Cruise: WS15264
Ship: R/V Walton Smith
Expo Code: 33WA20150921
Dates: September 21st -25th , 2015
Chief Scientist: Dr. Chris Kelble
Equipment: CTD Rosette
Total number of stations: 15
Location: Southwest Florida coastal region

The samples were run for Dr. Leticia Barbero of NOAA-AOML as part of the South Florida coastal water monitoring program.

Sample Collection

The discrete samples were collected from Niskin bottles attached to a 24 bottle configured rosette onboard the ship by the Lindsey Visser. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:
15 locations, 15 samples each 500-ml, no duplicate samples.
Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

pH:
15 locations, 15 samples each 500-ml, no duplicate samples.
Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Featherstone

TAlk:
15 locations, 15 samples each 500-ml, no duplicate samples.
Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Leticia Barbero and Dr. Denis Pierrot

Nutrients:
15 locations, 15 samples each 50-ml, no duplicate samples.
Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Charles Fischer

Sample Analysis
DIC:

Instrument ID	Date	Certified CRM (µmol/kg)	CRM Value (µmol/kg)	CRM Offset (µmol/kg)	Blank (Counts)	Avg. Sample Analysis Time
AOML 3	10/06/2015	2031.53	2026.25	5.28	28.0	19

Analysis date: 10/06/2015
Coulometer used: DICE-CM5015-AOML 3
Blanks: 28.0 counts/min
CRM # 1036 was used and with an assigned value of (includes both DIC and salinity):
Batch 144, c: 2031.53 µmol/kg, S: 33.571
CRM values measured: AOML 3: offset 5.28 µmol/kg (2026.25 µmol/kg).
Average run time, minimum run time, maximum run time: 19, 13 and 20 min.

Reproducibility: (# samples and average difference): No duplicate samples were collected.

CRM, salinity and $HgCl_2$ correction applied: Salinity correction was applied using TSG salinity.

Remarks

The volume correction was applied due to added $HgCl_2$ (Measured DIC*1.00037).
The first CRM of each cell was used for a CRM correction.

The DIC instruments were stable: the gas loop and CRM values did not change significantly throughout the life span of each cell.

Raised blank on AOML 3 (10/06/2015) from 18.7 to 28.0 before running the CRM.

The samples were analyzed using the DICE (AOML 3) and a new coulometer from UIC, Inc. CM5015 with CM5011 emulation software.

pH:

Analysis date: 10/06/2015
Spectrophotometer used: HP Agilent 8453

Reproducibility: (# samples and average difference): No duplicates were collected.

Remarks

The equations of Liu et al, 2011 formulated using the purified m-cresol purple indicator was used to determine pH of the samples. pH samples were analyzed at 20^0C at Full Scale (pH 0-14).

Temperature for each sample was measured before analysis using a Hart Scientific Fluke 1523 reference thermometer.

Approximately 80 mL of sample was extracted from each DIC sample bottle by syringe before DIC analysis to determine the pH.

TAlk:

The results posted are duplicate analyses from the same sample bottles used for DIC and pH.
Analysis dates: 12/14/2015
Titration system used: Open cell
CRM batch: 129, S = 33.361, certified TA = 2237.32 µmol/kg

2 CRM samples were run daily, before and after the seawater samples. The TA for the water samples was corrected using the daily averaged ratios between the certified and measured values of the 2 CRMs run. The following table shows the CRM measurements.

Cell System	Date	Time	Bottle #	TA	|ΔCRM|
1	12/14/15	11:04:35	977	2239.91	
1	12/14/15	18:55:01	639	2239.14	0.77

Reproducibility: No duplicates were collected.

<u>**Remarks**</u>

All samples were run on the same system. Sample 57130100 (bottle number 515) was damaged and could not be run for alkalinity.

