Uncertainty analysis for calculations of the marine carbonate system for ICOS-Oceans stations

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Motivation

Marine stations of the European infrastructure Integrated Carbon Observation System (ICOS) deliver high quality data to the Carbon Portal (CP). To ensure that every station fulfills the quality requirements of ICOS, they undergo a two-step labelling process. In the first step the station is evaluated on whether or not they can provide high quality data according to ICOS standards. In the second step the station must prove this by sending data and metadata to the Ocean Thematic Centre (OTC) showing that they measure data with the desired quality. The labelling scheme of ICOS-Oceans, as agreed during the Monitoring Station Assembly (MSA) meeting in Southampton in 2019, defines two goals with respect to the marine carbon cycle:

- Quantifying air-sea CO_2 fluxes
- Assessing the variability and drivers of these fluxes

Limitations of ocean fCO_2 measurement capabilities at Fixed Ocean Stations (FOS) mean that fluxes cannot be determined to the accuracy desired for large scale carbon budgets. Meanwhile, it is most common that Ship of Opportunity (SOOP lines) measure fCO_2 rather than other carbon system variables. Details about the labelling procedure can be found in the labelling document for ICOS marine stations, which is located on the OTC's website: https://otc.icos-cp.eu/. Stations are labelled as "Class 1" or "Class 2" (Table 1). Please note that there is no difference in quality between the two classes. A Class 1 station measures more variables than a Class 2 station.

Table 1: Measurement requirements for ICOS marine stations.

	Ship of Opportunity (SOOP) lines	**Fixed Ocean Station (FOS)**
Class 2 (minimum required variables)	fCO_2 (±2 µatm)	fCO_2 (±10 µatm) Alkalinity (TA) or Dissolved Inorganic Carbon (DIC) Oxygen
Class 1 (additional variables)	TA or DIC Oxygen	Surface: Nutrients (nitrate, silicate and phosphate)

For fCO_2 measurements onboard SOOP lines, the accuracy requirement for fCO_2 is ±2 µatm. If stations apply to be labelled as a Class 1 station, they need to provide one additional carbon variable (DIC or TA) and dissolved oxygen.

For FOS, the minimum requirement (Class 2) is that they measure fCO_2 with an accuracy of ±10 µatm and at least one additional variable of the carbonate system (DIC or TA) and dissolved oxygen.

This leads to two vital questions for the ICOS -Oceans stations:

A - How accurately should the second carbon variable be measured on SOOP lines and at FOS?

B - Can fCO_2 be calculated with a sufficient uncertainty by two other carbon parameters?

Knowing two of the four carbonate system variables ($f CO_2$, DIC, TA, pH) facilitates calculation of the whole marine carbonate system. As will be shown later, the variable pH is not recommended to be the variable accompanying $f CO_2$, as the resulting uncertainty from the error propagation is too high. It is still important for FOS to measure pH, since it is vital for validating the $f CO_2$ data. This document presents the calculations for the whole carbonate system, including the error propagation coming from the variables themselves and from the constants used.

To estimate a meaningful accuracy for the measurement of a second carbon variable it was decided to follow the Global Ocean Observing System (GOOS) essential ocean variables (EOV's) and the Global Ocean Acidification Observing network (GOA-ON) approach of "weather" and "climate goals" for uncertainty calculation (Newton et al. 2014):

The "weather goal" is defined as measurements of quality sufficient to identify

- relative spatial patterns and short-term variations
- supporting mechanistic responses to and impact on local, immediate ocean acidification dynamics
- This implies an uncertainty of:

pH	~0.02
TA, DIC	~10 µmol/kg
$f CO_2$	~2.5% relative uncertainty

The "climate goal" is defined as measurements of quality sufficient to

- assess long-term trends with a defined level of confidence
- 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:

pH	~0.003
TA, DIC	~2 µmol/kg
$f CO_2$	~0.5% relative uncertainty

According to the questions above, this document is divided in two sections:

A – This part investigates the sensitivity of one of the three calculated carbon parameters (DIC, TA and pH) based on the input variables ($f CO_2$ and DIC, TA, or pH). This is done separately for SOOP lines and FOS, as the quality requirements for these two station types are different.

B – This part investigates the resulting uncertainty of $f CO_2$ by using different pairs of input variables, which is important for validation of $f CO_2$ measurements at FOS.

All calculations were performed using the Matlab versions of CO2sys (van Heuven et al. 2009; Lewis and Wallace 1998; Orr et al. 2018) and the accompanied error calculations provided by Orr et al. (2015). The uncertainty of a variable is noted as u(variable name).

Please note: When using the Matlab version of the error propagation (errors.mat), be sure to update the file co2sys.mat provided by Orr et al. (2018), as there are minor changes compared to the version of van Heuven et al. (2009).

A – How accurately should the second carbon variable be measured on SOOP lines and at FOS?

The calculations in this section were done for different *f*CO_2 values between 250 and 700 µatm and for different temperatures between 5 and 25°C. TA and pH was calculated for each *f*CO_2 using a DIC value of 1950 µmol/kg at 15°C. This should ensure a comparable carbonate system for further calculations.

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*f*CO2 = [250, 300, 350, 400, 450, 500, 550, 600, 700] µatm
DIC = 1950 µmol/kg
Temperature = [5, 10, 15, 20, 25] °C
Salinity = 35; in pressure = out pressure = 5 dbar; SI = 0; PO4 = 0;
pH scale: total scale
K1K2 constants: (Lueker et al., 2000)
KSO4 constants: (Dickson, 1990)
TB (total boron): (Uppström, 1974)

Uncertainties in constants:
u(pK0) = 0.002
u(pK1) = 0.0055
u(pK2) = 0.01
u(pKb) = 0.01
u(pKw) = 0.01
u(pKspa) = 0.02
u(pKspc) = 0.02
u(Boron) = 0.02

Uncertainties in variables:
Salinity: u(S) = 0.1
Temperature: u(T) = 0.05

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SOOP lines

ICOS SOOP lines measure sea surface fCO_2 with an uncertainty of 2 µatm (u(fCO_2) = 2 µatm). For the other 3 variables, standard uncertainties were used that can be reached by well-equipped marine carbon labs.

