# Development of a Continuous Flow Analysis System for Trace Iron

-Data Report-

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# 2 Introduction

Iron levels in the surface ocean are generally very low—in the picomolar to nanomolar range—reaching levels as low as 0.1 nM as a result of biological uptake [Bruland and Rue 2001; Measures 1995]. Iron's role as an essential nutrient for phytoplankton suggests that it may play a major role in determining total biomass and community structure [Bruland 2001, Johnson, 2001]. In much of the ocean, iron is assumed to be the limiting nutrient [Bruland, Lohan 2003]. While this is especially true for the open ocean, coastal oceans may also experience iron limitation [Bruland, 2001, Hutchins and Bruland, 1998, Johnson, 2001].

To better understand iron's role in determining the rate of phytoplankton growth, and by extension, the rate of carbon uptake in the coastal ocean the measurement of iron was included as part of the SUCCES (Seasonal Upwelling Coastal Carbon Export and Sequestration) cruises in summer 2009. We needed to develop a system to measure iron concentrations using a continuous sample stream from our towed pump vehicles, SuperSucker and SeaSoar.

Iron's relative scarcity combined with its ubiquity in the human environment makes it a challenge to measure. Methods must be very sensitive but also minimize the potential for contamination by minimizing the exposure of samples to the open air. For our purposes, the system must also be able to quickly measure iron in a continuous sample stream to resolve iron gradients in the shelf waters.

Iron has been measured to a high degree of accuracy by several methods. Inductively coupled plasma mass spectrometry (ICPMS), a highly sensitive method, is very useful in the laboratory [Wu and Boyle, 1998] but is not a feasible method of shipboard analysis. Electrochemical techniques, including cathodic stripping voltammetry, can be used at sea and can give speciation data. Electrochemistry can only be used on discrete samples.

Two other analysis methods can be used to measure iron. Flow injection analysis (FIA) is the most common measurement of iron done at sea. FIA relies on discrete injections of sample into a constant carrier fluid that then mixes with a reagent stream and flows to the detector. FIA has been used for continuous analysis of surface waters [Measures, 1995; Johnson, 2001; Chase, 2005] because of its ease of use, efficient sampling, and high precision [Zhang 2001]. The total analysis time of approximately 5 minutes per sample (Measures 1995) leads to both smearing (due to load time) and lack of the desired temporal resolution. In classical continuous flow analysis (CFA), the sample stream continuously flows into the stream of reagents and this reaction mixture is continuously delivered to the detector. When used in this way, CFA generates results that may be "smeared."

To achieve our goal of very high frequency measurements, we have adapted the CFA method by segmenting the sample with injected air bubbles in a process called gas segmented continuous flow analysis (GSCFA). It would allow for high temporal resolution of our sample stream with minimal smearing. GSCFA has been used successfully by Hales, et. al. [2004] for high resolution nitrate measurements in similar shipboard settings. GSCFA allows for higher frequency measurements than FIA as there is no pre-concentration column, the absence of a column also reduces smearing. In addition, this method, like FIA, minimizes the sample handling which can lead to contamination [Weeks 2002].

We have developed a continuous flow analysis (CFA) system capable of high frequency measurements to profile the bottom boundary layer with chemistry based on previous flow injection analysis systems (FIA) utilizing N,N-dimethyl-p-phenylenediamine dihydrochloride (DPD) [Measures et al. 1995; Sedwick et al. 1997; Weeks and Bruland 2002; Chase 2005].

# 3 Methods

## 3.1 Equipment set up

*Refer to figure 1*

The CFA set up is contained in a plastic box that has been modified specifically for this purpose (see Figure 1). The input ports for DPD, buffer, and H2O2 all have check valves to prevent reagent contamination. There is also an input port for the sample and seven ports connected to the VCI ChemInert (06U-0396L) valve for the sample and standards.

Reagents were kept in a AirClean 600 PCR workstation clean air hood and pumped into the CFA box. PTFE 1/16" OD x 0.5mm ID plastic tubing is used to draw the reagents from the hood to the Ismatec (C.P. 7800-40) peristaltic pump. Various sizes of Cole Parmer peristaltic pump tubing are used to deliver the appropriate reagent mixture—DPD, acid, and air are delivered in tygon 0.38mm ID, buffer and sample in Pharmed BPT 0.89 mm ID, and H2O2 in Pharmed 0.51 mm ID.

The buffer and DPD are then mixed and run through a GE Healthcare HiTrap 1mL (17-0408-01) chelating column. H2O2 is then added to the reaction mixture. The sample is combined with 0.10N HCl and flowed through three 25-turn glass coils (approx ID 1mm). After acidification is complete, the reaction mixture and acidified sample are combined and flowed through one 25-turn glass coil before flowing to the photodiode detector and out of the box to a waste bottle. The photodiode is connected to a Macintosh computer via a National Instsruments USP 6009 card and data is collected using a LabView program written by Burke Hales.

The peristaltic pump is set at 35 which generates reagent flow rates of 0.92 mL/min for DPD (5.25 mM/min), 0.315 mL/min for buffer, 0.10 mL/min for H202, 0.328 mL/min for sample, and 0.092 mL/min for acid. This gives a total flow of 0.84 mL/min. The temperature of the acidification coil was controlled to 40°C while the reaction coil was not temperature controlled.

## 3.2 Reagents

DPD is ordered in a powdered form (both Sigma and Fluka were used during this research) and stored in the refrigerator to prevent oxidation. The reagent is prepared daily as a mixture of 0.6 g DPD in 60 mL of MilliQ H2O plus 4uL/mL HCl. Hydrogen peroxide is mixed as needed. The reagent is mixed as 125 mL of a 5% solution made from J.T. Baker Ultrex II ultrapure 30% H2O2.

1L of buffer is made from 170 mL isoplastically distilled NH4OH (~4M) and 70 mL J.T. Baker Ultrex II ultrapure glacial acetic acid and filled to 1L with MilliQH2O. The pH is then measured and adjusted to 6.3 with NH4OH. The acidification solution is 0.1 N HCl mixed in 500 mL batches from J.T. Baker Ultrex II ultrapure hydrochloric acid.

Two stock iron solutions (14.46 µM and 189 nM) were made in MilliQ (with 1 mL 6N HCl/125mL) from Ultra Scientific Analytical Solutions commercial iron standard (10,000 µg/mL). The standards used for running the instrument were made from these two standards with seawater (at pH 6) chelated in a GE Healthcare HiTrap 5mL chelating column. These standards were acidified at 4uL/mL. Standards varied from 0.4 nM to as high as 100 nM and still remained in a linear range.

## 3.3 Shipboard setup

*Refer to Figure 2*

On board R.V. Wecoma, water was pumped from the underwater towed vehicle Supersucker and then routed into the wet lab using nylon tubing. The sample was collected via a tangential flow filter (TFF) built and designed by Chris Holm. The TFF was fitted with a 0.2 micron 47 mm filter that had been rinsed in acid and stored in 10% HCl. A bypass loop was constructed around the TFF to prevent flow disruptions downstream. A Polyethylene line from the surface towed iron fish was also plumbed to the GSCFA so it could run either supersucker or surface fish sample.

## 3.4 Sample collection

Discrete samples were collected on the cruises in several different ways. Some samples were collected at the sink outlet of the supersucker. These were collected in a syringe rinsed with the flow three times and then filtered with an acid rinsed 0.45 micron Supor membrane PALL Life Sciences IC Acrodisk 25mm syringe filter and acidified. Other samples were collected at the input to the GCFA system. These samples were collected with a syringe in two ways: via the tangenial flow filter or from the sample flow and filtered as with the samples collected at the sink. All samples were treated with 240 µL 6N HCl per 60 mL of sample.

CTD samples were collected in a similar manner. We were second to sample the CTD bottles (after methane sampling). A PALL SUPOR AcroPak 200 0.2 micron cartridge filter was affixed to the spout and allowed to flush for about a minute before collecting 60 mL samples. These samples were also acidified with 240 µL 6N HCl per 60 mL of sample.

