word on these matters.

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1 Background

The formation of (particulate and dissolved) organic carbon from dissolved inorganic carbon by primary production in the ocean is a central element of the marine carbon cycle. Both as the basis of the marine foodweb and a significant sink for atmospheric CO₂, this organic carbon plays an important role in the Earth system. Global (climate) change will inevitably effect the magnitude and character of marine productivity. In order to indentify, quantify and eventually predict such changes, we need a global observatory that provides routine data a well-constrained quality.

Today, global marine primary production is estimated from satellite-based observation of ocean color or general circulation model with biological modules. In-situ data are too sparse for this purpose and therefore are used more for ground-truthing exercises. We currently lack a global observatory that is suitable for this. However, Biogeochemical Argo, a new component of the OneArgo program, holds great potential to meet the requirements and deliver the data necessary to routinely quantify (among other quantities) marine net primary production.

First attempts to quantify the net amount of carbon removed from the atmosphere via the biological pump, commonly referred as the net community production (NCP; *e.g.*, Laws, 1991), from Argo data focussed on float-based oxygen. While initial attempts were limited by the accuracy of the oxygen measurements, a major break-through in O₂ measurement methodology (*i.e.*, in-air calibration, Bittig and Körtzinger, 2015; 2017) made oxygen-based biological production estimates possible (*e.g.*, Bushinsky and Emerson, 2015). In a similar mass-balance approach, float-based nitrate data were used successfully to estimate NCP (*e.g.*, Plant et al., 2016, Baetge et al., 2020). Indeed, it is generally assumed that new production is associated almost exclusively with the uptake of nitrate derived from subsurface waters in the open ocean (Eppley and Peterson, 1979). The combination of these two approaches were very useful by revealing a dichotomy between oxygen- and nitrate-based productivity estimates that points at non-Redfieldian biological production and possibly other unknown factors. This highlighted the added value of independent NCP estimates from the suite of parameters offered by BGC Argo floats.

The use of float-based pH measurements to quantify NCP is still a relatively new variant of mass-balance type NCP estimation methods (*e.g.*, Briggs et al., 2018). It would provide the most direct observation-based approach to estimate carbon NCP. For this purpose, float-based pH measurements would need to be combined with estimates of total alkalinity in order to calculate the dissolved inorganic carbon content as the quantity of interest. So far, this approach has been hampered by the relative small number of BGC Argo floats with pH sensors (except for the Southern Ocean) and the not well constrained accuracy of float-based pH observations in the upper ocean.

1.1 Chemistry of the Marine Carbon Dioxide System

A series of chemical equilibria govern the dissolution of CO₂ in water and its reaction with water. This gives rises to a suite of different chemical species, which are connected through the corresponding equilibrium reactions; these are: CO₂ in aquatic solution, carbonic acid, bicarbonate and carbonate ions (*i.e.*, CO₂(aq), H₂CO₃, HCO₃⁻, CO₃²⁻). Unfortunately, the concentrations of these individual species of the carbon dioxide system in solution can not be measured directly. There are, however, four parameters that can be measured at high accuracy. These are used, together with ancillary information, to obtain a complete description of the CO₂ system in seawater (Dickson et al., 2007).

These four measurable parameters are:

- Total dissolved inorganic carbon (DIC)
- Total alkalinity (TA)
- Fugacity/partial pressure of CO₂ in gas phase in chemical equilibrium with seawater ($f\text{CO}_2/p\text{CO}_2$)
- Total hydrogen ion concentration (pH)

It is possible, in theory, to obtain a complete description of the marine CO₂ system in a sample of sea water at a particular temperature and pressure provided that the following information is known (Dickson et al., 2007):

- Solubility constant for CO₂ in sea water (K_0),
- Equilibrium constants for each of the acid-base pairs that are assumed to exist in the solution,
- Total concentrations of all the non-CO₂ acid-base pairs,
- Values of at least two of the four CO₂-related parameters: DIC, TA, $f/p\text{CO}_2$, pH

For a mass-balance approach to estimated NCP, DIC would be quantity of choice as it will reflect the net exchange of inorganic carbon inputs and outputs to/from the biological community. In order to assess rates of NCP, changes in biological reactants and products (*i.e.*, DIC) from two consecutive measurements or during seasonal sections can be exploited in combination with a correction from additional changes associated with the net ecosystem calcification or air-sea CO₂ fluxes (Borges et al., 2008; Mathis et al., 2010). Also, because the mixed layer depth constitutes one of the major factors controlling ocean primary production, calculations have to be done considering this parameter. If DIC cannot be measured directly, which due to limitations in sensor technology currently is the case for BGC-Argo floats, two other of the four measurement parameters of the marine CO₂ system are required for its calculation. Therefore, float-based pH – the only marine CO₂ system parameter currently measurable operationally from floats – needs to be combined with a second parameter. In the present absence of suitable sensors for $p\text{CO}_2$, DIC or TA, a reasonable work-around is to predict TA using algorithms that employ variables such as T, S, pressure (P), and O₂, which are measured on floats. One such option for this alkalinity estimation is LIAR (Locally Interpolated Alkalinity Regression; Carter et al., 2016), which uses data from the Global Ocean Data Analysis Project (GLODAPv2) data set (Olsen et al., 2016). In a regional context, simple TA vs. salinity regressions can often be employed with good success (*e.g.*, Takahashi et al., 2014). Generally, such TA predictions have a typical overall uncertainty on the order of 6 $\mu\text{mol kg}^{-1}$ (*e.g.*, Williams et al., 2017). As the data coverage of the GLODAPv2 data product is far from perfect, both in terms of spatial and annual variability (seasonal cycle), the robustness of TA algorithms based on it (or other data products) is globally not uniform. Regional and/or seasonal biases are therefore to be expected which have the potential to compromise the accuracy of DIC calculated from measured pH and predicted TA.