u(fCO_2) = 2 µatm, u(DIC) = u(TA) = 2 µmol/kg; u(pH) = 0.001

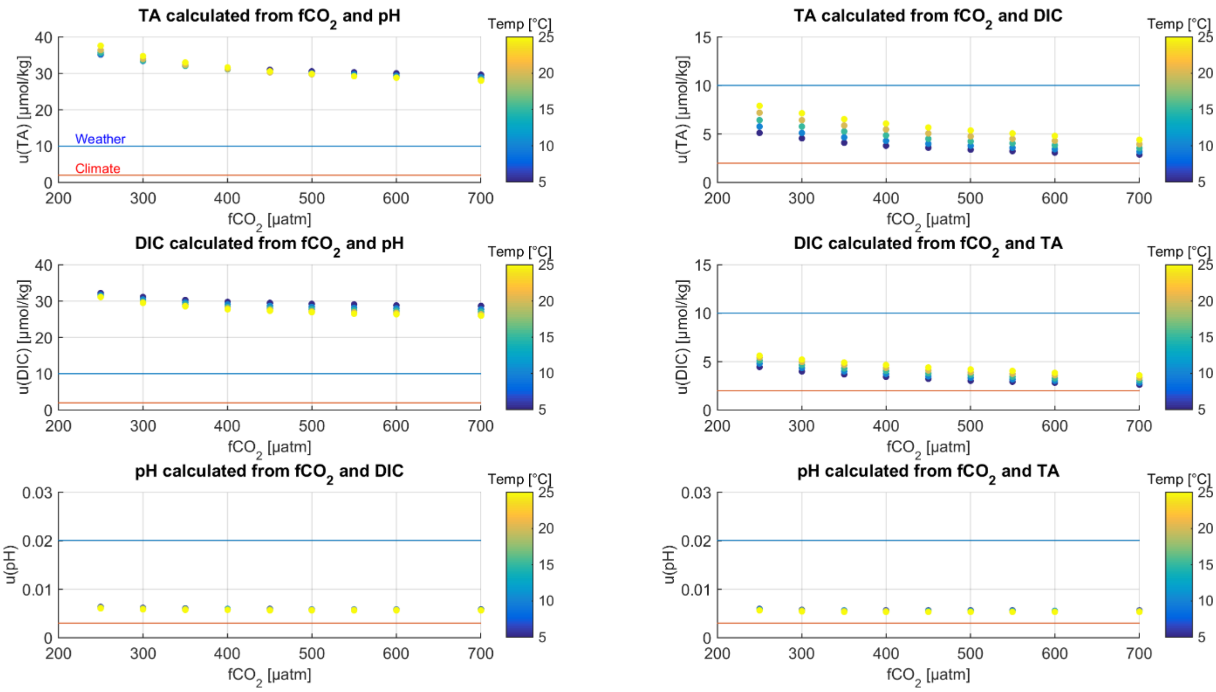

Figure 1a: Uncertainty of calculated variables of the marine carbonate system using fCO_2 and a second carbon variable. Standard uncertainties (u(fCO_2) = 2 µatm, u(DIC) = u(TA) = 2 µmol/kg; u(pH) = 0.001) were used for this calculation. The blue and red lines denote the “weather” and “climate goal”, respectively, for each variable according to Newton et al. (2014).

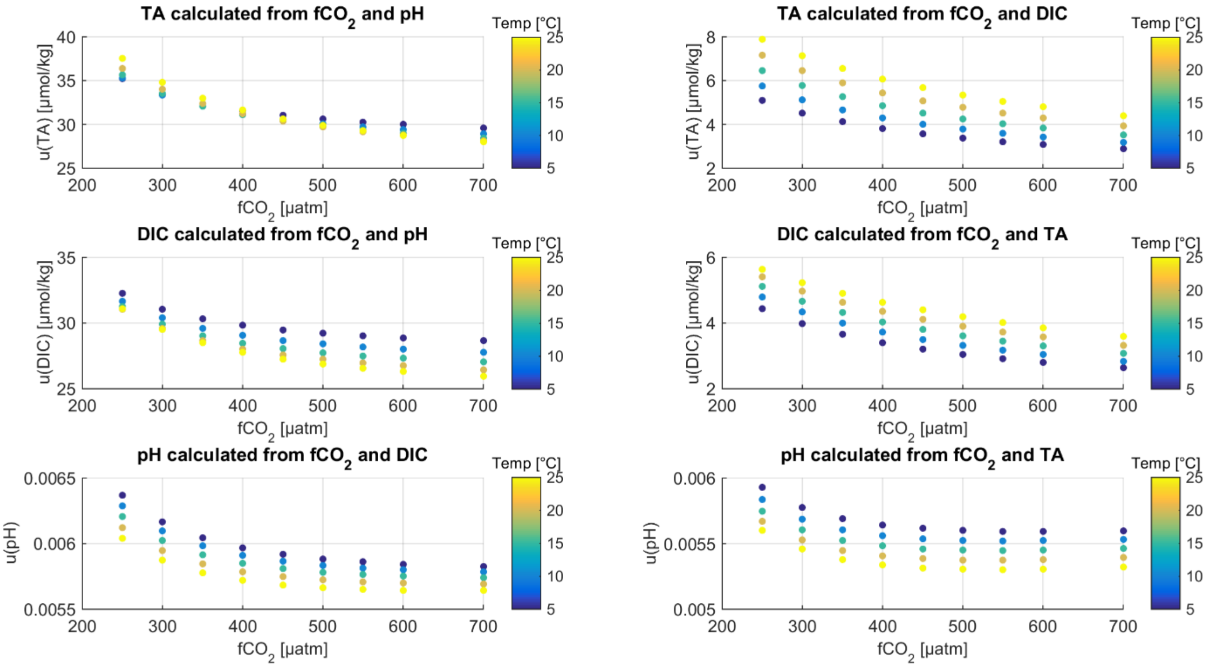

Figure 1b: Same as Figure 1a but without the lines for the "weather" and "climate goal" for better scaling.

Figure 1a shows that when fCO_2 and any second carbon variable are measured, one will never meet the thresholds for the "climate goal" when calculating the other two variables. Following the definition of the "weather goal" instead, the uncertainties of the second carbon variable were adjusted (Figures 2 and 3), so that the calculated variables met the "weather goal". When using lower uncertainties for the input variables the resulting uncertainty of the calculated variables will be better. In Figure 2 and 3, the maximum uncertainty for the second input variable (beside fCO_2) was set to result in uncertainty estimates for the calculated variables within the "weather goal". When using fCO_2 and pH, none of the resulting uncertainties fulfills the "weather goal". Thus, pH and fCO_2 cannot be used for any calculations of the marine carbonate system for ICOS quality assessments. As mentioned above, nonetheless, pH is included in the following calculations in order to capture the entire system.

Input variables: fCO_2 and DIC

The output from the calculations shown in Figure 1 showed, that with an uncertainty for fCO_2 of 2 µatm, the uncertainty of DIC can increase to 5 µmol/kg and the uncertainty for calculated TA and pH are below the thresholds for the "weather goal" of 10 µmol/kg and 0.02 pH units, respectively.

u(fCO_2) = 2 µatm, u(DIC) = 5 µmol/kg

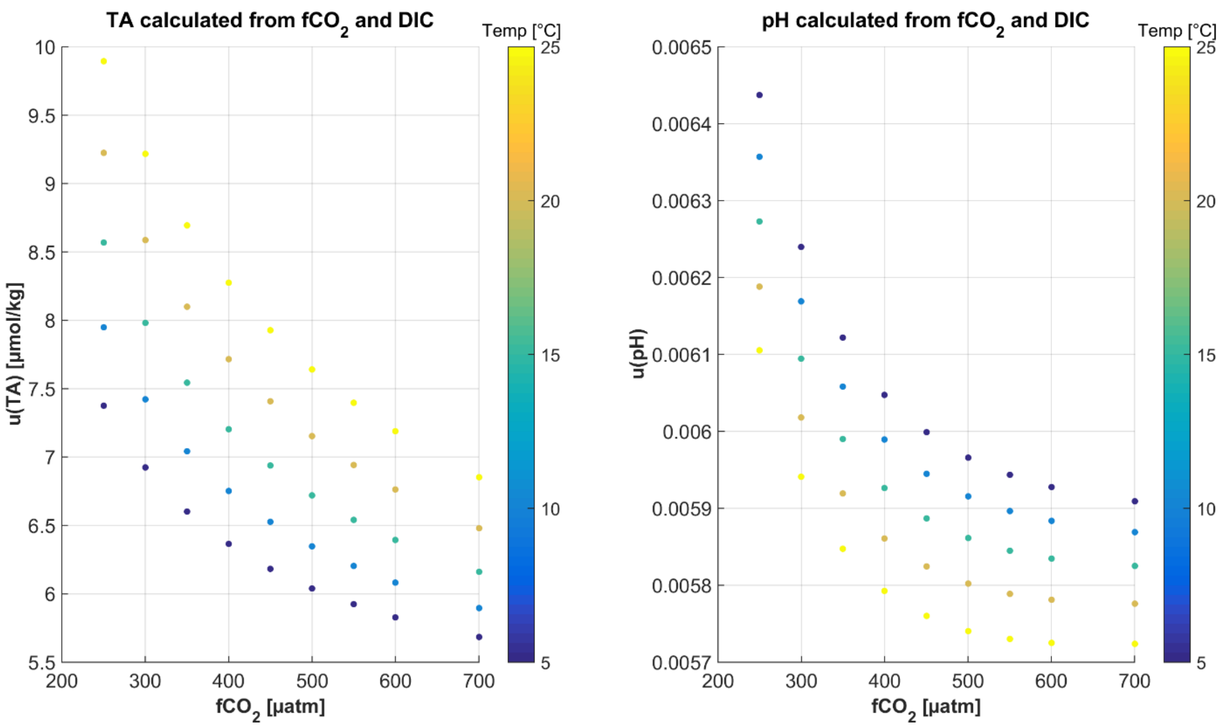

Figure 2: Uncertainty of TA and pH calculated from fCO_2 and DIC. With the assigned uncertainty of 5 µmol/kg for DIC, TA and pH can be calculated to meet the "weather goal".