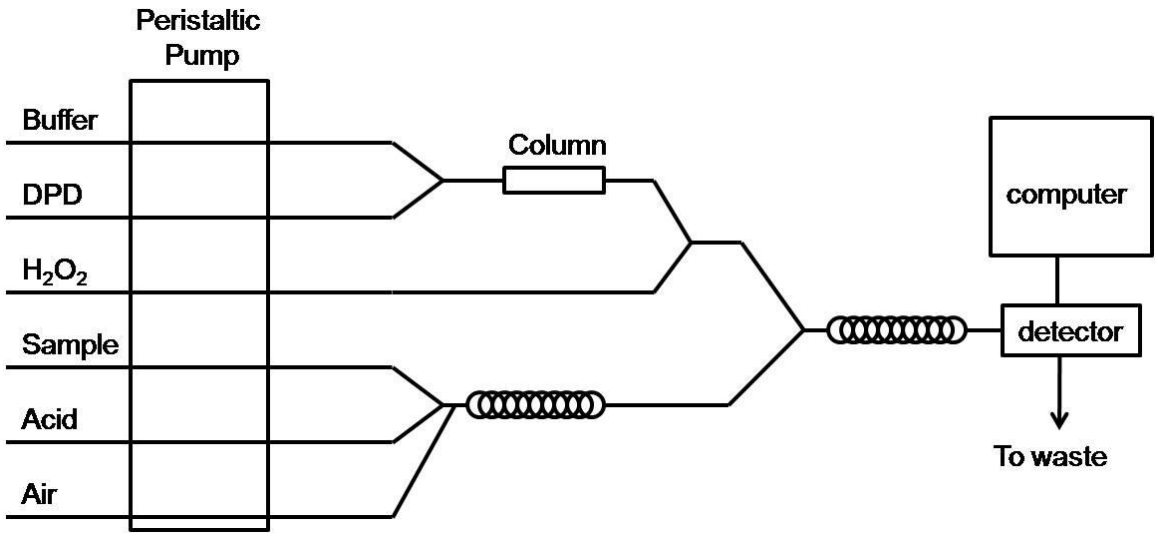


Figure 1: GCFA Schematic

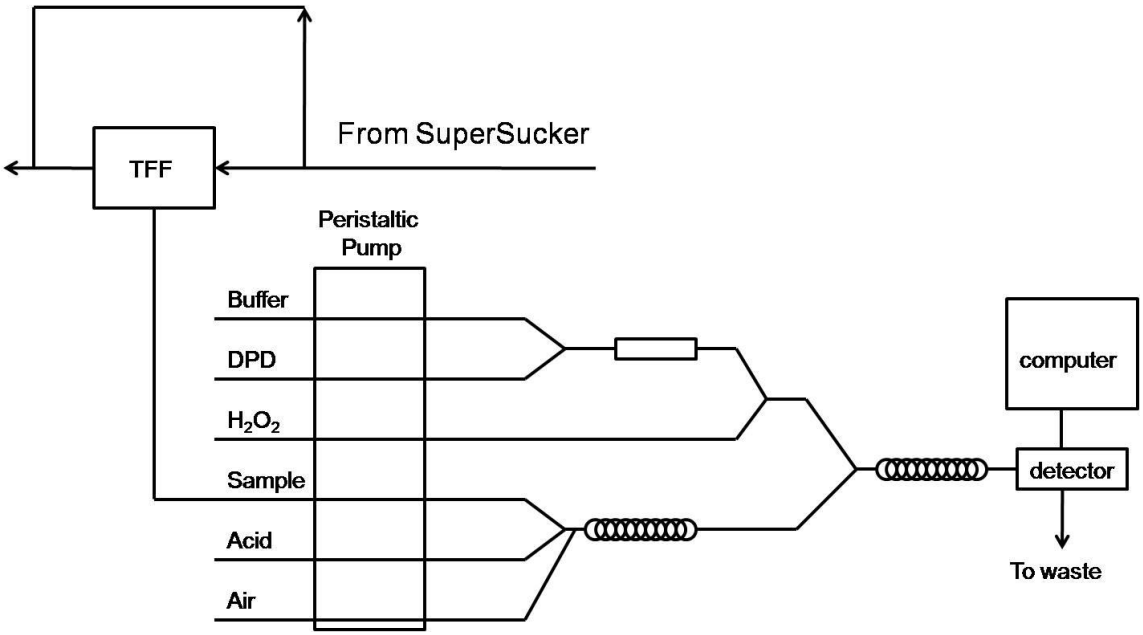


Figure 2: GCFA as on SXS Cruises

# 4 Results

## 4.1 Lab tests

The system was tested in the lab to prepare it for deployment on the SUCCES cruises throughout 2008 and through the early summer of 2009. After deployment on SXS2, the system was tested further, especially with respect to the disagreement between discrete and inline samples (see May 26 and final discussion), before it was deployed on SXS3

### 4.1.1 High-low comparisons and response time

Several tests of a high-low response were conducted to determine the response time of the system. These tests were rather inconclusive as the response time seemed to vary in an undermined fashion.

The run conducted in February 2009 (see chart below) illustrated the typical response of an inital fast response followed by a longer and slower secondary tapering. This test was done with two standards alternating back and forth. There does appear to be a drift problem evident in this sample—this result was not consistently reproducible. The high standard in this case was beyond the linear range of the system at 225.5 nM which may have had other effects on the system.

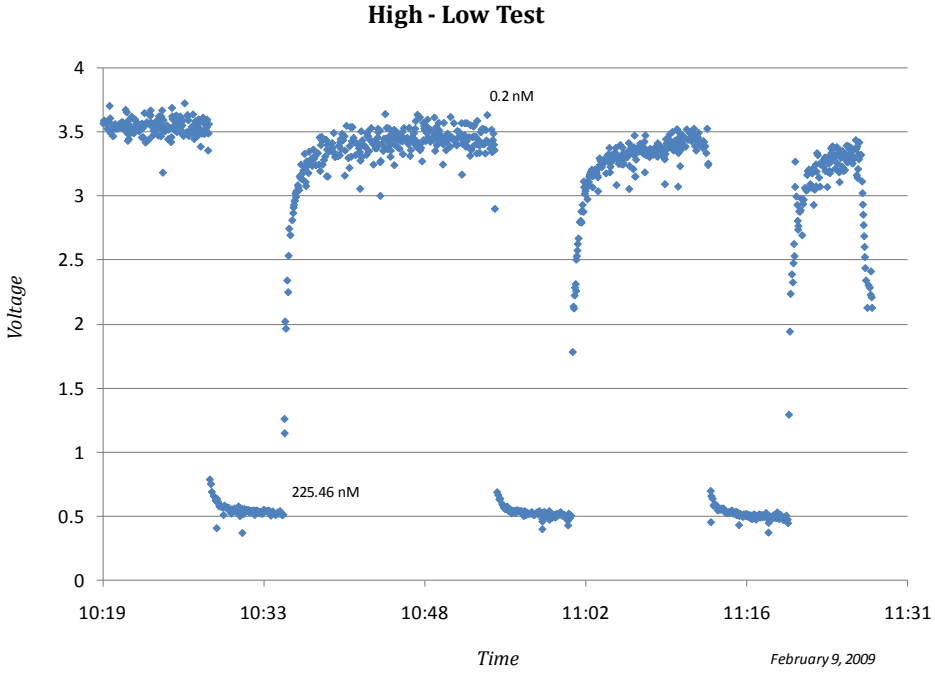


Figure 3: Laboratory high-low testing (1)

A test using two different standards (mixed at the same time as the example above) showed very little drift in the lower standard but still maintains the fast initial response followed by a slower magnitude tapering.

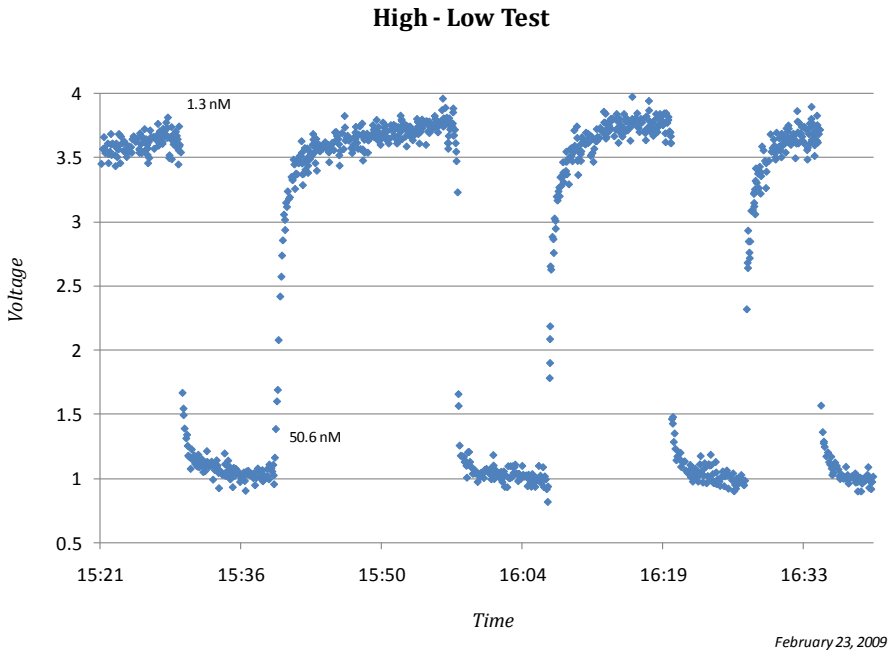


Figure 4: Laboratory high-low testing (2)

The system has shown the ability to give repeatable fast results. In the test (chart below) conducted on August 7, 2008 a one meter plastic reaction coil was used. There was no inline acidification. This test shows little to no drift, consistancy in the curve shape, and relatively fast responses.