1.2 Quality Requirements for DIC

In order to be most widely useful, float pH-based $f\text{CO}_2$ data therefore would have to reach an accuracy of $\pm 5 \mu\text{atm}$ or better. Indeed, to be included in the “Surface Ocean CO₂ Atlas” (SOCAT), the publicly available synthesis product for quality-controlled surface ocean $f\text{CO}_2$ measurements, data have to reach the minimum accuracy requirements defined by three levels of accuracy: $\pm 2 \mu\text{atm}$ (flags A and B), $\pm 5 \mu\text{atm}$ (flags C and D), and $\pm 10 \mu\text{atm}$ (flag E). It is unlikely, that calculated $f\text{CO}_2$ data not having a demonstrable accuracy of $\pm 5 \mu\text{atm}$ may get included in the main SOCAT synthesis product at all. It is also noteworthy that the highest quality flag A is only assigned to data with an estimated accuracy of $\pm 2 \mu\text{atm}$ which is further corroborated by the existence of a high-quality crossover with another data set (flagged A or B).

The definition of the essential ocean variables (EOV) by the Global Ocean Observing System (GOOS) and the two-tier quality approach taken by the Global Ocean Acidification Observing network (GOA-ON) (Newton et al., 2015) state the following “weather” and “climate” goals:

The “**weather goal**” is defined as measurements of a quality sufficient to identify relative spatial patterns and short-term variations and support the understanding of mechanistic responses to and

impact on local, immediate ocean acidification dynamics. This implies an uncertainty of: $\text{pH} \pm 0.02$, $\text{TA/DIC} \pm 10 \mu\text{mol kg}^{-1}$ and $f\text{CO}_2 \pm 2.5\%$ ($= 10 \mu\text{atm}$ at $400 \mu\text{atm}$).

The “**climate goal**” is defined as measurements of a quality sufficient to assess long-term trends with a defined level of confidence and support detection of the long-term anthropogenically driven changes in hydrographic conditions and carbon chemistry over multi-decadal time scales. This implies an uncertainty of: $\text{pH} \pm 0.003$, $\text{TA/DIC} \pm 2 \mu\text{mol kg}^{-1}$ and $f\text{CO}_2 \pm 0.5\%$ ($= 2 \mu\text{atm}$ at $400 \mu\text{atm}$).

1.3 Uncertainties of Calculations in the Marine CO₂ System

When marine CO₂ system variables are used to calculate others, errors both from the input parameters as well as from the thermodynamic constants used are propagated. This has been explored by Orr et al. (2018) and applied to specific ICOS cases (Steinhoff, 2020). The case relevant for BGC-Argo in the context of NCP is the combination of pH (measured directly by floats) and TA (predicted via specific algorithms) to calculate DIC (Fig. 1). The calculation based on the protocol developed by Orr et al. (2018) includes a formal error propagation of the errors of the input parameters and of all thermodynamic constants applied in calculations. As such it is a conservative error estimate.