Input variables: fCO_2 and TA

The output from the calculations shown in Figure 1 indicates, that with an uncertainty for fCO_2 of 2 µatm, the uncertainty of TA can increase to 10 µmol/kg and the uncertainty for calculated DIC and pH are below the thresholds for the “weather goal” of 10 µmol/kg and 0.02 pH units, respectively.

u(fCO_2) = 2 µatm, u(TA) = 10 µmol/kg

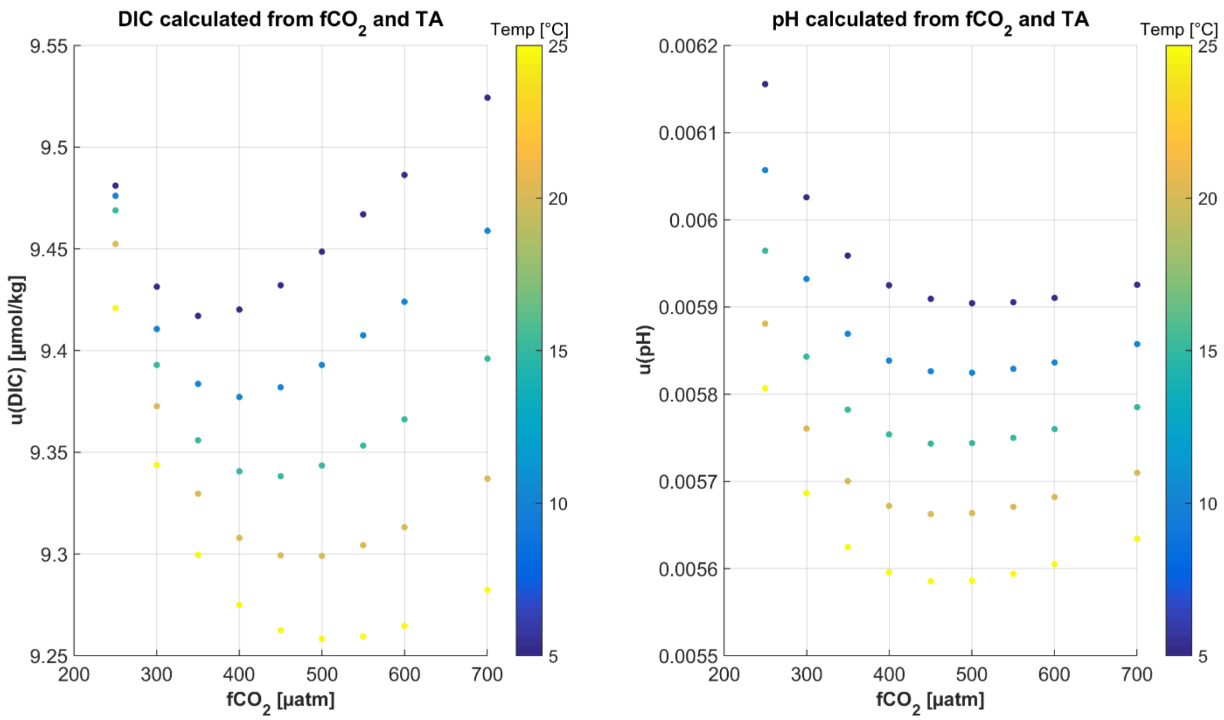

Figure 3: Uncertainty of DIC and pH calculated from fCO_2 and TA. With the assigned uncertainty of 10 µmol/kg for TA, DIC and pH can be calculated to meet the “weather goal”.

Figure 1a also shows that if one is aiming for the “climate goal”, this will not be reached by using fCO_2 and any other carbon parameter. The “climate goal” can only be reached with measured data. It also shows that using pH together with fCO_2 always leads to results with uncertainties higher than even the “weather goal”. As mentioned above, pH and fCO_2 should not be used for any calculations of the marine carbonate system for ICOS quality assessments. Table 2 summarizes the findings from above.

Table 2: “Weather goal” SOOP lines: Resulting uncertainties depending on the chosen input uncertainties. Green fields mean that the “weather goal” is met, red fields mean that the uncertainty is too high to meet the “weather goal”. The uncertainty of fCO_2 is always 2 µatm.

fCO_2 + one of the variables below	Input uncertainty of input variable	DIC [µmol/kg]	pH	TA [µmol/kg]
DIC	5 µmol/kg		<<0.02	<10
pH	0.001	>25		>27
TA	10 µmol/kg	<10	<<0.02	

FOS

ICOS FOS measure sea surface fCO_2 with an uncertainty of 10 µatm (u(fCO_2) = 10 µatm). For the other 3 variables, standard uncertainties were used that can be reached by well-equipped marine carbon labs, as for the SOOP lines.