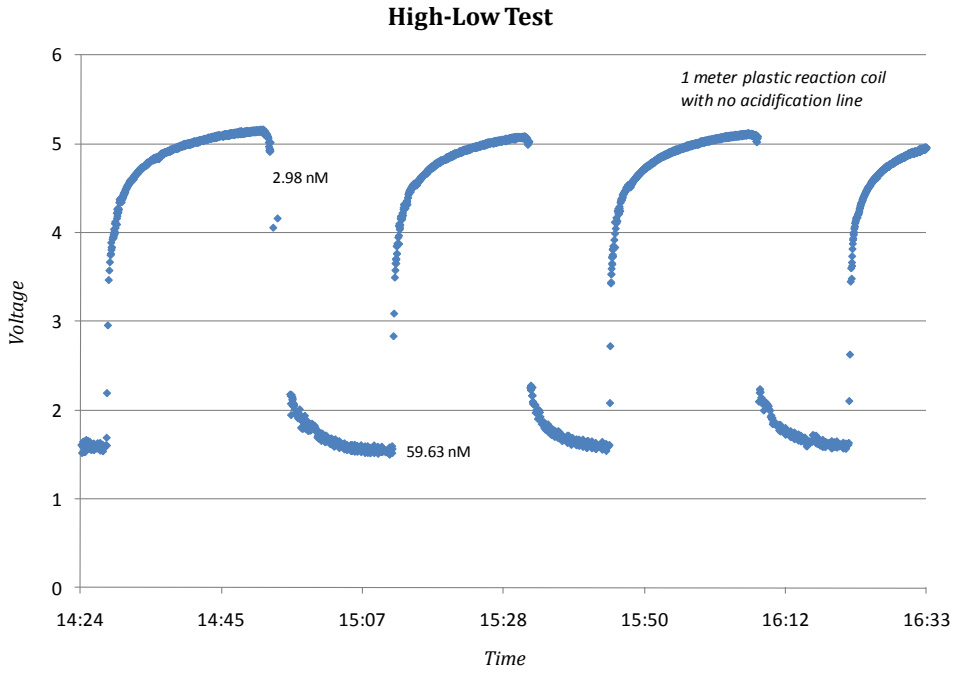


Figure 5: Laboratory high-low testing (3)

An overlaid look at the data shows the February dates had very similar response times. This is to be expected because very little changed in the system

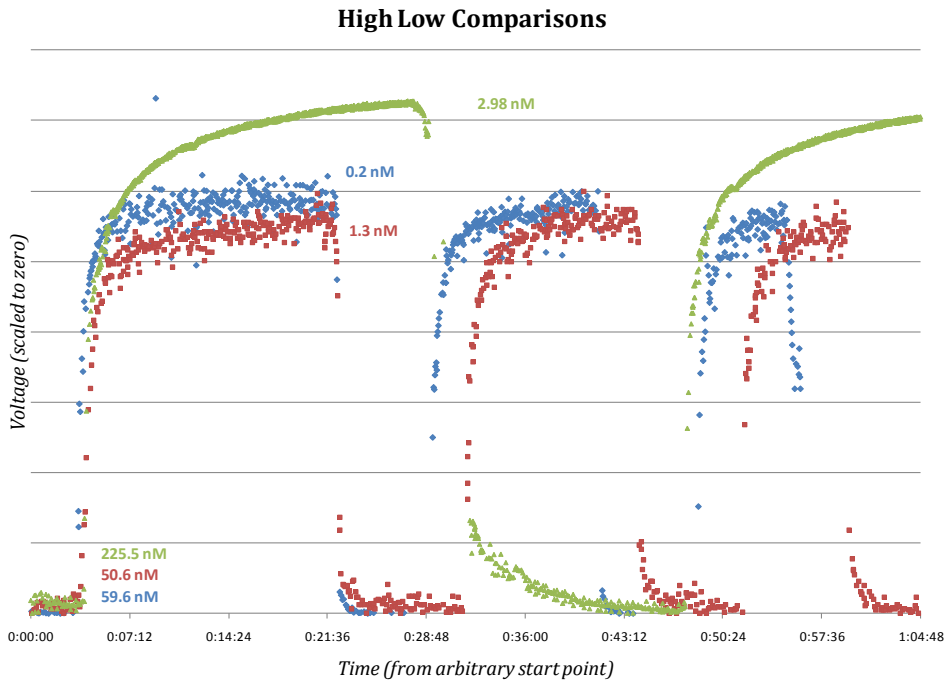


Figure 6: High-Low Test Comparison

### 4.1.2 Acidification and pH

Acidification was ruled out as a possible cause of the discrete and underway mismatches through a series of laboratory tests.

First, a set of five 60 mL standards (0.19, 0.91, 2.81, 9.26, 51.19), plus a blank, was mixed and acidified to the usual level of acidification used for standards (240 µL 6N HCl/60 mL sample). These samples were run in the GCFA with the inline acidification line removed. After each sample was run, they were acidified with an additional 240 µL 6N HCl and run again as “double acidified” samples. The standards and blank were acidified one more time with 240 µL 6N HCl and run as “triple acidified” samples. There were no significant differences between the absorbancies of single, double, and triple acidified standards as seen in the chart below.

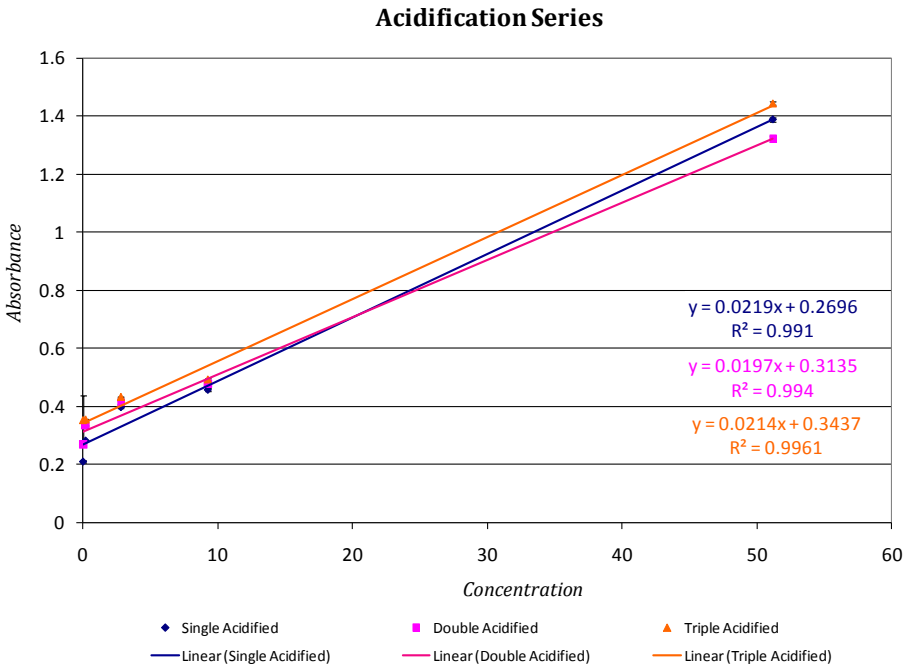


Figure 7: Acidification Series

A second test of acidification was conducted to be sure that the acidification line itself was not the cause of the offsets. For this test, a sample of approximately 20 nM was made up in unchelated seawater and allowed to sit for approximately 1 hour to allow for any iron to stick to the sides of the bottle. This sample was then run and acidified via the inline acidification system with 0.25, 0.10, and 0.05 N HCl. This sample was then transferred to a new bottle and acidified with 240 µL 6N HCl and run with the same range of acids. There is still some variation in the absorbances however the magnitude of this variation is not large enough to completely explain the difference between discrete and underway measurements.

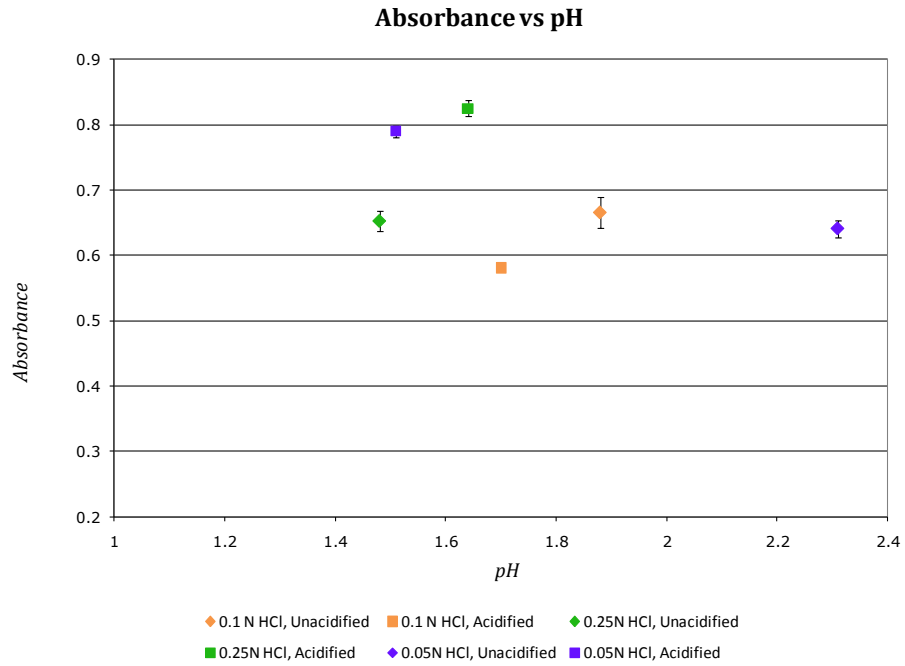


Figure 8: pH effects

### 4.1.3 Temperature

The effect of temperature was also tested as a possible source of the discrete and underway sample mismatch. This test was conducted by making up a 125 mL sample of approximately 20 nM. The sample was allowed to sit for approximately one hour for iron to stick to the sides of the bottle. The sample was then divided into four vials. The two of the vials were acidified and two were left unacidified. One of each sample was then placed into a 10°C chiller. The samples were then run with both 0.05 and 0.10 N HCl to control for the effects of pH.