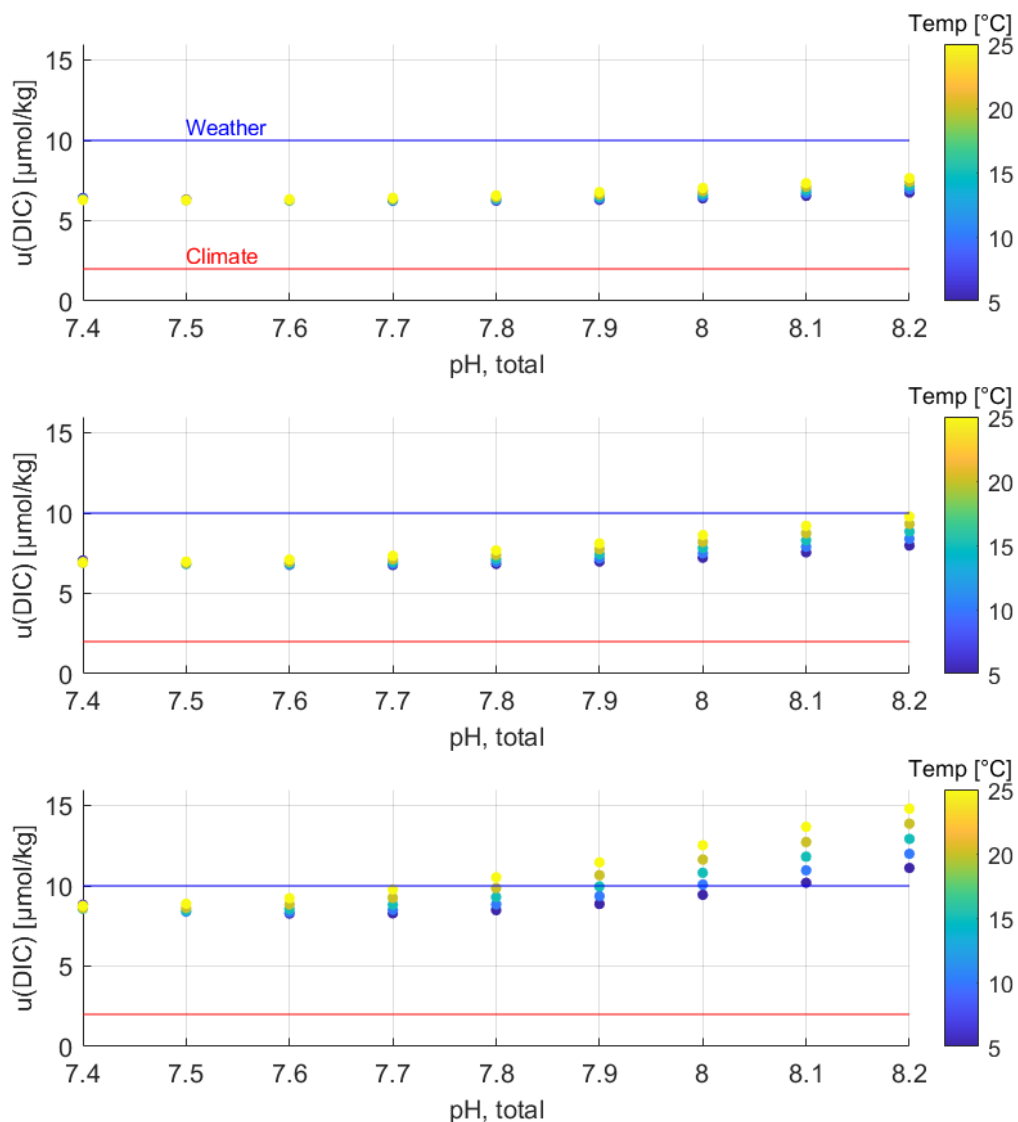


Fig. 1: Resulting uncertainty in DIC ($u(\text{DIC})$, y-axis) vs. pH (x-axis) when using pH and TA as input parameters. The calculations were made using $u(\text{pH}) = 0.003$ (top panel), 0.01 (middle panel) and 0.02 (bottom panel). All calculation were made for $u(\text{TA}) = 6 \mu\text{mol kg}^{-1}$. The results are shown at five different temperatures (color-coded). The calculation scheme propagates both the uncertainties of the input parameters as well as the uncertainties of the thermodynamic constants applied in the calculations.

According to this, DIC can be calculated with an uncertainty of 6-7.5 $\mu\text{mol kg}^{-1}$ when using pH and TA as input with uncertainties of $u(\text{pH}) = 0.003$ pH units (“climate goal”) and $u(\text{TA}) = 6 \mu\text{mol kg}^{-1}$. This overall uncertainty is in fact dominated by the contribution of $u(\text{TA})$ which at present prevents the achievement of the “climate goal” DIC independent of the quality of pH (Fig. 1., top panel). The additional DIC uncertainty incurred for $u(\text{pH}) = 0.003$ pH units is relatively small at 1-2 $\mu\text{mol kg}^{-1}$. If float pH can routinely be constrained to $u(\text{pH}) = 0.01$ pH units, the resulting calculated DIC (middle panel) would under all typical conditions meet the “weather goal”. In contrast, for $u(\text{pH}) = 0.02$ pH units, the “weather goal” for DIC can only be systematically met at low pH (i.e., high $f\text{CO}_2$) encountered in low oxygen waters in the interior ocean. Elsewhere, it would exceed it by up to 5 $\mu\text{mol kg}^{-1}$. We note that the “weather goal” uncertainty in DIC of 10 $\mu\text{mol kg}^{-1}$ is about the same magnitude as the seasonal DIC cycle in most of the surface ocean, which ranges between 5 and 20 $\mu\text{mol kg}^{-1}$ with a median value of 14 $\mu\text{mol kg}^{-1}$ (Keppler et al., 2020). This comparison reveals that the spring-to-fall NCP, which is mostly responsible for the observed seasonal DIC cycle, can likely not be estimated at better or even the same quality from float pH than is currently possible from float O_2 .