u(fCO_2) = 10 µatm, u(DIC) = u(TA) = 2 µmol/kg, u(pH) = 0.001

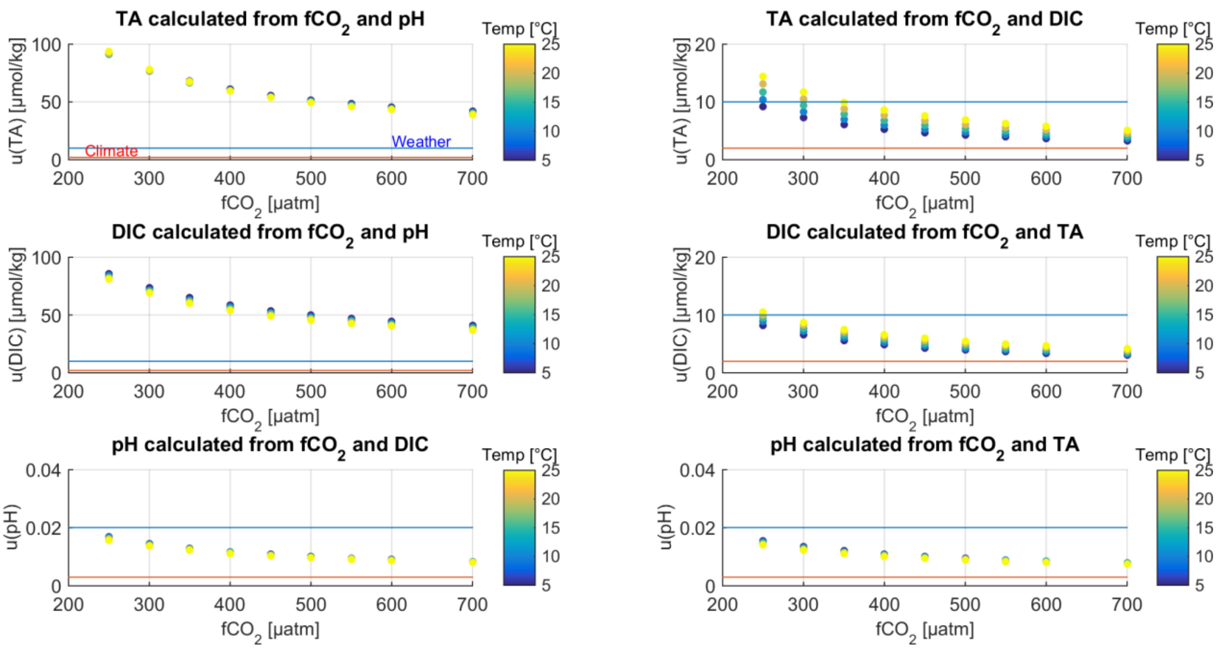

Figure 4a: Uncertainty of calculated variables of the marine carbonate system using fCO_2 and a second carbon variable. Standard uncertainties (u(fCO_2) = 10 µatm, u(DIC) = u(TA) = 2 µmol/kg; u(pH) = 0.001) were used for this calculation. The blue and red lines denote the "weather" and "climate goal", respectively, for each variable according to Newton et al. (2014).

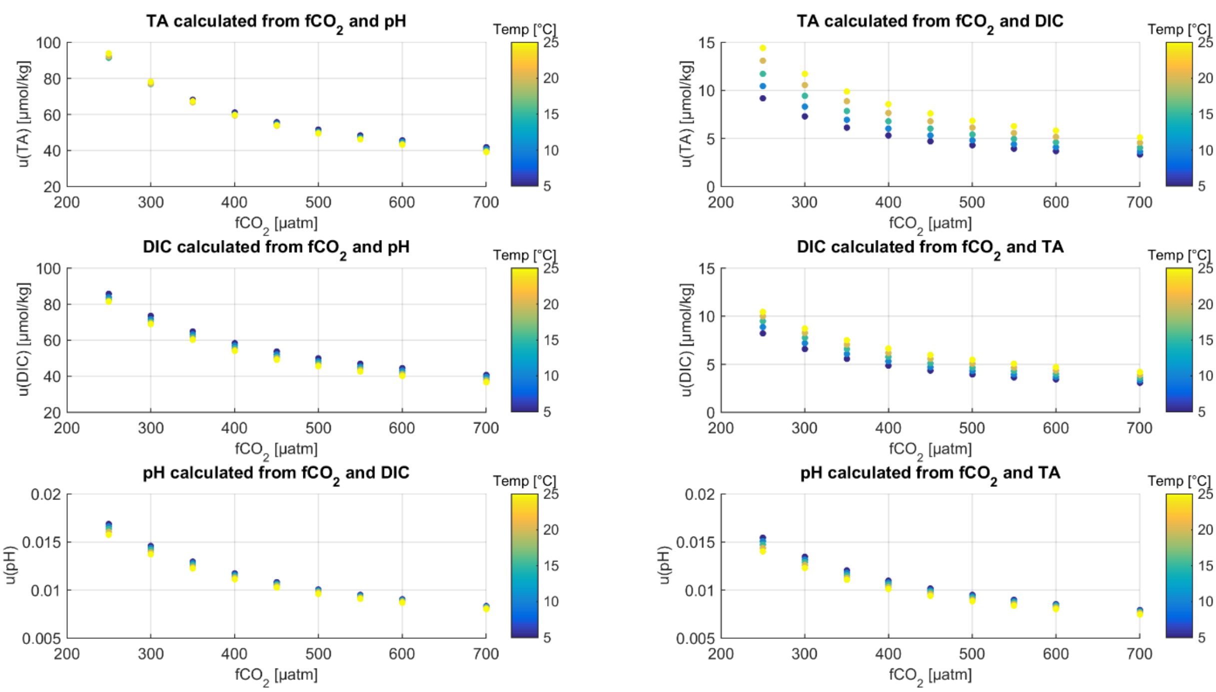

Figure 4b: Same as Figure 4a but without the lines for the "weather" and "climate goal" for better scaling.

Figure 4a shows that when fCO_2 (with u(fCO_2)=10 µatm) and any second carbon variable are measured, one will never meet the thresholds for the "climate goal" when calculating the other two variables. Following the definition of the "weather goal" instead, the uncertainties of the second carbon variable were adjusted (Figures 5 and 6), so that the calculated variables met the "weather goal". In Figure 5 and 6, the maximum uncertainty for the second input variable (beside fCO_2) was set to result in uncertainty estimates for the calculated variables within the "weather goal". When using fCO_2 and pH, none of the resulting uncertainties fulfills the "weather goal". Thus, pH and fCO_2 cannot be used for any calculations of the marine carbonate system for ICOS quality assessments. As mentioned above, nonetheless, pH is included in the following calculations in order to capture the entire system.

Input variables: fCO_2 and DIC

The output from the calculations shown in Figure 4b showed that with an uncertainty for fCO_2 of 10 µatm, the uncertainty of DIC must be as low as possible (2 µmol/kg) and the uncertainty for calculated alkalinity and pH are below the thresholds for the "weather goal" of 10 µmol/kg (only for fCO_2 values greater than 350 µatm) and 0.02 pH units, respectively.

u(fCO_2) = 10 µatm, u(DIC) = 2 µmol/kg

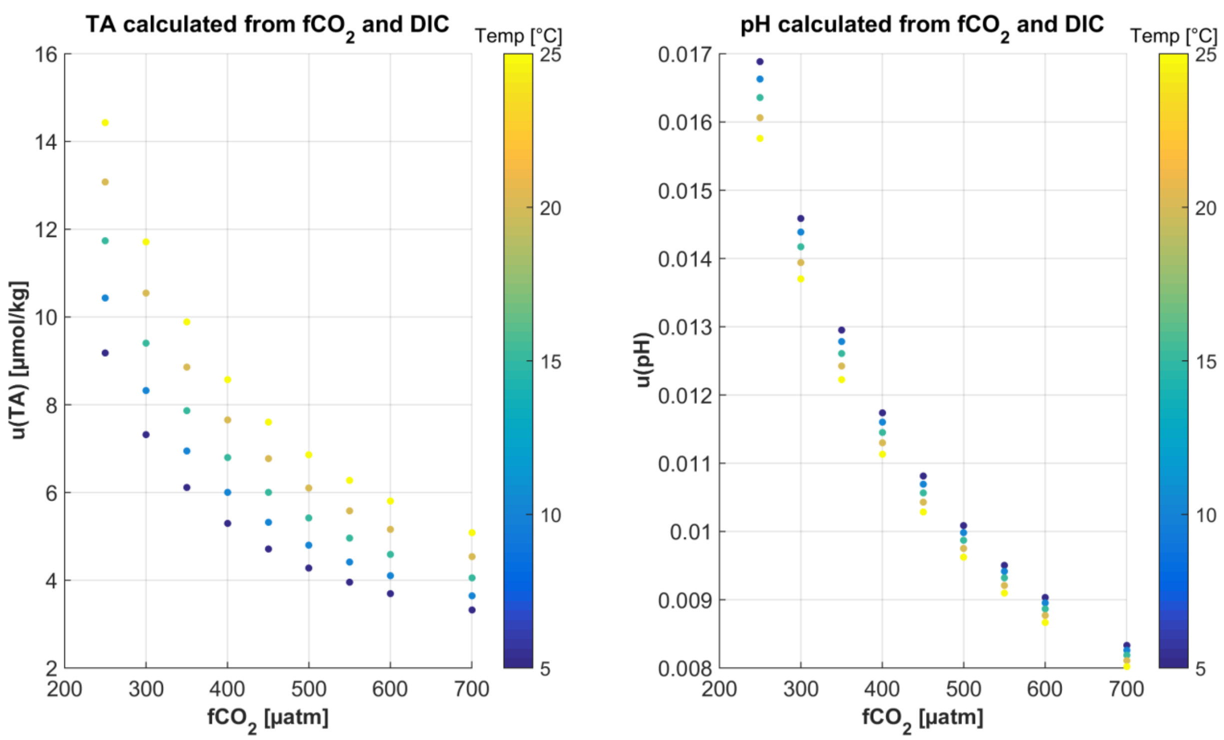

Figure 5: Uncertainty of TA and pH calculated from fCO_2 and DIC. With the assigned uncertainty of 2 µmol/kg for DIC, TA (for fCO_2 >350 µatm) and pH can be calculated to meet the "weather goal".