The results of this test are shown in the figure below. There is a large variation between the samples acidified to the higher pH levels (pH 2.3, and pH 1.9) and the lower pH levels (pH 1.7 and pH 1.5) however in practice the sample is always acidified to at least pH 1.7. There is no significant trend between the sample run at 10°C and the sample run at room temperature. This is probably partially attributable to the acidification tubing being heated to 40°C which may minimize the temperature differences during the reaction. Within the pH 1.7 and pH 1.5 samples the variation is similar to that seen during the acidification tests pointing towards a yet undetermined source of variation.

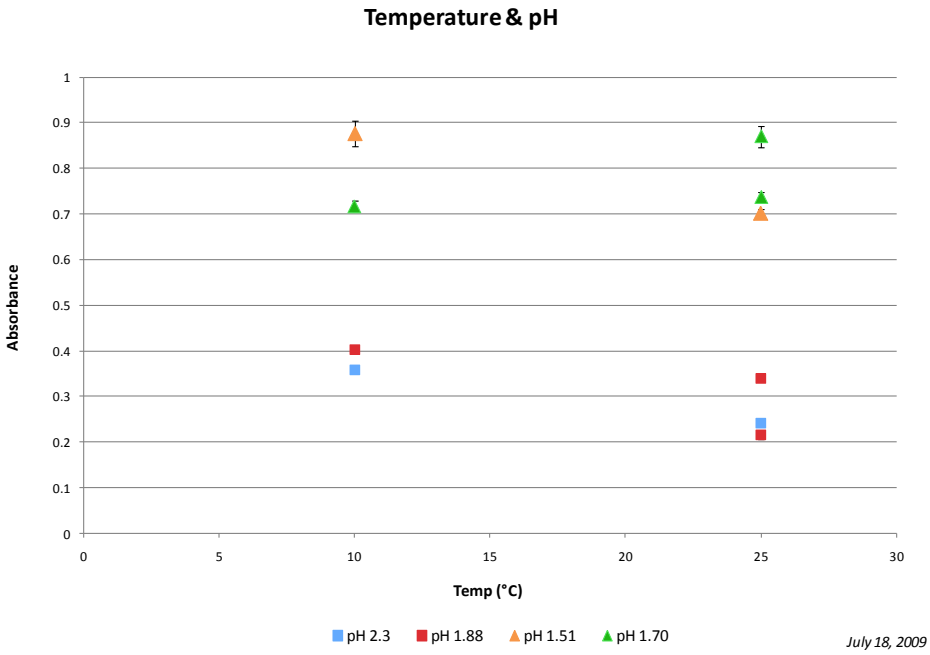


Figure 9: Temperature effects

## 4.2 Lab results

The discrete samples collected during SXS2 did not match the values measured during the underway analyses. *See section 4.3.1.1.3 (May 26).*

The above tests were conducted during June and July 2009 to determine the origin of the mismatch and to resolve the problem before the beginning of SXS3. The problem still appeared to be an issue (see cruise discussion in section 5).

### 4.2.1 Lab results files

**Table 1: Laboratory data files**

| Date | File | Contents |
|---|---|---|
| 6/13/2008 | 6132008.xlsx | Standard Curve, 5m plastic |
| 6/16/2008 | 6162008.xlsx | Standard Curve, 5m plastic |
| 6/24/2008 | 6242008.xlsx | Standard Curve, 5m plastic |
| 6/25/2008 | 6252008.xlsx | Standard Curve, 5m plastic |
| 6/30/2008 | 6302008.xlsx | Standard Curve, 4m plastic |
| 7/1/2008 | 7012008.xlsx | Standard Curve, 4m plastic |
| 7/7/2008 | 7072008.xlsx | Standard Curve, 3m plastic |
| 7/10/2008 | 7102008.xlsx | Standard Curve, 4m plastic, 40°C |
| 7/21/2008 | 7212008.xlsx | Standard Curve, 3m plastic |
| 7/23/2008 | 7232008.xlsx | High-Low drift test |
| 7/25/2008 | 7252008.xlsx | Standard Curve, 3m plastic |
| 7/28/2008 | 7282008.xlsx | High-Low drift test |
| 8/1/2008 | 8012008.xlsx | Standard Curve, 3m plastic |
| 8/5/2008 | 8052008.xlsx | 1m plastic coil tau estimation |
| 8/6/2008 | 8062008.xlsx | 2m plastic coil tau estimation |
| 8/8/2008 | 8082008.xlsx | 2m plastic high-low |
| 8/11/2008 | 8112008.xlsx | 3m plastic high-low |
| 8/12/2008 | 8122008a.xlsx | 4m plastic high-low |
| | 8122008b.xlsx | 5m plastic high-low |
| 8/27/2008 | 8272008.xlsx | PreSXS1 acidification testing |
| 11/2/2008 | 11022008.xlsx | Standard Curve |
| 11/21/2008 | 11212008.xlsx | Glass tubing |
| 1/5/2009 | 1052009.xlsx | Pump samples |
| 2/9/2009 | 2092009.xlsx | High-low drift test |
| 2/23/2009 | 2232009.xlsx | High-low drift test |
| 3/2/2009 | 3022009.xlsx | Pump samples |
| 4/13/2009 | 4132009.xlsx | Standard curve, 5m plastic |
| 4/14/2009 | 4142009.xlsx | Standard curve, 3m plastic |
| 4/23/2009 | 4232009.xlsx | No-bubble run |
| 4/27/2009 | 4272009.xlsx | Manual bubble run |
| 6/18/2009 | 6182009.xlsx | 1x, 2x, 3x acidification test |
| 6/22/2009 | 6222009.xlsx | SXS2 Samples |
| 7/16/2009 | 7162009.xlsx | pH effect test |
| 7/18/2009 | 7182009.xlsx | Temperature effect test |
| 9/14/2009 | 9142009.xlsx | SXS3 samples |
| 9/15/2009 | 9152009.xlsx | SXS3 samples |
| 9/16/2009 | 9162009.xlsx | SXS3 samples |
| 9/23/2009 | 9232009.xlsx | New vs cruise standards |
| 10/7/2009 | 10072009.xlsx | Holm/Lakin standard comparison |
| 10/8/2009 | 10082009.xlsx | Fluka vs Sigma DPD test |
| | HighLowComparisons.xlsx | Figure 6 and data |

## 4.3 Cruise Results

*Internal lag times are estimated from the recorded time for changing to a new standard to the beginning of the fast initial change in voltage.*

### 4.3.1 SXS2 (May) Cruise

#### *4.3.1.1 Daily Results*

*Times given in the notes section reflect the time the information was recorded.

##### 4.3.1.1.1 May 23—Transect 1, 45°N (SXS2_xsct1)

A transect of 45°N was run on May 23. The system was started several hours before supersucker flow in order to improve bubble quality over results in port call. Some improvement were made during the standards run but most of the bubble progress was made during the early part of the days supersucker flow. The improvements included replacing the bpt links between the glass tubing sections in the acidification coil with Tygon which seemed to improve the bubbles as well as giving us a better view of what happened to the bubbles inside the tubing. It was also determined that a close fit of the glass tubing inside the Tygon connections is imperative to maintaining the bubbles inside the acidification coil so the connections were also changed to Tygon and adjusted in the reaction coil. The reaction coil was also shortened from 4 25-turn coils to 3 coils.

The run was interrupted by some valve switching problems related to the writing of new data files (the system was being run on valve position 2 but when a new file would start it would revert to position 1 and draw air). The system pulled large amounts of air at the end of the run and the second standards run was indecipherable.