Thus, the currently achievable uncertainty in predicted TA of about 6 $\mu\text{mol kg}^{-1}$ (Bittig et al., 2018; Carter et al., 2018), which corresponds to an uncertainty in DIC of about 6 $\mu\text{mol kg}^{-1}$, represents a major obstacle to higher accuracy of calculated DIC. Additionally, it should be noted that regional/seasonal biases in estimated TA may occur and that during times and in regions of high surface concentrations of phosphate and silicate, a small additional uncertainty in TA arises from the fact that these nutrient concentrations cannot be measured by floats. Another potential complication is the existence of uncharacterizable organic alkalinity in coastal waters or during phytoplankton bloom situations which can render TA a somewhat ill-defined property (Kerr et al., 2021). So clearly, TA is a somewhat problematic variable in the context of DIC calculation from float pH. In contrast to the situation found for calculating $f\text{CO}_2$ from float pH, the calculation of DIC is more forgiving with respect to $u(\text{pH})$.

1.4 Comparison between SOOP-based and Float-based Surface Carbon Observations

The global Ship-of-Opportunity network (SOOP) is operated in the European Research ICOS (see above) and the ‘Surface Ocean CO_2 Reference Observing Network’ (SOCONET). **SOCONET** is a volunteer group of established operators who provide quality global surface ocean CO_2 data. Participants perform automated measurements of surface water and atmospheric CO_2 from Ships-of-Opportunity and moorings.

The data from these networks are submitted routinely and according to specific requirements to the SOCAT, where they undergo defined quality control measures. SOCAT is a synthesis activity for quality-controlled, surface ocean $f\text{CO}_2$ observations by the international marine carbon research community (>100 contributors). The data are publicly available, discoverable and citable. The SOOP network and the SOCAT data product are relevant for BGC-Argo in two ways:

- (1) BGC Argo float-based pH observations can be converted to $f\text{CO}_2$ and potentially be submitted to the SOCAT data-base. This, however, requires better understanding of the quality of pH-based surface $f\text{CO}_2$ observations by the Argo observation network as discussed above.

- (2) The SOOP network and the SOCAT database represent a data repository that can actively be employed in the quality assessment and to some extent also in the routine quality control of Argo float-based pH. This is an idea we are specifically exploring in Euro-Argo RISE.

For this purpose, SOCONET/ICOS, which typically only features routine $p\text{CO}_2/f\text{CO}_2$ observations, need to be augmented and harnessed for BGC-Argo. The addition of TA as a second analytical variable of the marine CO_2 system to the suite of autonomous SOOP observations has been demonstrated to be methodologically feasible now (Seelmann et al., 2019; 2020a; 2020b). We have therefore added TA to the measurement portfolio of our existing North Atlantic SOOP line (ICOS station DE-SOOP-Atlantic Sail) in 2019 using the Contros HydroFIA™ TA system (-4H-JENA engineering GmbH, Jena, Germany). This serves two purposes in the context of BGC-Argo:

- (1) From high-quality co-located and synchronous SOOP-based $f\text{CO}_2$ and TA observations, pH can be calculated at relatively high quality to serve as a direct comparison for BGC-Argo floats.
- (2) SOOP-based routine TA observations allow for improved parameterizations of (surface) TA which can be employed in the conversion of float pH into $f\text{CO}_2$, which is required for integration into the SOCAT database. Such improved TA parameterizations may help to reduce regional and/or seasonal biases present in surface TA algorithms.

As a further augmentation of the existing North Atlantic SOOP, we have implemented autonomous pH measurements using the Contros HydroFIA™ pH system (-4H-JENA engineering GmbH, Jena, Germany) with similar spectrophotometric technology in 2021. With these, a direct comparison with the BGC-Argo float network is possible, which potentially allows for a direct and uncompromised quality assessment.

In order to compare SOOP-based and float-based surface carbon observations, we searched for direct crossovers between float surfacings and SOOP passages. SOCAT has defined a crossover by the following criterion x that combines distance d (in km) and time t (in d), where one day of separation in time is heuristically equivalent to 30 km of separation in space. In SOCAT, the value used for x is 80 km:

$$\sqrt{(\Delta d)^2 + (30 \cdot \Delta t)^2} \leq x \text{ km}$$

2 Results

2.1 North Atlantic pH Float Pilot Study

Through great synergy with the operational German Argo Programme as well as several nationally funded research projects (OA-TWS-IOC, DArgo2025, C-SCOPE), we were able to start in 2018 and carry out beyond today a pilot study for float-based carbon observations in the subpolar North Atlantic and their synergistic coupling with an existing SOOP line. A total of 10 pH/O₂ floats from two manufacturers have been purchased and deployed as part of the pilot study so far (Table 1, Fig. 2). Further floats will be deployed in 2023.

Table 1: BGC-Argo floats with pH and O₂ sensors deployed in the Labrador Sea and subpolar North Atlantic as part of a pilot study for float-based carbon observations.