Input variables: fCO_2 and TA

The output from the calculations shown in Figure 4b showed that with an uncertainty for fCO_2 of 10 µatm the uncertainty of TA can increase to 4 µmol/kg and the uncertainty for calculated DIC and pH are below the thresholds for the "weather goal" of 10 µmol/kg (only for fCO_2 values greater than 250 µatm) and 0.02 pH units, respectively.

u(fCO_2) = 10 µatm, u(TA) = 4 µmol/kg

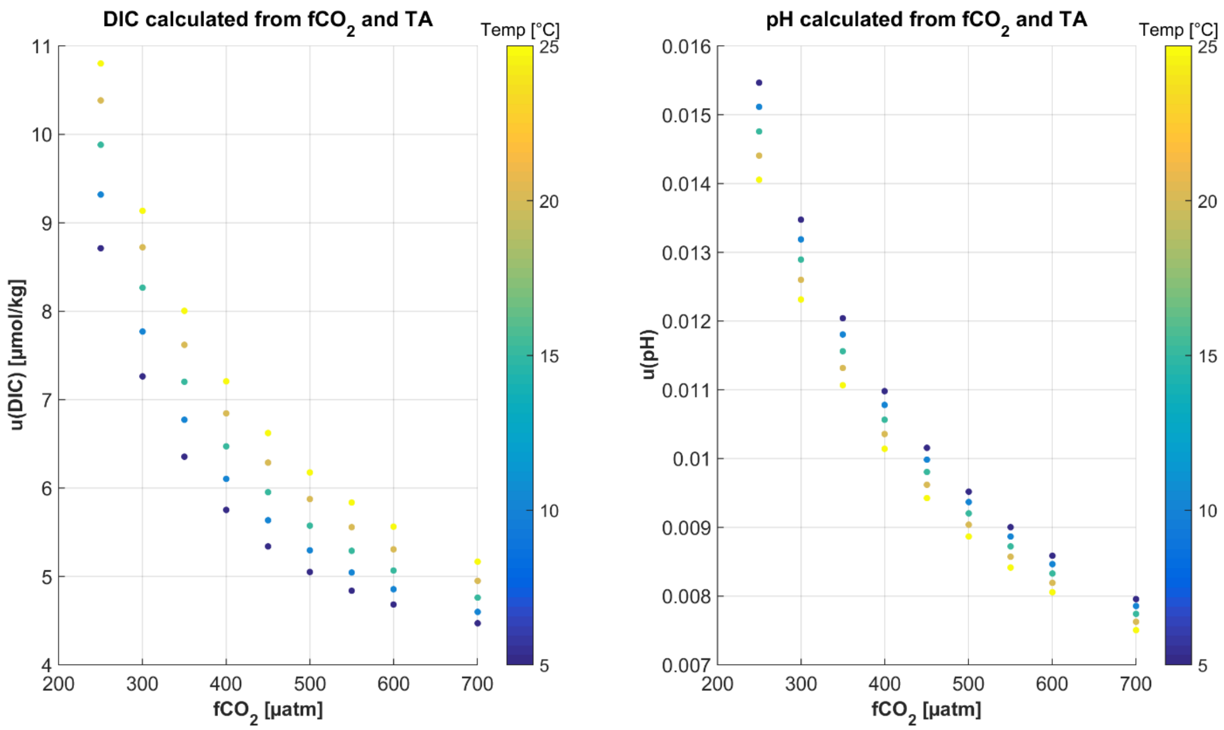

Figure 6: Uncertainty of DIC and pH calculated from fCO_2 and TA. With the assigned uncertainty of 4 µmol/kg for TA, DIC (for fCO_2>300 µatm) and pH can be calculated to meet the "weather goal".

Figure 4a also shows that if one is aiming for the "climate goal", this will not be reached by using fCO_2 and any other carbon parameter. The "climate goal" can be only be reached with measured data. It also shows that using pH together with fCO_2 always leads to results higher than the "weather goal". As mentioned above for SOOP lines, pH and fCO_2 should not be used for any calculations of the marine carbonate system for ICOS quality assessments. Table 3 summarizes the findings from above.

Table 3: "Weather goal" FOS: Resulting uncertainties depending on the chosen input uncertainties. Green fields mean that the "weather goal" is met, red fields mean that the uncertainty is too high to meet the "weather goal". The uncertainty of fCO_2 is always 10 µatm.

fCO_2 + one of the variables below	Input uncertainty of input variable	DIC [µmol/kg]	pH	TA [µmol/kg]
DIC	2 µmol/kg		<<0.02	<10*
pH	0.001	>30		>30
TA	4 µmol/kg	<10*	<<0.02	

*for fCO_2>300 µatm

- **Concluding part A**

When aiming for uncertainties of marine carbon variables that fulfill the “climate goal” as defined by Newton et al. (2014), the carbon variables need to be measured. Due to the error propagation, the resulting uncertainty when calculating variables from fCO_2 and another variable is always above the threshold of 2 µmol/kg for DIC and TA and 0.003 for pH.

It was shown that using fCO_2 and pH will always result in uncertainties higher than the uncertainty limits stated for the “weather goal” (10 µmol/kg for DIC and TA, 0.02 for pH).

Figures 2 and 3 and Table 1 show that SOOP lines need to provide the additional variable DIC with an uncertainty of 5 µmol/kg or TA with an uncertainty of 10 µmol/kg, in order to become a Class 1 station.

Figures 5 and 6 and Table 2 show that FOS need to provide the additional variable DIC with an uncertainty of 2 µmol/kg or TA with an uncertainty of 4 µmol/kg, in order to become a Class 1 station.

B - Can fCO_2 be calculated with a sufficient uncertainty by two other carbon parameters?