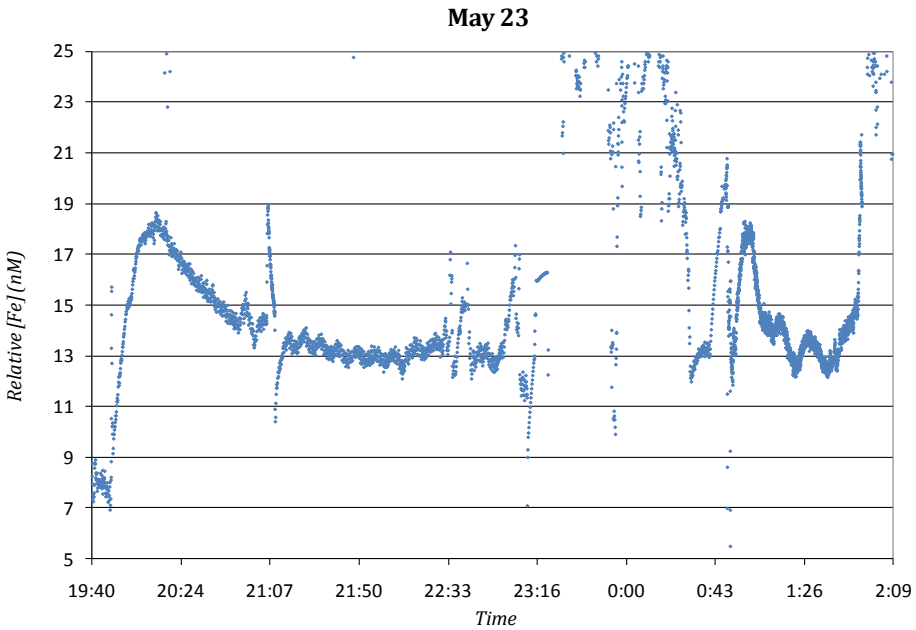


Figure 10: Relative Fe (SXS2_xsct1)

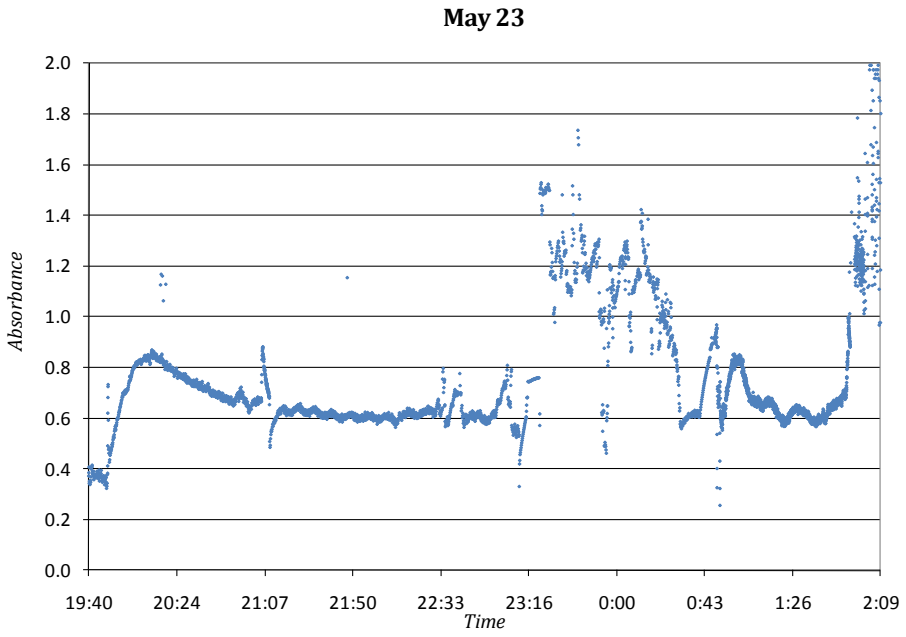


Figure 11: Absorbance (SXS2_xsct1)

**Table 2: SXS2_xsct1 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection limit* | | *Slope* |
|---|---|---|---|---|---|---|---|
| MilliQ | 0.5826 | 0.0186 | n/a | | 0.92 | | 0.0466 |
| Std 1 | 0.6780 | 0.0143 | n/a | | *(Std1)* | | |
| Std 2 | 0.7651 | 0.0196 | n/a | | | | |
| Std 3 | 1.6402 | 0.0461 | n/a | | | | |
| Std 4 | 3.0571 | 0.3232 | n/a | | | | |
| *Average* | | 0.0843 | | | | | |

**Internal Lag time:** ≈15 minutes

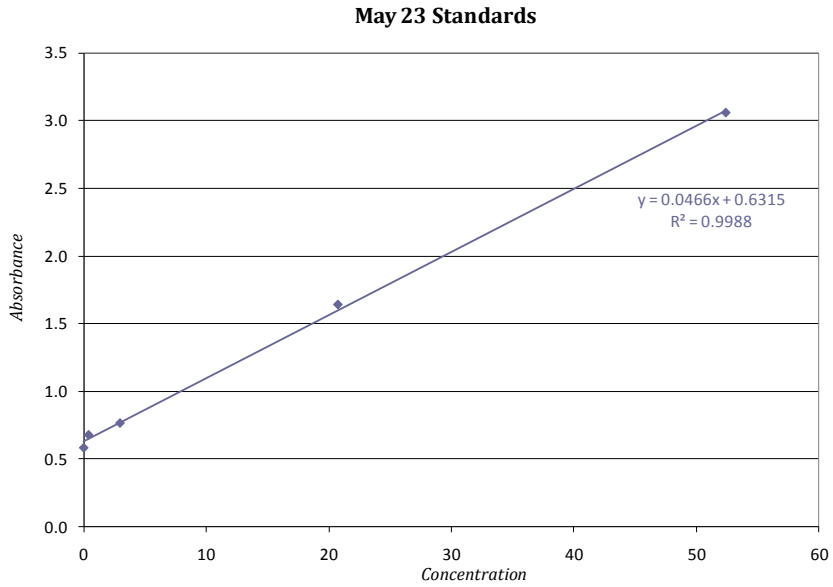


Figure 12: SXS2_xsct1 standards

**Table 3: SXS2_xsct1 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| MilliQ | 0 | 5/23/09 | 17:44 | 0.5826 | 0.01856 |
| Std 1 | 0.4 | 5/23/09 | 17:55 | 0.6778 | 0.01427 |
| Std 2 | 2.96 | 5/23/09 | 18:05 | 0.7651 | 0.01963 |
| Std 3 | 20.75 | 5/23/09 | 18:20 | 1.6402 | 0.04610 |
| Std 4 | 52.41 | 5/23/09 | 18:41 | 3.0571 | 0.32318 |

**Table 4: SXS2_xsct1 notes**

| | | |
|---|---|---|
| 5/23/09 | 15:50 | reagents running |
| 5/23/09 | 17:10 | replacing glass tubing links, improving bubbles |
| 5/23/09 | 17:33 | begin standards |
| 5/23/09 | 19:08 | air stuck in the line |
| 5/23/09 | 19:26 | begin supersucker transect (45°N); allow lines to flush ~10 minutes before running |
| 5/23/09 | 19:35 | begin supersucker flow to GCFA |
| 5/23/09 | 20:50 | accidental valve switch |
| 5/23/09 | 22:13 | noticed slow upward trend of voltage; there are small oscillations within the trend |
| 5/23/09 | 22:39 | acidification/reagents junction made more direct |
| 5/23/09 | 23:34 | changed to larger pump tubing for bubbles with inconclusive results; also changed to larger ID link between bubble injection and acidification line which seemed to make things worse so returned to smaller ID; perfected fits between glass tubing which seems to make the flow more even |
| 5/24/09 | 0:52 | changed to tygon links in the reaction coil; switched from 4 coils to 3 |
| 5/24/09 | 1:56 | drawing air during standards; abandon run |

#### 4.3.1.1.2 May 25—Patch day 1 (SXS2_srvy1)

May 25, 2009 was the first day of surveying the tracer patch during SXS2. The system was run with only three 25-turn glass coils in the acidification line and one 25-turn coil as the reaction line. Some experimentation was done with the temperature but increasing the temperature to 50°C only seemed to boost noise so it was returned to 40°C. Two discrete samples were run (#128 and #111) during the run. A vertical profile was conducted at the end of the day (5/26, 6:04) that included some surface pumping before shutting down.

Overall, the days run was very noisy. This is most likely related to bubble issues but could also be caused by contamination from the supersucker line or opening the system lines for adjustment.