WMO	Float Type	Depl. Time	Depl. Area	Status*
3901667	Apex/Webb	June 2018	Labrador Sea	Inactive, 38 cycles, faulty pressure sensor → warranty replacement 7900566
3901668	Apex/Webb	June 2018	Labrador Sea	Inactive, 182 cycles
3901669	Apex/Webb	June 2018	Labrador Sea	Inactive, 179 cycles
7900566	Apex/Webb	August 2020	Labrador Sea	Inactive, 107 cycles, faulty GPS system
6904110	Provor/nke	July 2021	Subpolar N.A.	Active, 82 cycles, pH sensor failure after few profiles
6904111	Provor/nke	July 2021	Subpolar N.A.	Active, 101 cycles, pH sensor failure after few profiles
6904112	Provor/nke	July 2021	Subpolar N.A.	Active, 81 cycles Compromised pH sensor quality
6904114	Provor/nke	August 2021	Labrador Sea	Active 69 cycles Compromised pH sensor quality
6904115**	Provor/nke	August 2021	Labrador Sea	Inactive, 63 cycles, pH sensor failure after few profiles
6904231	Provor/nke	October 2022	Labrador Sea	Active, 26 cycles pH quality not yet assessed

*As of Dec. 13, 2022.

** Float recovery in August, 2022.

Unfortunately, the 10 floats suffered from an unusually high number of manufacturer-related technical issues or failures either of the pressure sensor (3901167, warranty replacement by 7900566), the GPS system (7900566), or the pH sensor itself (6904110, 6904111, 6904112, 6904114, 6904115). The latter was related to a problem with the reference electrode which was reported to have occurred over the serial number range 10000 to 11117 (Communication Ken Johnson, AST-23 meeting, April 2022) and caused the affected pH sensors to deliver reduced data quality and in many cases show early sensor failure. This has severely compromised both the quality and the amount of pH data. In the end, only a little more than half of the floats are at all useful towards the goals of the pilot study.

We note the observation that in our analyses the two long-lasting floats deployed in 2018 (3901668 + 3901669) showed the best results, and are thus assumed to represent the optimum case for achievable performance of this current technology. Floats deployed in 2021 (690411x) with the later reported

manufacturing issues show significantly less promising results in almost all characteristics. It has to be seen how the manufacturing quality will develop in the future.

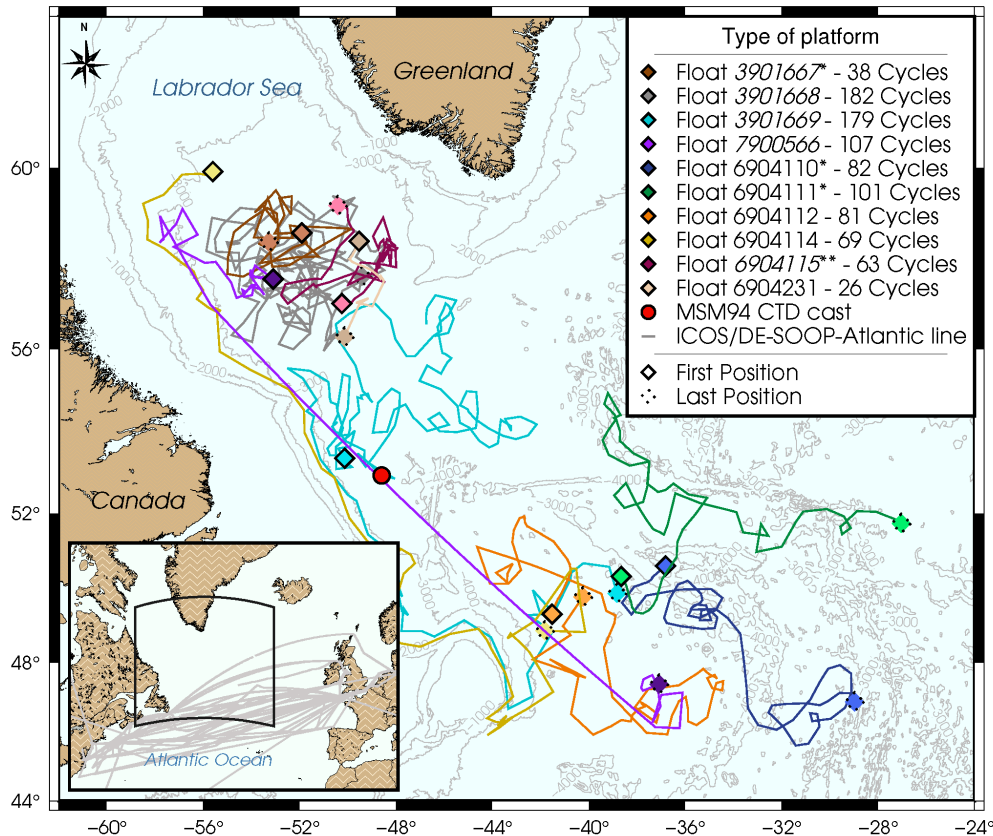


Fig. 2: Map of the Northwest Atlantic with Labrador Sea and North Atlantic Current showing the trajectories of all 10 pH/O₂ floats deployed so far in our pilot study. In the legend, floats in italic are inactive. * Float with a faulty pressure and/or pH sensor. ** Float recovered. Dotted points show the last locations as of December 13th, 2022.