The calculations in this section were done for four different fCO_2 levels between 250 and 600 µatm and for different temperatures between 5 and 25°C. TA and pH was calculated for each fCO_2 using a constant DIC value of 1950 µmol/kg at 15°C. This should ensure a consistent carbonate system for further calculations.
For each pair of input variables, four different uncertainties were used for the calculation of fCO_2:

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*f*CO2 = [250, 350, 450, 600] µatm
DIC = 1950 µmol/kg
Temperature = [5, 10, 15, 20, 25] °C
Salinity = 35; in pressure = out pressure = 5 dbar; SI = 0; PO4 = 0;
pH scale: total scale
K1K2 constants: (Lueker et al., 2000)
KSO4 constants: (Dickson, 1990)
TB (total boron): (Uppström, 1974)

Uncertainties in constants:
u(pK0) = 0.002
u(pK1) = 0.0055
u(pK2) = 0.01
u(pKb) = 0.01
u(pKw) = 0.01
u(pKspa) = 0.02
u(pKspc) = 0.02
u(Boron) = 0.02

Uncertainties in variables:
Salinity: u(S) = 0.1
Temperature: u(T) = 0.005

u(pH) = [0.001, 0.002, 0.003, 0.004]
u(TA) = [1, 2, 3, 4]
u(DIC) = [1, 2, 3, 4]

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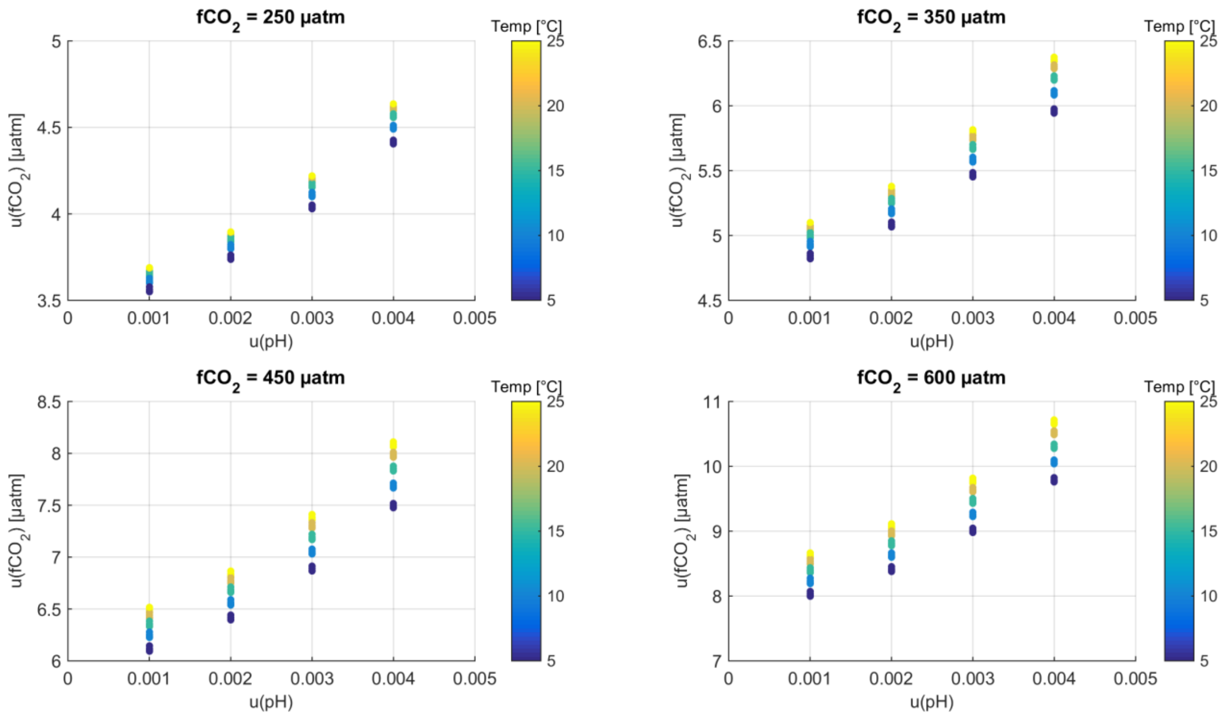
The following figures show the resulting uncertainty in fCO_2 (u(fCO_2)) by using two variables with different uncertainties. Each figure shows the results at four different fCO_2 levels and different temperatures. The top part of the figures shows the u(fCO_2) plotted as the uncertainty of the first input variable and the bottom part shows the same u(fCO_2) plotted versus the uncertainties of the second input variable.

Using TA and pH as input variables:

u(fCO_2) vs. u(pH)



u(fCO_2) vs. u(TA)

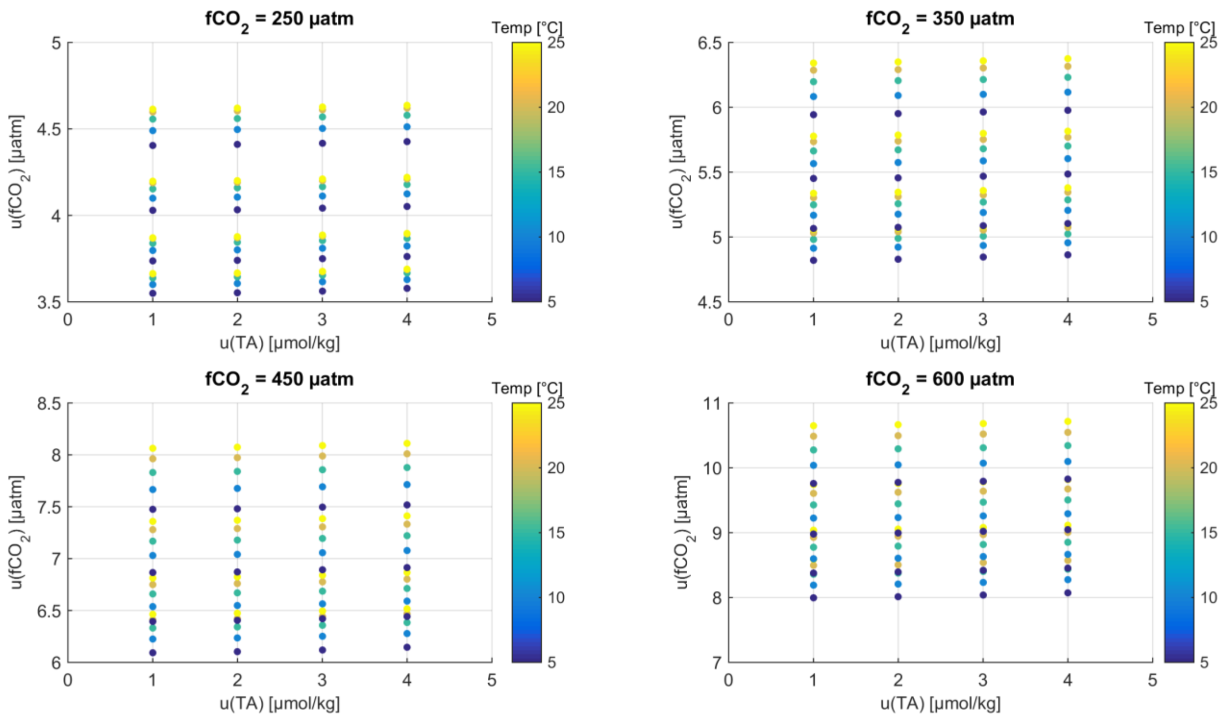
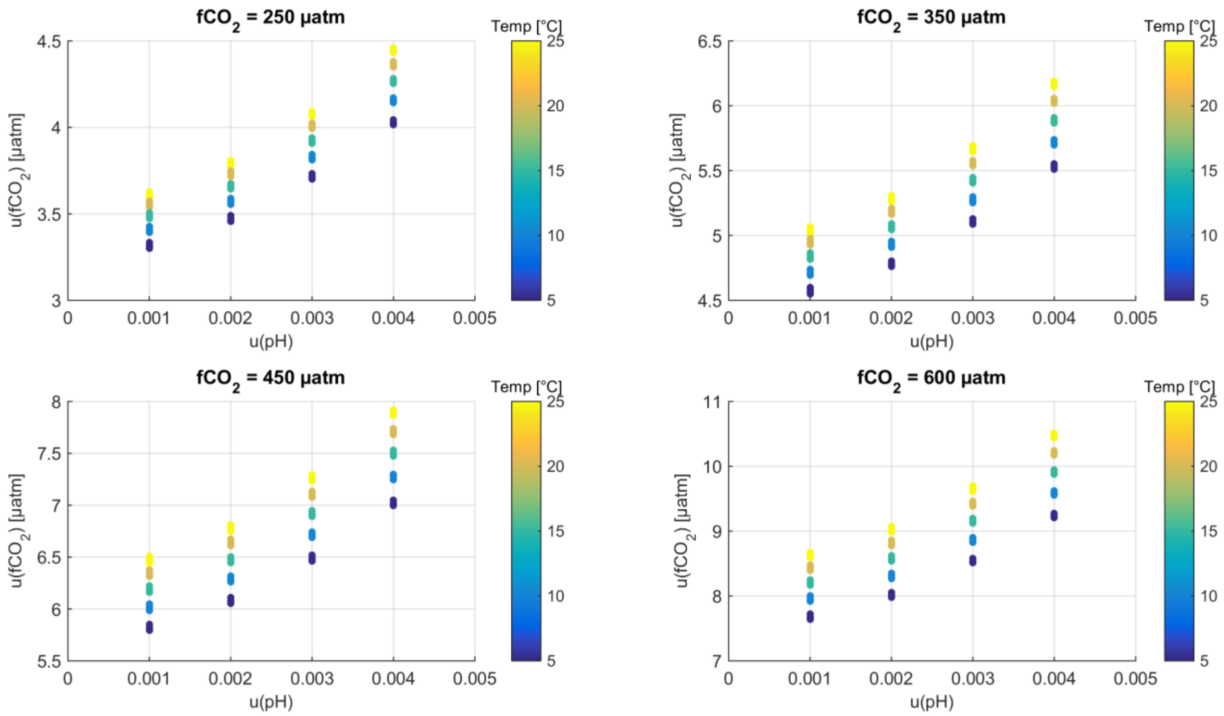