<u>*Comments*</u>

The latitude, longitude, date, and time reported with the DIC, pH and TAlk measurements were taken from the sample field log. The field log values are provided for reference; no post-cruise assurance of accuracy has been done to this data. The Niskin bottles are approximately one half meter above the CTD sensors on the rosette. Therefore, Temp and Sal are bin-averaged CTD values representing the next shallower

depth from that recorded by the CTD (CTD Depth) at the time the Niskin bottles were fired with the exception of the surface values, which are the same as the CTD Depth values (as per the log sheet).

The Sample ID is the sample station, cast number and Niskin bottle number for the discrete samples.

DIC (W) Bottle 509 was taken underway, not at any station.

Nutrients:
Analysis Date: 10/01/2015
Nutrient samples were analyzed using a Seal Analytical high resolution digital colorimeter auto-analyzer 3 (AA3). A series of standards for each method were run before sample analysis to obtain a calibration curve for data reduction.
Method 353.4 was used to determine the concentration of nitrate and nitrite for each station (Zhang et al., 1997b). This method used automated, gas-segmented, continuous flow colorimetry for the analysis of nitrate and nitrite. Samples were first passed through a copper-coated cadmium reduction column. Nitrate was reduced to nitrite in a buffer solution. The nitrite was then determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a color azo dye. The absorbance measured at 550 nm is linearly proportional to the concentration of nitrite + nitrate in the sample. Nitrate concentrations are obtained by subtracting nitrite values, which have been separately determined without the cadmium reduction procedure, from the nitrite + nitrate values.
Method 365.5 was used to determine the concentration of orthophosphate for each station (Zimmermann and Keefe, 1997; Zhang et al., 2001). This method used automated colorimetric and continuous flow analysis for the determination of low-level orthophosphate concentrations. Ammonium molybdate and antimony potassium tartrate react in an acidic medium with orthophosphate to form an antimony-phospho-molybdate complex. This complex was reduced to a blue-colored complex by ascorbic acid. The absorbance measured at 880 nm is proportional to the phosphate concentration in the sample.
Method 366.0 was used to determine the concentration of soluble silica for each station (Zhang and Berberian, 1997). This method used automated, gas-segmented, continuous flow colorimetry for the analysis of dissolved silicate concentration. In this method, β-molybdosilicic acid was formed by the reaction of the silicate contained in the sample with molybdate in acidic solution. The β-molybdosilicic acid was then reduced by ascorbic acid to form molybdenum blue. The absorbance of the molybdenum blue, measured at 550 nm, is linearly proportional to the concentration of silicate in the sample.

Zhang, J-.Z. and Berberian, G.A. (1997). Determination of dissolved silicate in estuarine and coastal waters by gas segmented flow colorimetric analysis, *U.S. Environmental Protection Agency, (EPA Method 366.0),* EPA-600-R-97-072.

Zhang, J-.Z., Fischer, C.J. and Ortner, P.B. (2001). Continuous flow analysis of phosphate in natural waters using hydrazine as a reductant. *Intern. J. Environ. Anal. Chem.* 80(1): 61-73.

Zimmermann, C.F., and C.W. Keefe (1997). Determination of orthophosphate in estuarine and coastal waters by automated colorimetric analysis. *U.S. Environmental Protection Agency (EPA method 365.5)*, EPA-600-R-97-072.

Zhang, J.-Z., Ortner, P.B. and Fischer, C.J. (1997b). Determination of nitrate and nitrite in estuarine and coastal waters by gas segmented continuous flow colorimetric analysis. *U.S. Environmental Protection Agency (EPA Method 353.4)*, EPA-600-R-97-072.

Operation Manual (2008), AutoAnalyzer 3 high resolution, Seal Analytical. *Publication No. MB7-31EN-02*, (February 2008).

UPDATE:
Between March and May of 2021, all of the data for the discrete samples was put into a uniform format. The supporting information was checked for accuracy, especially the expocode, date, time, and positions. Additionally, pH results were recalculated to 20 and 25 degrees Celsius.