On all floats, the standard delayed-mode cookbook procedures for pH (pump-offset correction, CANYON-B reference, segment method, 1500 dbar reference level, 0.005 pH units mCP dye offset correction, temperature correction) were applied according to Johnson et al. (2017). A more detailed description of these correction procedures is provided in Euro-Argo RISE deliverable 4.7.

We note that the two reference methods CANYON-B vs. LIR yielded corrected pH values that differed by about 0.02 pH units. The choice of the reference method, therefore, incurs a huge uncertainty much above the desired accuracy level. Also, the choice of the reference depth (*e.g.*, 1500 vs. 1900 dbar) contributed about 0.01 to the uncertainty of pH. As no objective criteria exist to guide the choice of both reference method and depth, the resulting uncertainty is on the order of a few hundred of a pH unit which is far in excess of tolerable levels. This may be a peculiarity of the subpolar North Atlantic with its complex water masses, deep convection, and deep penetration of anthropogenic CO₂. It points, however, at a critical shortcoming of the current delayed-mode quality control which requires an additional control mechanism, ideally at the surface, for independent assessment and possibly also the correction of float-pH data.

2.2 SOOP-based pH Observations

On the SOOP-Atlantic line, pH was measured at 15 min intervals using the Contros HydroFIA™ pH system in unattended mode. The continuous flow of uncontaminated and bubble-free seawater was provided via a cross-flow filter to avoid particle contamination of the optical path. Before and after each 5-week roundtrip (2 trans-Atlantic crossings each) the instrument was calibrated in port against fresh CRM (Certified Reference Material) provided by the Dickson Lab (batch 190, accuracy ± 0.0014 pH units).

Each system calibration typically has about 8 (5-10) repeat pH measurements on a single, freshly opened CRM bottle. These pre- and post-calibration runs are pretty stable for each meta-cresol purple (mCP) indicator bag which lasts for 4 roundtrips (Fig. 3). Some variability between mCP batches and even bags of the same batch is evident. Therefore an individual pH correction is applied to each mCP bag based on the error-weighted mean of the 5 calibration runs bracketing 4 roundtrips of the vessel. The standard error of this weighted mean is typically < 0.002 pH units. The overall accuracy of SOOP-pH is estimated to be ± 0.003 pH units. There is an indication of a temporal drift of the pH measurements which do not show in the individual mCP bag calibration. It is currently unclear whether this is due to some deterioration in the system's optical path or aging within the stored mCP indicator bags.

