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# Calculation uncertainty of pCO2 from discrete samples of TA, DIC, and pH

At the marine MSA meeting in Trieste we discussed ways to validate the sensor pCO2 data. One frequently used method is to compare the sensor pCO2 with calculated pCO2 from discrete pH, DIC, TA data. At the meeting, we showed some plots indicating that using TA and pH for such a calculation was better than using DIC and TA. However, we promised to perform a more thoroughly study of these calculations where uncertainties in both the input (DIC, TA, pH, T, S) and the equilibrium constants (K0, K1, K2, KB, Kw) were included. The aim of this study was to decide a possibly change of the accuracy for the core parameter pCO2 (Table 3b, Fixed Stations, in the ICOS Marine Station Labelling Step 2 document).

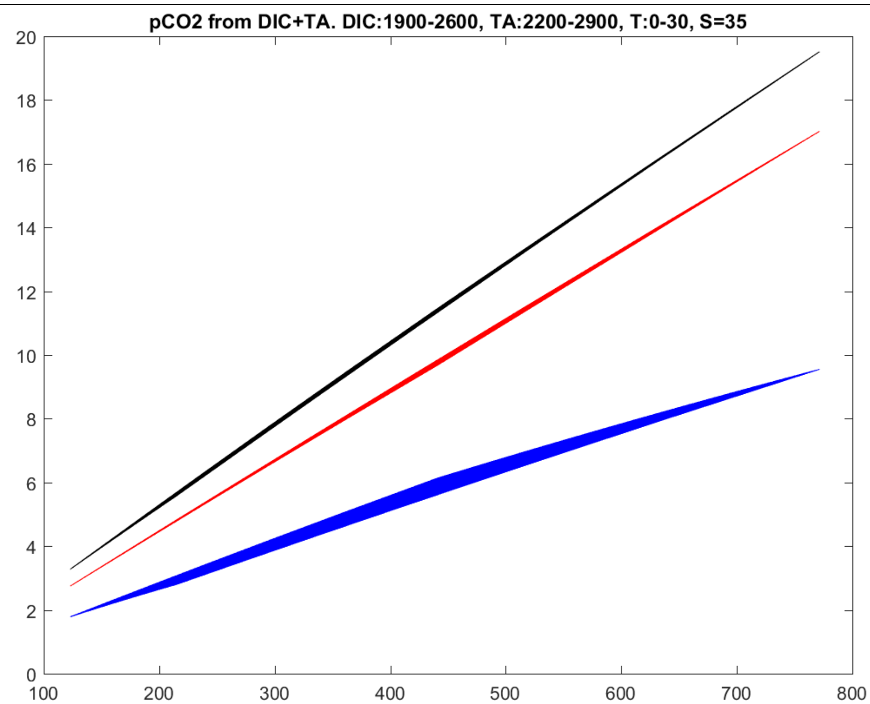
Siv Lauvset has now performed the study and here we send the results.

In the study, Siv has used CO2SYS Matlab version 2.0, pK1 and pK2 from Lueker et al. (2000), K0 from Weiss (1974), KB (and KS) from Dickson (1990), Boron conc. from Uppström (1974), and pH on total scale. Both PO4 and Si are assumed to be zero, and have zero uncertainty. In the uncertainty calculation, she has used the m-files from James Orr (https://github.com/jamesorr/CO2SYS-MATLAB/blob/master/src/).

Uncertainties for pK1 (0.0055) and pK2 (0.01) are from Lueker et al. (2000), and uncertainties for pK0, pKb, pKw, pKspa, pKspc are 0.002, 0.01, 0.01, 0.02, 0.02, respectively (as is default in Orr's program). We have assumed uncertainties in DIC of 1.5 µmol/kg, in TA of 3 µmol/kg, and in pH of 0.005.

