Robust Sensor for Extended Autonomous Measurements of Surface Ocean Dissolved Inorganic Carbon

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Supporting Information

10-port Valve Flow Pathways

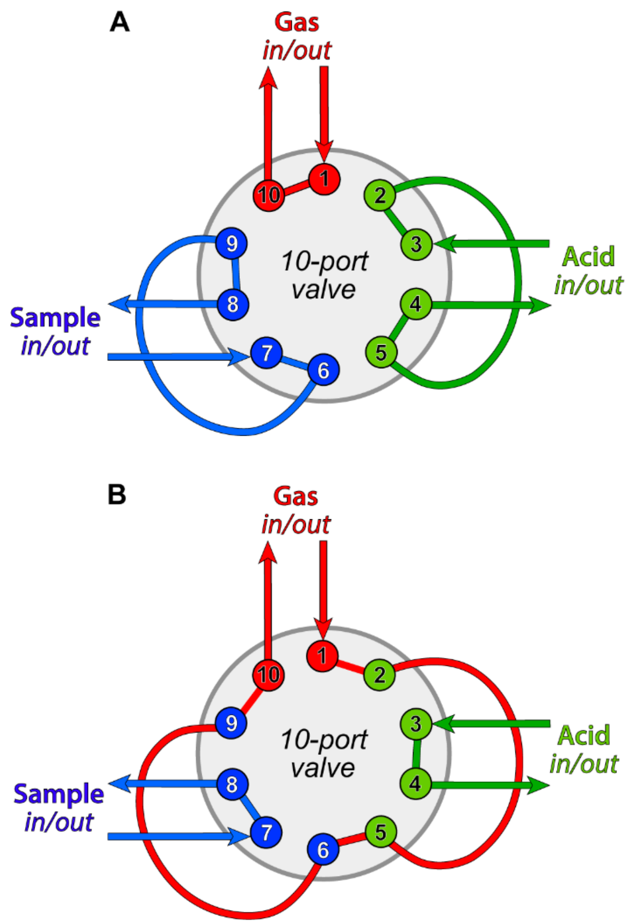

Figure S1. 10-port valve flow pathways used to control sample and acid additions. The sample and acid loops are filled during separate sequences of the measurement when the valve is in position **A**. The valve is then switched to position **B** to inject the fluid into the equilibration chamber. Loops are not drawn to scale.

Seattle Aquarium Flow-Through System

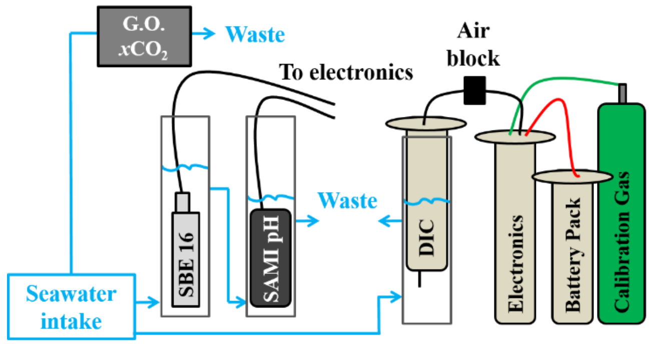

Figure S2. Diagram of the Seattle Aquarium flow-through system. Water from ~12m depth was pumped through a valve manifold that fed into the three flow-through pathways depicted. Discrete bottle samples were collected from a valve on the manifold for later coulometric DIC analysis.

Honolulu, HI Deployment Drift Correction

In December of the Honolulu, HI deployment, xCO_2 measurements began to drift with time. After thorough review of the raw LI-820 diagnostic data and multiple discussions with a technician at LICOR, we identified the source of the drift to be an interference (debris) in the optical chamber. The drift was initially identified from the increasing xCO_2 values in the field and confirmed as an infrared detector malfunction during post-deployment calibration in the laboratory. The DIC bottle samples were not used in this correction or for justifying the correction. The adjustment was made simply for xCO_2 quality control purposes prior to DIC calculation. This correction was unique to the Hawaii deployment and is not part of the usual post-deployment quality control.

Due to the strong relationship between the LICOR response and temperature (which is why the sensor is calibrated prior to every measurement), and the nature of the field malfunction, we applied a small non-linear temperature correction to account for temperature interferences resulting from the detector drift issue. Again, this correction was to account for a temporary issue with the LICOR detector used on this one deployment and would not normally be part of the system calculations. This modest correction had an average influence of 1.4 ppm on the xCO_2 values and improved the overall DIC measurement accuracy from 6±14 µmol kg^{-1} to 1±11 µmol kg^{-1}.

Honolulu, HI Calculated vs. Direct Measurement Comparisons

Table 1. Mean and standard deviation of the difference between calculated and measured values for xCO_2, pH and DIC. Differences between bottle DIC and the calculated and MADIC measured DIC values are also given. May 2014 data are omitted from these computations due to a $SAMI^2$-pH sensor clog.

	Mean Difference	**StDev.**
$xCO_{2\ Calc} - xCO_{2\ Meas}$	-3	9
$pH_{Calc} - pH_{Meas}$	0.006	0.009
$DIC_{Calc} - DIC_{Meas}$	-27	43
$DIC_{Bottle} - DIC_{Calc}$	21	37
$DIC_{Bottle} - DIC_{Meas}$	1	11