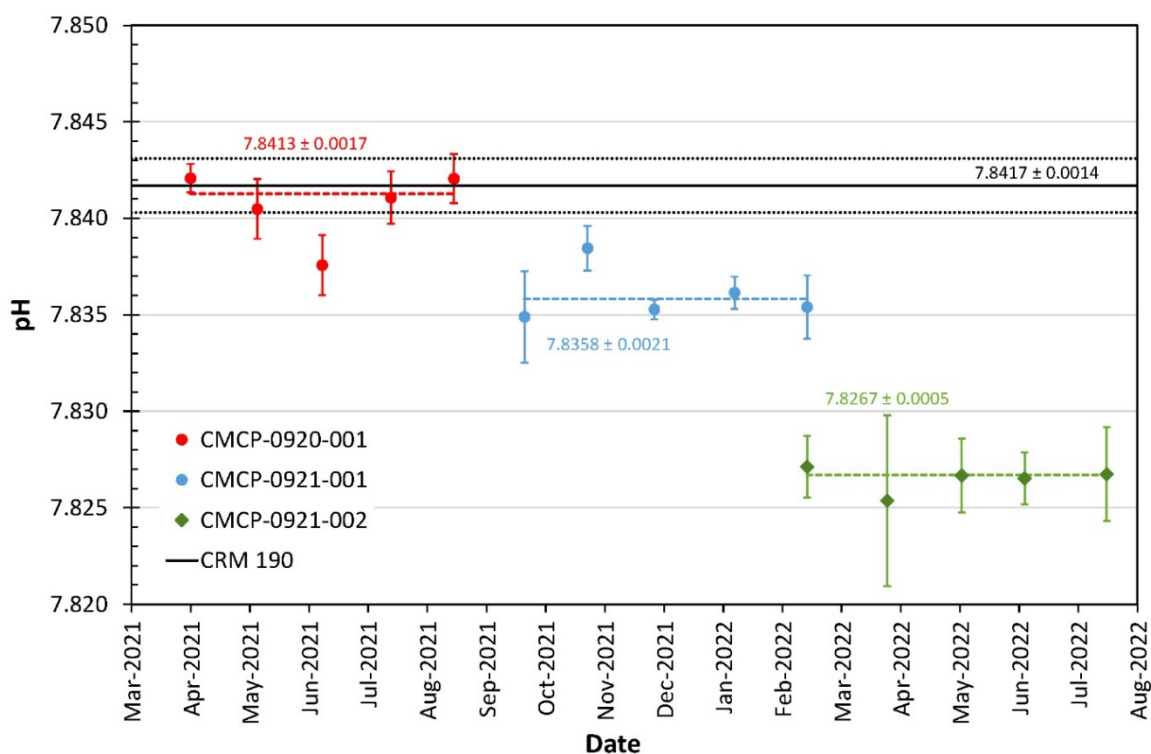


Fig. 3: pH measurements performed on CRM batch 190 with the Contros HydroFIA™ pH system before and after each 5-week roundtrip of our Ship-of-Opportunity M/V Atlantic Sail. Four consecutive roundtrips are always carried out with one reagent bag of the mCP indicator (CMCP-mmyy of batch preparation-number of bag). Adjustments of measured pH to the nominal pH value assigned to the CRM (7.8417 ± 0.0014 at 25°C) are based on the error-weighted mean of all CRM measurements carried out per individual mCP bag (typically at 5 different times with 5-10 repeat measurements each, values shown in plot).

2.3 SOOP-Float pH Crossover Analysis

We have adopted the SOCAT crossover criterion which tries to optimize between spatial and temporal mismatch to search for SOOP-float crossovers. We have explored a larger range in x (80-400 km) and we have also experimented with additional crossover criteria such as maximum offset in temperature and/or salinity. Given the limitations of our dataset (mostly due to massive manufacturing problems of the 2020/1 pH sensor series) no robust recommendations can be drawn from these experiments. To operationalize this approach, regional refinements and most likely additional crossover criteria (*e.g.*, max. temperature difference) and procedures (*e.g.*, correction of SOOP pH to the temperature of the float pH) will have to be developed by further studies.

SOOP data falling into a given SOCAT-like crossover criterion for a given float surfacing were extracted and averaged. Likewise, the mixed layer pH data (typically upper 15 m) of a float surfacing were extracted and averaged. Standard deviations of these averages give an indication of the coherence of the extracted data portions and hence their statistical weight.

For 2021 and the major part of 2022, we achieved several crossovers between surfacings of three pH/O₂ floats (WMO 3901669, WMO 6904111, WMO 6904112) and our SOOP line in the subpolar North Atlantic. All of these are in the western subpolar North Atlantic where the coincidence of Atlantic waters of southern provenience and Labrador Sea waters of polar origin complicate the crossover analysis.

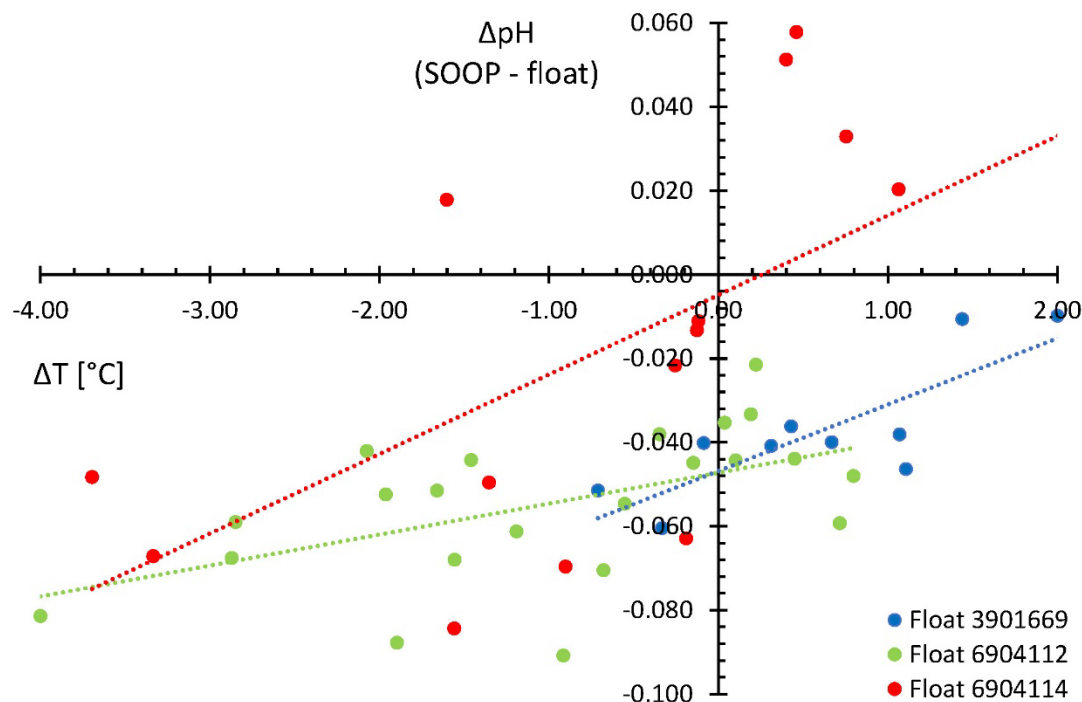


Fig. 4: Offset between SOOP pH and fully corrected float pH (y-axis) as a function of temperature difference (x-axis) for crossovers ($x = 400$ km, $\Delta T = 4^\circ\text{C}$) of three different floats.