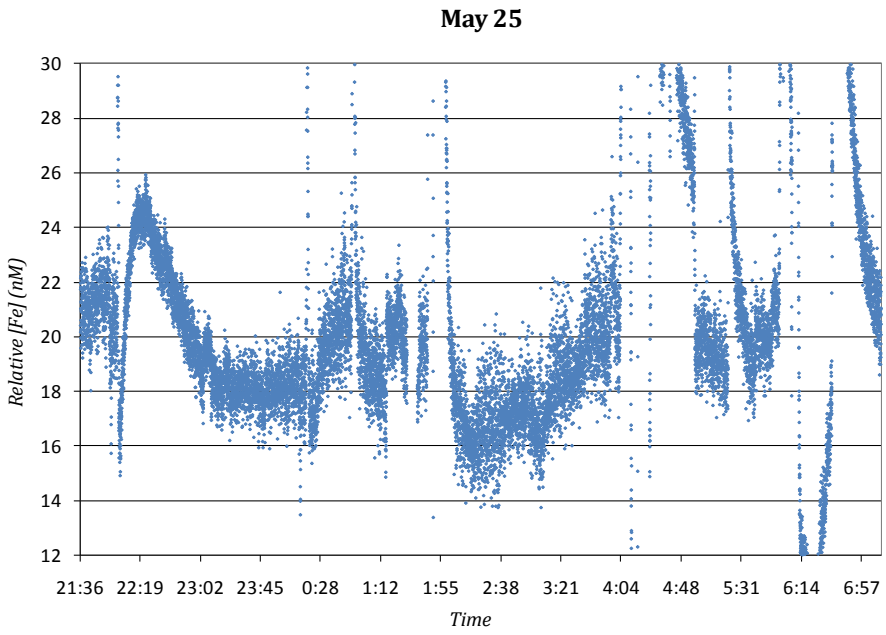


Figure 13: Relative [Fe] (SXS2_srvy1)

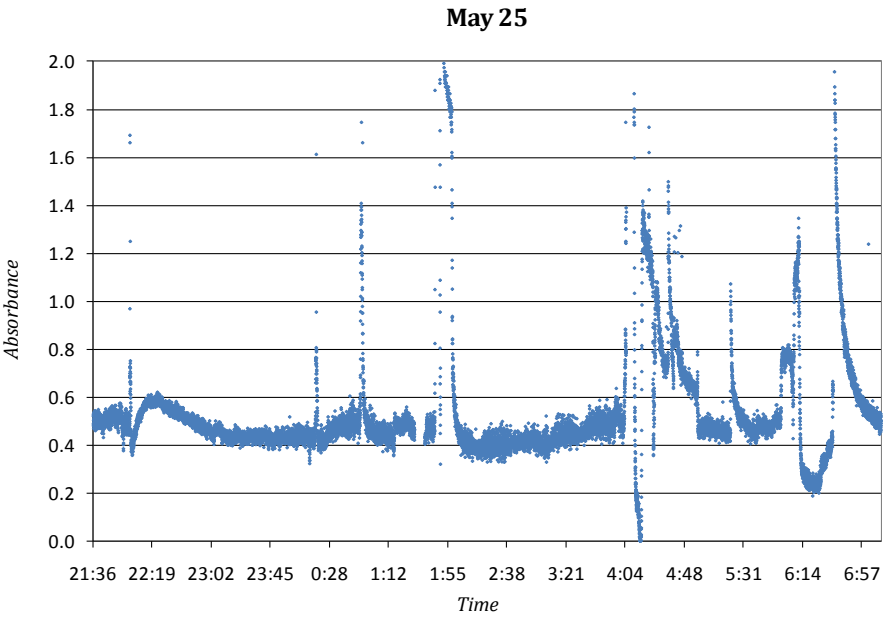


Figure 14: Absorbance (SXS2_srvy1)

**Table 5: SXS2_srvy1 standards**

| **Summary** | | | | | | | |
|---|---|---|---|---|---|---|---|
| *Standard* | *Absorbance* | *Stdev* | *Drift (Abs 3-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
| MilliQ | 0.8015 | 0.2796 | 0.2761 | | 5.066 | | 0.0239 |
| Std 1 | 0.9286 | 0.2620 | 0.4102 | | (2st Std1) | | *Slope 1:* |
| Std 2 | 0.9890 | 0.0468 | 0.3065 | | | | 0.0273 |
| Std 3 | 1.7363 | 0.1518 | 0.0520 | | | | *Slope 2:* |
| Std 4 | 2.0416 | 0.2648 | -0.4264 | | | | 0.0321 |
| *Avg* | | 0.1813 | | | | | *Slope 3:* |
| | | | | | | | 0.0139 |

**Internal Lag time:** ≈ 7 minutes

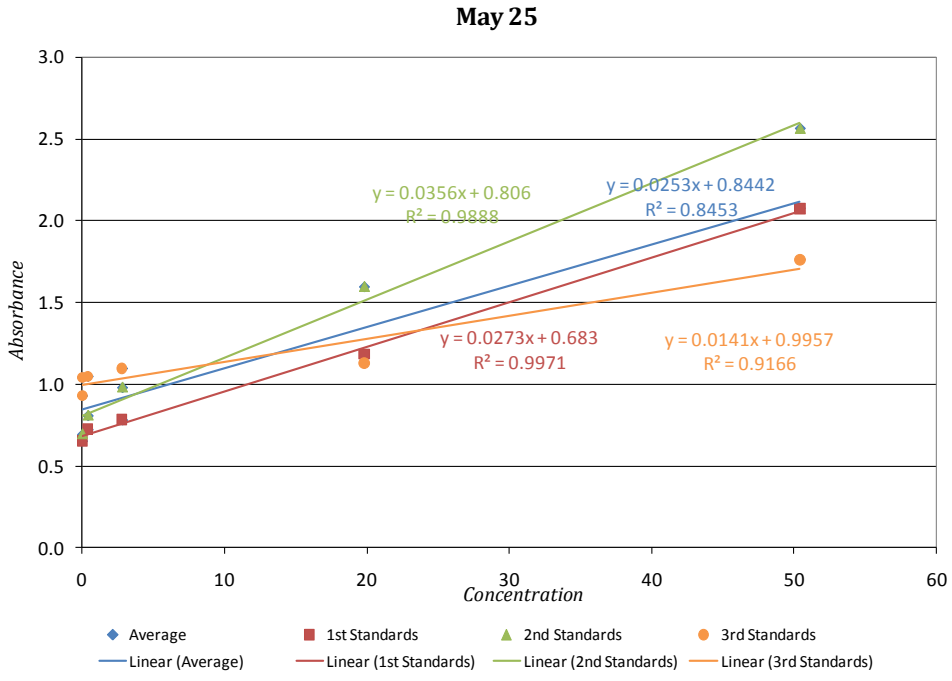


Figure 15: SXS2_srvy1 standards

**Table 6: SXS2_srvy1 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| Std 1 | 0.4 | 5/25/2009 | 15:39 | 0.7248 | 0.04925 |
| Std 3 | 19.8 | 5/25/2009 | 15:49 | 1.1840 | 0.03147 |
| Std 2 | 2.81 | 5/25/2009 | 16:00 | 0.7831 | 0.04634 |
| Std 4 | 50.41 | 5/25/2009 | 16:12 | 2.0746 | 0.06301 |
| MilliQ | 0 | 5/25/2006 | 16:26 | 0.6546 | 0.03609 |
| MilliQ | 0 | 5/25/2009 | 20:38 | 0.6947 | 0.03698 |
| Std 3 | 19.8 | 5/25/2009 | 20:50 | 1.5953 | 0.05201 |
| Std 1 | 0.4 | 5/25/2009 | 21:03 | 0.8091 | 0.03851 |
| Std 4 | 50.41 | 5/25/2009 | 21:15 | 2.5615 | 0.07372 |
| Std 2 | 2.81 | 5/25/2009 | 21:25 | 0.9807 | 0.05481 |
| MilliQ | 0 | 5/26/2009 | 5:10 | 1.0434 | 0.03640 |
| Std 1 | 0.4 | 5/26/2009 | 5:37 | 1.0492 | 0.04120 |
| Std 2 | 2.81 | 5/26/2009 | 5:47 | 1.0978 | 0.04550 |
| Std 3 | 19.8 | 5/26/2009 | 5:53 | 1.1288 | 0.04339 |
| Std 4 | 50.41 | 5/26/2009 | 6:02 | 1.7623 | 0.03743 |
| MilliQ | 0 | 5/26/2009 | 7:36 | 0.9307 | 0.69332 |

**Table 7: SXS2_srvy1 discrete samples**

| **Discrete Samples** | | | | | | | |
|---|---|---|---|---|---|---|---|
| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Conc.* | *Date run* |
| 5/25/2009 | 19:13 | SXS Consistancy Standard | | | | | |
| 5/25/2009 | ?? | #111 | 0.9880 | n/a | 0.05280 | 39.52 | 5/25/2009 |
| 5/25/2009 | 22:31 | #128 | 1.0190 | n/a | 0.03070 | 40.76 | 5/25/2009 |
| 5/26/2009 | 1:40 | #119 | | | | | |
| 5/26/2009 | 6:25 | #122 | | | | | |

**Table 8: SXS2_srvy1 notes**

| | | |
|---|---|---|
| 5/25/09 | 15:05 | begin reagents |
| 5/25/09 | 15:26 | begin standards |
| 5/25/09 | 17:01 | increased temperature of acidification heater |
| 5/25/09 | 17:20 | temperature stabilized at 50°C |
| 5/25/09 | 17:50 | adjusted connections, switched to acid with brij |
| 5/25/09 | 19:13 | changed from 1.3 ID bubble pump tubing to 0.86ID |
| 5/25/09 | 19:23 | turned temperature back down to 40°C |
| 5/25/09 | 20:28 | increased temperature to 50°C |
| 5/25/09 | 20:36 | begin standards |
| 5/25/09 | 21:56 | begin supersucker flow |
| 5/25/09 | 22:31 | begin discrete samples #128 and #111 |
| 5/26/09 | 0:12 | unflitered line |
| 5/26/09 | 0:43 | filtered line |
| 5/26/09 | 1:32 | program froze |
| 5/26/09 | 1:38 | program restart |
| 5/26/09 | 1:50 | valve problem; fixed |
| 5/26/09 | 4:13 | begin standards |
| 5/26/09 | 6:04 | TFF vertical profile followed by surface test |
| 5/26/09 | 6:28 | acidified milliQ |