Figure 7: Uncertainty of fCO_2 calculated from TA and pH for four different fCO_2 levels and different temperatures. The upper four panels show the impact of the uncertainty of pH (u(pH)) and the lower panels show the impact of u(TA).

Using DIC and pH as input variables:

u(fCO_2) vs. u(pH)



u(fCO_2) vs. u(DIC)

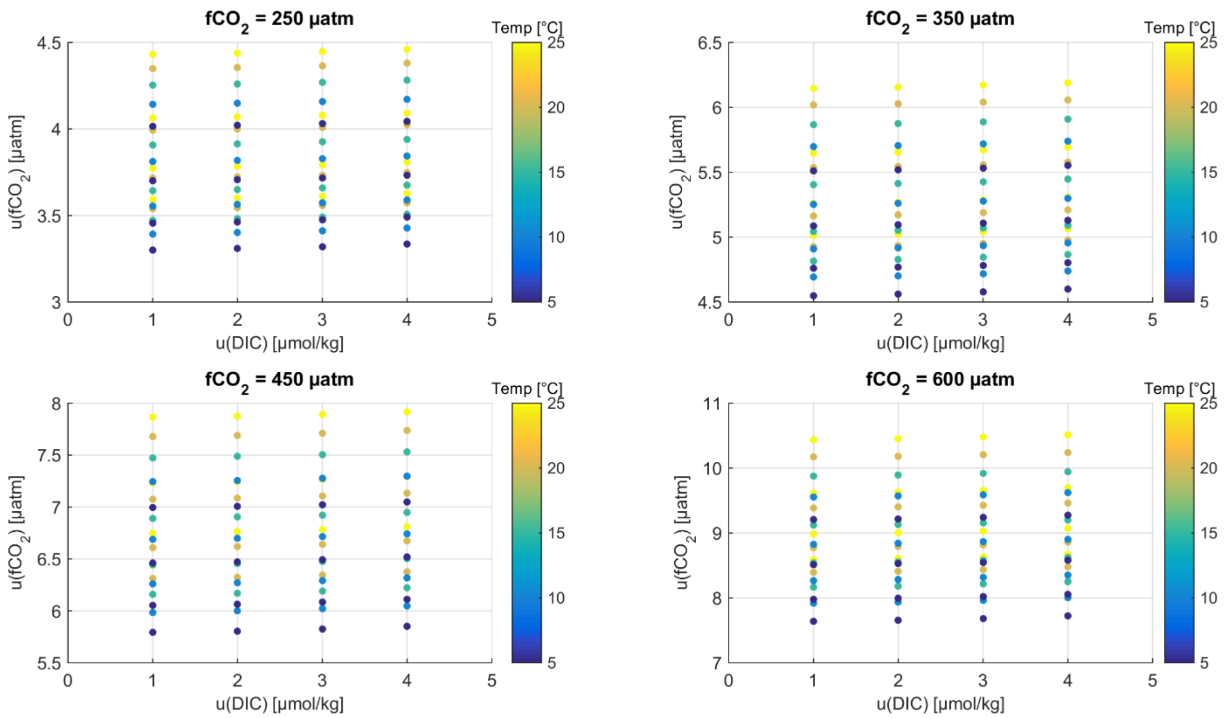
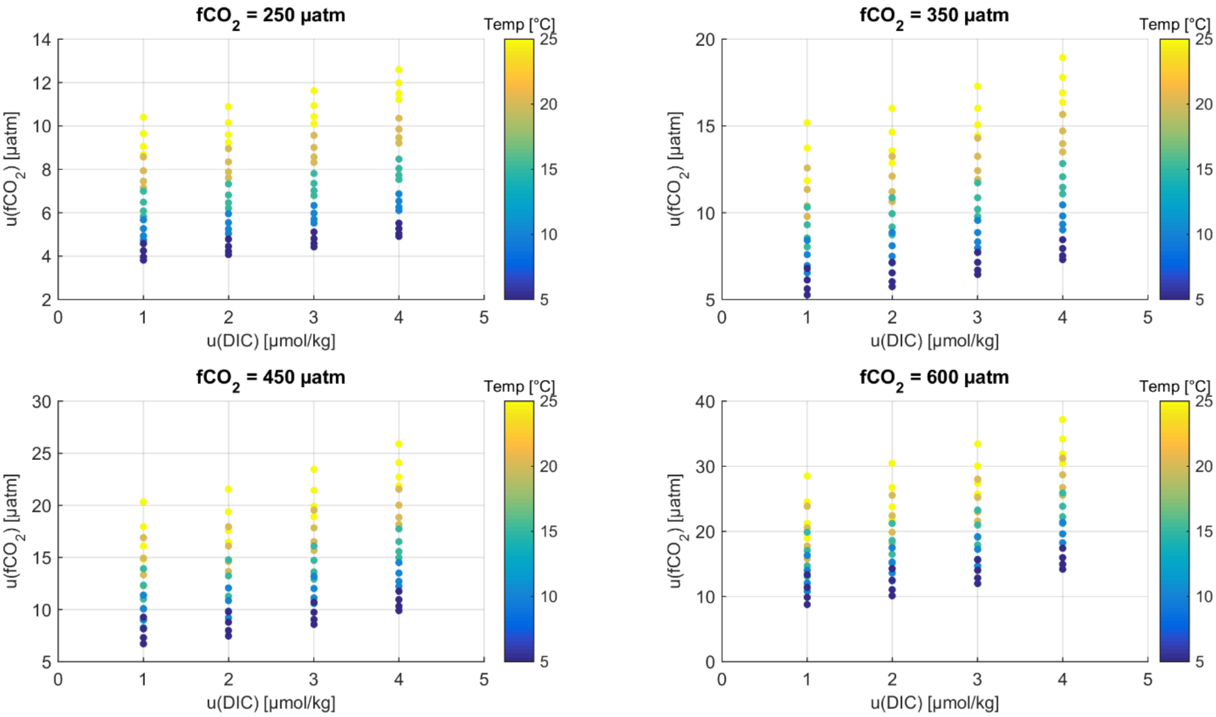


Figure 8: Uncertainty of fCO_2 calculated from DIC and pH for four different fCO_2 levels and different temperatures. The upper four panels show the impact of u(pH) and the lower panels show the impact of u(DIC).