In order to yield a larger number of crossovers we applied a rather large search window of $x = 400$ km. The resulting list of crossovers was reduced by the addition requirement $-4.0 < \Delta T < 4.0$ which excluded a few data points. For each crossover, the SOOP-pH was corrected from SOOP-T to float-T using SOOP-TA. We assume that the remaining differences in pH are not driven by differences in T but represent a bias in SOOP-pH and possibly a contribution from different water mass properties represented in the SOOP and float data. We then plotted ΔpH (SOOP – float) as a function of ΔT (Fig. 6). The ΔpH at $\Delta T = 0$ should then represent the pH offset between SOOP and float. By fitting a linear regression to the

data, the pH offset can be estimated more robustly. We think this regression using crossovers achieved with a relatively wide search window yields a more robust ΔpH estimate as an average of a small number of crossovers found with a smaller search window. Another option would be to apply a temperature correction of the SOOP pH data to the float T at each crossover. Clearly, the method of choice for the detection and evaluation of SOOP-float crossovers needs to be explored more in-depth with a larger dataset of floats from different regions.

The results of our analysis (Table 4) show for two of the three floats (3901669 and 6904112) a relative good linear relationship between ΔpH and ΔT , which allows the estimation of the pH offset at $\Delta T = 0$ with a reasonably small error. Interestingly, the resulting ΔpH is almost identical for the two floats. For the third float (6904114), more scatter leads to a less well-constrained pH offset which in fact is indistinguishable from $\Delta\text{pH} = 0$. The mean ΔT of the crossovers is within $\pm 1^\circ\text{C}$ for each float. The corresponding ΔS of these crossovers is on the order ± 0.5 . Calculating the pH offset as a function of ΔS yields ΔpH values which are statistically indistinguishable from the ones based on ΔT (but have slightly larger uncertainty). This indicates that the water mass correction achieved through the regression approach is generally effective.

Table 4: Statistics of the crossover analysis for SOOP and float pH data.

Float	$\Delta\text{pH at } \Delta T=0$		ΔT		ΔS	
	mean	std dev	mean	std dev	mean	std dev
3901669	-0.047	0.004	0.87	1.00	0.41	0.50
6904112	-0.047	0.004	-0.98	1.29	-0.40	0.58
6904114	-0.005	0.010	-0.56	1.57	-0.56	1.57

3 Conclusions & Recommendations

Although the results only represent a limited number of floats, few crossovers and a relatively small regional domain, three conclusions can already be drawn:

- (1) Results found for each float are rather similar and indicate that float pH may be biased by up to several hundredths of a pH unit at the surface. In fact, two of the three floats show a virtually identical offset of -0.047 ± 0.004 pH units, i.e. the float-pH is systematically higher on average by this amount when compared to SOOP-pH. Such a bias in pH would correspond to a (T- and pH-dependant) DIC bias on the order of -20 to $-30 \mu\text{mol kg}^{-1}$. When such DIC uncertainties are considered, the resulting NCP changes vary between 2 and 3 % of the initial NCP value. In addition, besides the float-pH uncertainty, the error propagation, as well as the uncertainties related to the assumptions made to derive NCP rates (*i.e.*, calculated air-sea CO_2 fluxes, net ecosystem calcification estimates), have to be considered as potential sources of error.
- (2) The accuracy of DIC calculated from float-based pH observations is currently limited by the necessity to employ a parameterization for TA as the other needed marine CO_2 system variable. The associated uncertainty in predicted TA of about $6 \mu\text{mol kg}^{-1}$ translates into an uncertainty in DIC of about the same magnitude. The “climate goal” for DIC of $2 \mu\text{mol kg}^{-1}$ therefore cannot be met regardless of the quality of the pH observations. With an overall uncertainty of 0.01 in pH the resulting DIC would systematically conform to the “weather goal” in for DIC of $10 \mu\text{mol kg}^{-1}$. It remains questionable though, how well NCP can be estimated from DIC at an uncertainty that is of similar magnitude as the entire seasonal cycle of surface DIC in most of ocean.
- (3) With larger amounts of SOOP-float crossover data and optimized crossover criteria, an independent quality control and perhaps even correction of float surface pH can be achieved in areas of good SOOP coverage. SOOP could thus be implemented in the DMQC routine for float pH. Algorithms synchronizing float profiling routines with SOOP line schedules and projected crossings may even be employed to actively chase crossovers in a systematic way.

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