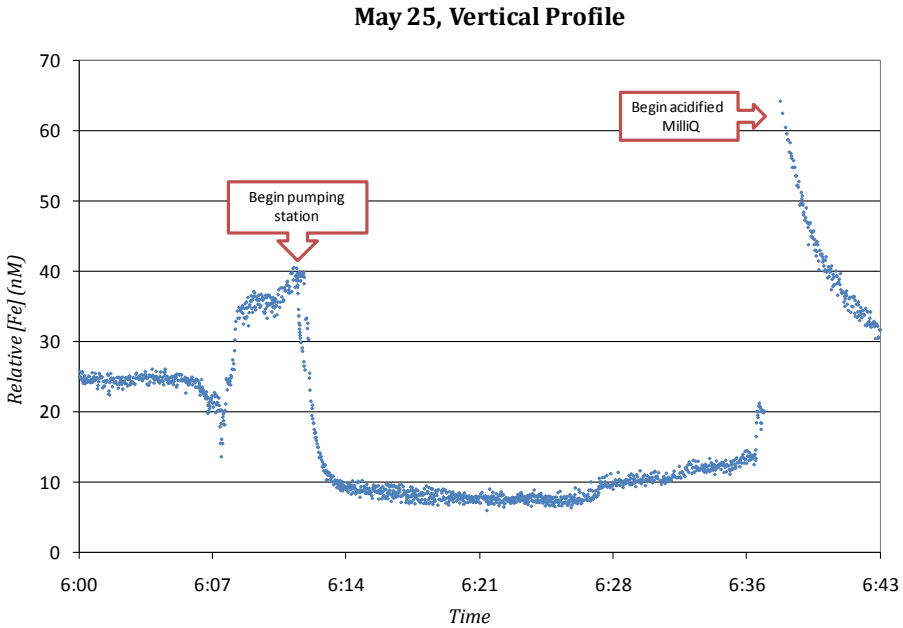


Figure 16: May 25th vertical profile

#### 4.3.1.1.3 May 26—Patch day 2 (SXS2_srvy2)

May 26, 2009 the second day of patch surveying. The signal exhibited little to no variation and was very noisy. The TFF and unfiltered lines were both run. The standards were fairly consistent throughout the entire day. A discrete sample was collected and ran immediately after collection but the sample was off.

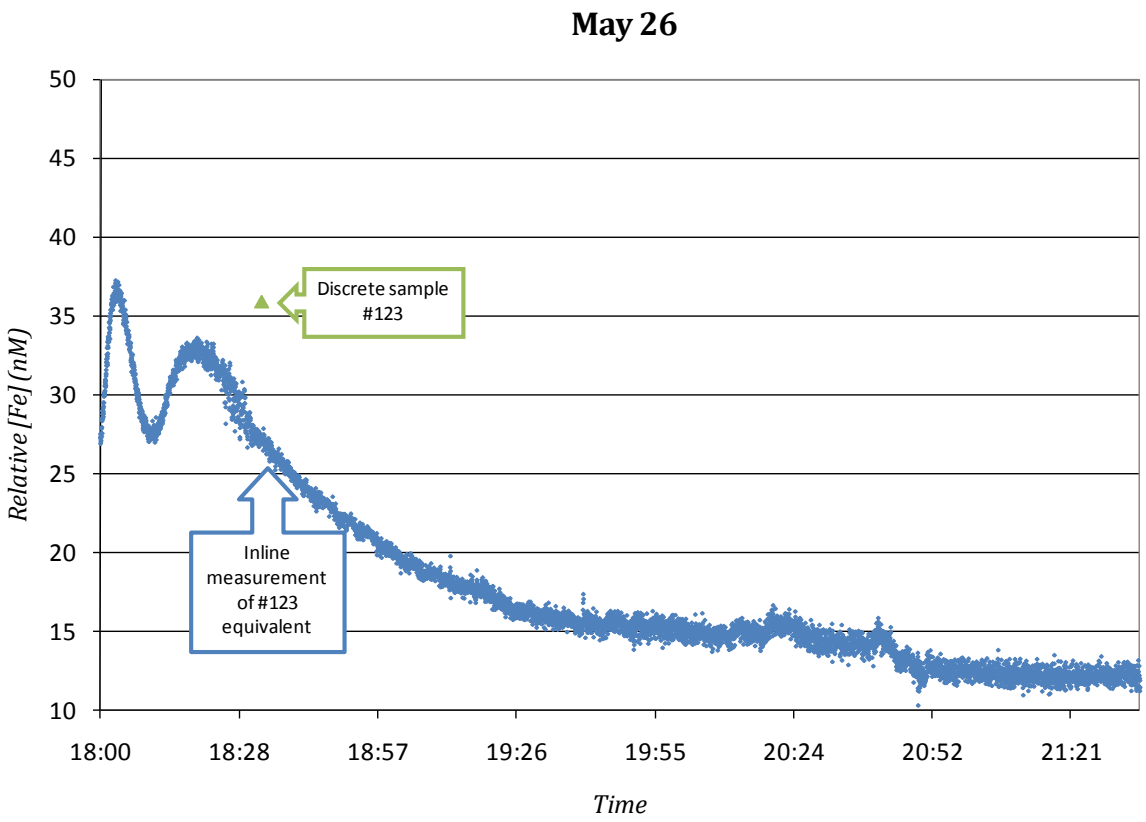


Figure 17: SXS2_srvy2 discrete discrepancy

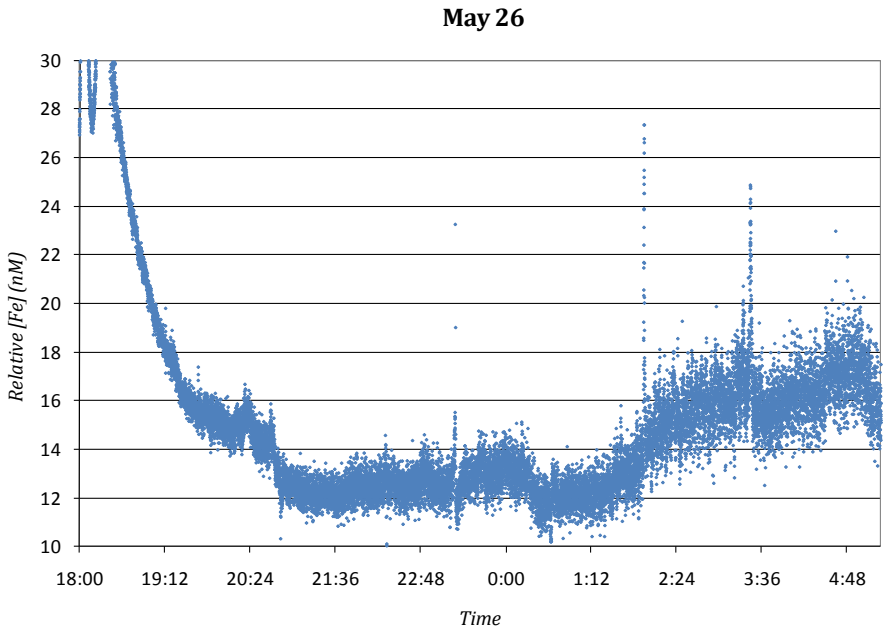


Figure 18: Relative [Fe] (SXS2_srvy2)

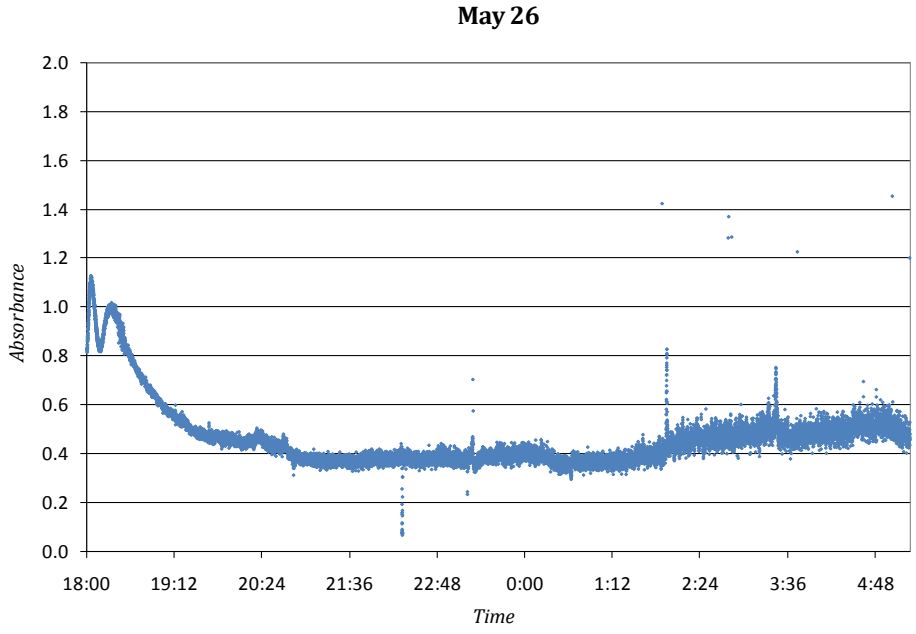


Figure 19: Absorbance (SXS2_srvy2)