Using DIC and TA as input variables:

u(*f*CO_2) vs. u(DIC)



u(*f*CO_2) vs. u(TA)

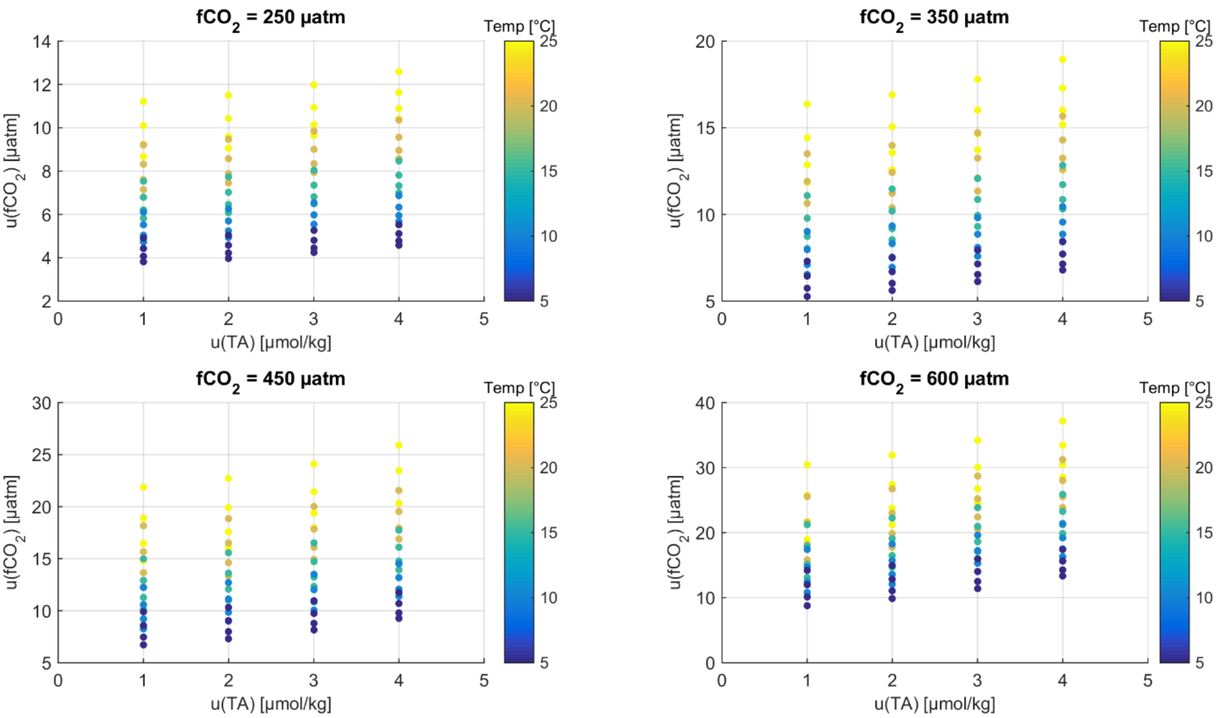


Figure 9: Uncertainty of *f*CO_2 calculated from DIC and TA for four different *f*CO_2 levels and different temperatures. The upper four panels show the impact of u(DIC) and the lower panels show the impact of u(TA).

Concluding part B

- Calculating fCO_2 from two carbonate variables is only suitable for FOS as there is no combination that results in an uncertainty for calculated fCO_2 better than 3.5 µatm.
- Using TA and pH: fCO_2 can be calculated with an uncertainty better than 10 µatm for fCO_2 values below ca. 600 µatm when u(pH)<0.003 and u(TA)<4 µmol/kg.
- Using DIC and pH: fCO_2 can be calculated with an uncertainty better than 10 µatm for fCO_2 values below ca. 600 µatm when u(pH)<0.003 and u(DIC)<4 µmol/kg.
- DIC and TA can only be used for water temperatures below 15°C and fCO_2 levels below 450 µatm.

Summary

When calculating carbon variables using CO2sys, the error propagation should always be included. When using the error propagation code from Orr et al. (2018), one also needs to update the CO2sys files as they also include minor changes to account for the error propagation.

The labelling scheme of ICOS-Oceans, as agreed during the Monitoring Station Assembly (MSA) meeting in Southampton in 2019, defines two goals with respect to the marine carbon cycle:

- Quantifying air-sea CO_2 fluxes
- Assessing the variability and drivers of these fluxes

Limitations of ocean fCO_2 measurement capabilities at FOS mean that fluxes cannot be determined to the accuracy desired for large scale carbon budgets. Meanwhile, it is most common that SOOP lines measure fCO_2 rather than other carbon system variables. Therefore, fCO_2 needs to be measured with an accuracy of 2 µatm on SOOP lines and 10 µatm at FOS. To estimate a meaningful accuracy for the measurement of a second carbon variable it was decided to use the definitions of the "weather goal" and the "climate goal" as defined by Newton et al. (2014) for the Global Ocean Acidification Observing Network (GOA-ON).

One important outcome is that when aiming for data with uncertainties fulfilling the "climate goal" these data need to be measured. There is no combination of fCO_2 and a second carbon variable that allow the calculation of the other two variables with sufficient uncertainty. Using fCO_2 and pH will result in uncertainties that are above the thresholds for the "weather goal". Using the results from part A, uncertainty estimates can be added to the variables in Table 1, so that it can be rewritten as shown in Table 4:

Table 4: Updated measurement requirements for ICOS marine stations.

	SOOP lines	FOS
Class 2 (minimum required variables)	fCO_2 (±2 µatm)	fCO_2 (±10 µatm) Alkalinity **(±4 µmol/kg)** or DIC **(±2 µmol/kg)** Oxygen
Class 1 (additional variables)	Alkalinity **(±10 µmol/kg)** or DIC **(±5 µmol/kg)** Oxygen	Surface: Nutrients (nitrate, silicate and phosphate)

Part B investigated which variables can be used and to what uncertainty they need to be measured to evaluate fCO2 measurements at ICOS stations. Using two variables of the marine carbonate system to calculate fCO_2 is only suitable for FOS. There is no combination that results in an uncertainty for calculated fCO_2 better than 3.5 µatm. Of course, the results depend heavily on temperature and often on the fCO_2 level itself. When evaluating a FOS, the results need to be analyzed in detail for each station.

When using TA and pH, fCO_2 can be calculated with an uncertainty better than 10 µatm for fCO_2 values below ca. 600 µatm using u(pH)<0.003 and u(TA)<4 µmol/kg. The uncertainty of pH has the larger effect. The fCO_2 can be calculated with an uncertainty of below 5 µatm at low fCO_2 levels (<350 µatm) and temperatures below 15°C.

When using DIC and pH, fCO_2 can be calculated with an uncertainty better than 10 µatm for fCO_2 values below ca. 600 µatm using u(pH)<0.003 and u(DIC)<4 µmol/kg. Again, the uncertainty of pH has the larger effect. The fCO_2 can be calculated with an uncertainty of below 5 µatm at low fCO_2 levels (<350 µatm) and temperatures below 20°C.

When using DIC and TA, fCO_2 can be calculated with an uncertainty better than 10 µatm only for water temperatures below 15°C and fCO_2 levels below 450 µatm. The pair DIC-TA should not be used for evaluating ICOS FOS, as it gives sufficient results only in a limited temperature range.

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