## pCO2 calculated from DIC and TA:

*Plot 1:*

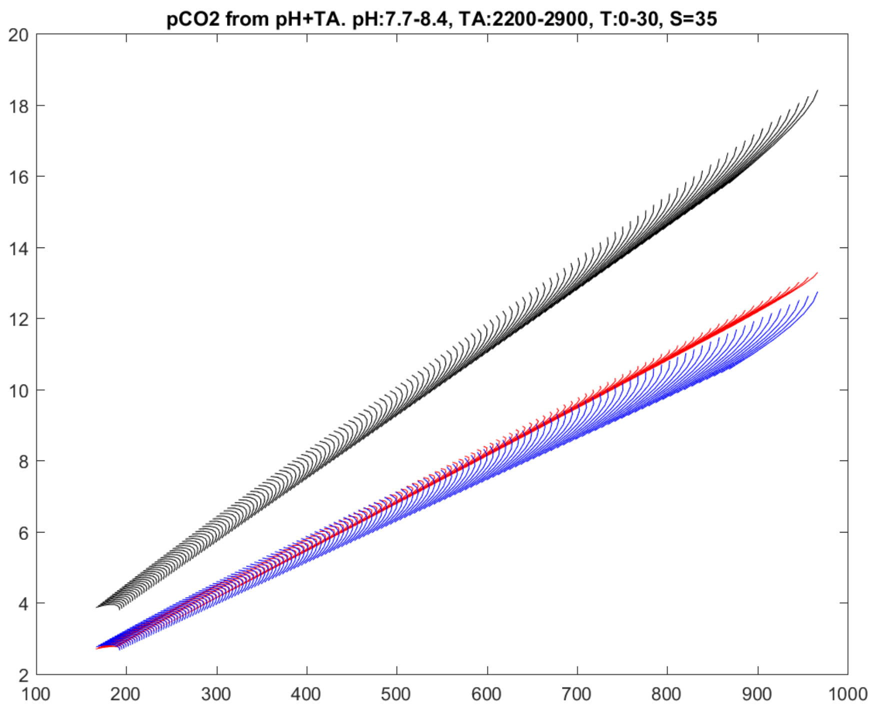



Blue: errors only in input (DIC, TA, temperature and salinity); Red: errors only in constants; Black: all errors. Envelope given by range in temperature.

Plot 1 shows the result when DIC and TA are used to calculate pCO2. The x-axis is the span in pCO2 and the y-axis is the pCO2 calculation uncertainty. The plot is made for a span in TA (2200-2900 µmol/kg), DIC (1900-2600 µmol/kg), temperature (0 to 30°C) and a constant salinity of 35. The plot shows that the uncertainties in the constants dominates the total pCO2 calculation uncertainty, while the uncertainties in DIC and TA contribute less. As an example, at a pCO2 of 400 µatm, the total pCO2 calculation uncertainty (the squared standard error) is approximately 11 µatm. At this pCO2, the pCO2 calculation uncertainty resulting from uncertainties in the constants (mostly K1 and K2) is approximately 8 µatm, and that resulting from uncertainties in DIC and TA is 5 µatm (uncertainties from temperature and salinity do not have a significant contribution).
A further study (not shown here) also shows that the uncertainty in TA is more important for the total calculation uncertainty that the uncertainty in DIC.

**pCO2 calculated from pH (total scale) and TA:**

*Plot 2:*




Blue: errors only in input (pH, TA, temperature, and salinity); Red: errors only in constants; Black: all errors. Envelope given by range in temperature.

Plot 2 shows the result when pH and TA are used to calculate pCO2. The x-axis is the span in pCO2 and the y-axis is the pCO2 calculation uncertainty. The plot is made for a span in pH (7.7-8.4), TA (2200-2900 µmol/kg), temperature (0 to 30°C) and a constant salinity of 35. The plot shows, that the uncertainties in the constants (mostly K0 and K2) is equally important for the total pCO2 calculation uncertainty as the uncertainties in pH and TA (again, the temperature and salinity uncertainties do not have a significant contribution). As an example, at a pCO2 of 400 µatm, the total pCO2 calculation uncertainty (the squared standard error) is approximately 8 µatm. At this pCO2, the pCO2 calculation uncertainty resulting from uncertainties in the constants (mostly K0 and K2) as well as from uncertainty in DIC and TA is approximately 5 µatm. However, the total pCO2 calculation uncertainty increase for increasing pCO2.

A further study (not shown here) shows that the uncertainty in pH is much more important for the total calculation uncertainty than the uncertainty in TA.

**Conclusion from the uncertainty calculation exercise**

Siv's exercise shows that calculated pCO2 from discrete samples of TA and DIC are not particularly useful for validating pCO2 data from sensors. The reason is the large uncertainties in the carbonate system constants, which is out of our hands to improve. This issue is for the global marine carbon community to solve, and there might be an effort towards this starting this fall.

We recommend using the combination TA-pH to calculate pCO2, since this combination gives the lowest calculation uncertainty. In this exercise, a pH uncertainty of 0.005 is used, and if this uncertainty is improved, the pCO2 calculation uncertainty will also improve.

**Suggestion on how to proceed**

As for now, we suggest to change the ICOS criteria for pCO2 sensors for FOS stations (continuous/quasi-continuous samples) to **±10 µatm**, which is in line with the SOCAT criteria E for alternative sensors. The discrete pH samples should be measured with an accuracy of 0.005 or better. We are aware that the change of criteria is of limited value for the stations, which measure very high pCO2 values.

Further, we encourage the PIs to perform parallel CO2 measurements in the field, i.e. when a CO2 sensor is to be retrieved, the user should ensure that the old sensor and the new, calibrated sensor are measuring in seawater side by side for a couple of hours before the old sensor is retrieved. This can be used to determine a possible drift of the old sensor and will act as a validation of that sensor. This field exercise requires that the station has more than one pCO2 sensor in the stock.

OTC will start looking into possibilities for in situ calibration/validation by e.g. using marine drones equipped with a CO2 reference system.