**Table 9: SXS2_srvy2 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 3-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| MilliQ | 0.5900 | 0.0449 | n/a | | 4.46 | | 0.0302 |
| Std 1 | 0.8053 | 0.0449 | -0.0363 | | (Std1 avg) | | *Slope 1:* |
| Std 2 | 0.8825 | 0.1343 | -0.0870 | | | | 0.0207 |
| Std 3 | 1.5004 | 0.0559 | -0.0825 | | | | *Slope 2:* |
| Std 4 | 2.2742 | 0.1267 | -0.3537 | | | | 0.0342 |
| *Average* | | 0.1127 | | | | | *Slope 3:* |
| | | | | | | | 0.0233 |

**Internal Lag time:** ≈ 7 minutes

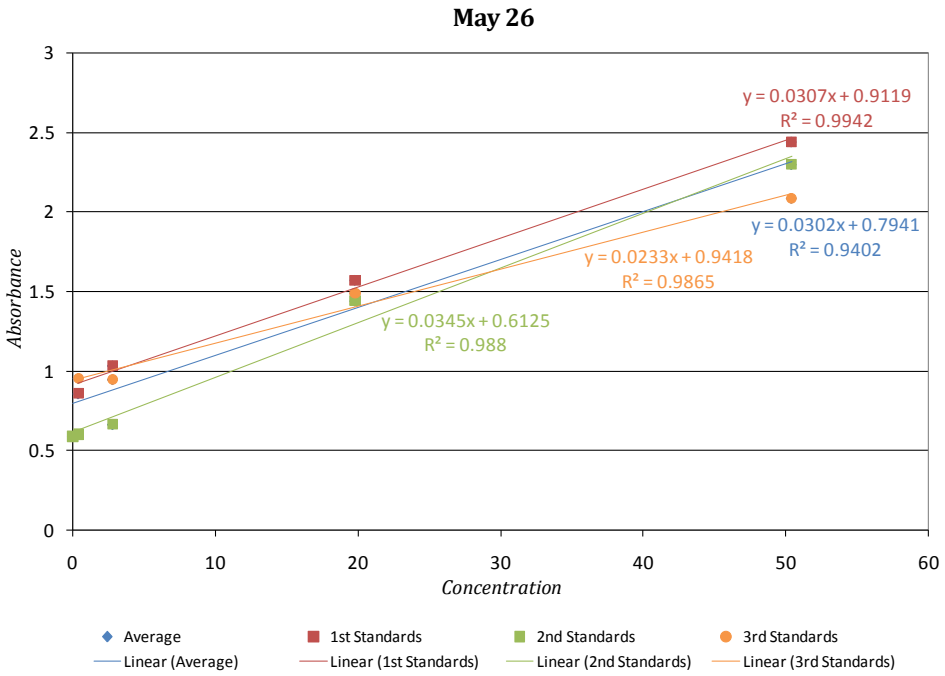


Figure 20: SXS2_srvy2 standards

**Table 10: SXS2_srvy2 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| Std 3 | 19.8 | 5/26/09 | 14:12 | 1.5714 | 0.07189 |
| Std 1 | 0.4 | 5/26/09 | 14:23 | 0.8585 | 0.06954 |
| Std 4 | 50.41 | 5/26/09 | 14:32 | 2.4394 | 0.14349 |
| Std 2 | 2.81 | 5/26/09 | 14:47 | 1.0345 | 0.33084 |
| Std 1 | 0.4 | 5/26/09 | 16:33 | 0.6020 | 0.03182 |
| MilliQ | 0 | 5/26/09 | 16:57 | 0.5900 | 0.37923 |
| Std 2 | 2.81 | 5/26/09 | 17:04 | 0.6654 | 0.03042 |
| Std 3 | 19.8 | 5/26/09 | 17:18 | 1.4408 | 0.04760 |
| Std 4 | 50.41 | 5/26/09 | 17:27 | 2.2975 | 0.13580 |
| Std 1 | 0.4 | 5/27/09 | 7:40 | 0.9553 | 0.03324 |
| Std 2 | 2.81 | 5/27/09 | 7:50 | 0.9475 | 0.04161 |
| Std 3 | 19.8 | 5/27/09 | 8:04 | 1.4889 | 0.04835 |
| Std 4 | 50.41 | 5/27/09 | 8:14 | 2.0857 | 0.10090 |

**Table 11: SXS2_srvy2 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Concentration* | *Date run* |
|---|---|---|---|---|---|---|---|
| 5/26/09 | 18:27 | #123 | 1.0843 | | 0.02217 | 35.91 | 5/26/09 |
| 5/26/09 | 20:23 | #113 | 1.3857 | | 0.01494 | 76.32 | 6/22/09 |
| 5/26/09 | 21:25 | #124 | 1.3617 | | 0.01543 | 74.77 | 6/22/09 |
| 5/26/09 | | #131 | 1.3169 | | 0.03264 | 71.88 | 6/22/09 |
| 5/26/09 | 22:39 | #117 | 1.6391 | | 0.02712 | 92.66 | 6/22/09 |
| 5/27/09 | 0:56 | #115 | 1.2897 | | 0.05613 | 70.12 | 6/22/09 |
| 5/27/09 | 0:01 | #118 | 1.2689 | | 0.01706 | 68.78 | 6/22/09 |
| 5/27/09 | 1:49 | #120 | 1.2505 | | 0.01518 | 67.59 | 6/22/09 |

**Table 12: SXS2_srvy2 notes**

| | | |
|---|---|---|
| 5/26/09 | 13:29 | begin reagents |
| 5/26/09 | 13:51 | begin standards |
| 5/26/09 | 14:39 | running bulk acidified seawater while waiting for supersucker |
| 5/26/09 | 16:21 | standards |
| 5/26/09 | 17:23 | begin supersucker flow |
| 5/26/09 | 18:27 | running discrete sample #123 |
| 5/27/09 | 1:48 | unfiltered line |
| 5/27/09 | 3:20 | TFF line |
| 5/27/09 | 5:11 | begin standards |

#### 4.3.1.1.4 May 27—Patch day 3 (SXS2_srvy3)

May 27 the third day of patch surveying during SXS2. The day ran without many major issues beyond a program freeze. The system was alternated between the TFF and the unfiltered line. Overall, the system seems to have been more variable than usual despite the relatively low detection limit.

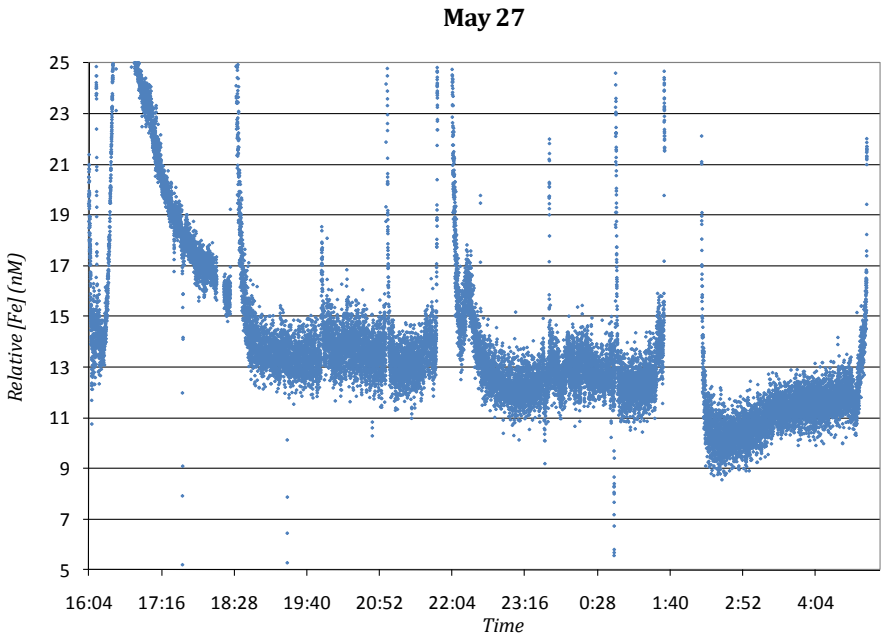


Figure 21: Relative [Fe] (SXS2_srvy3)

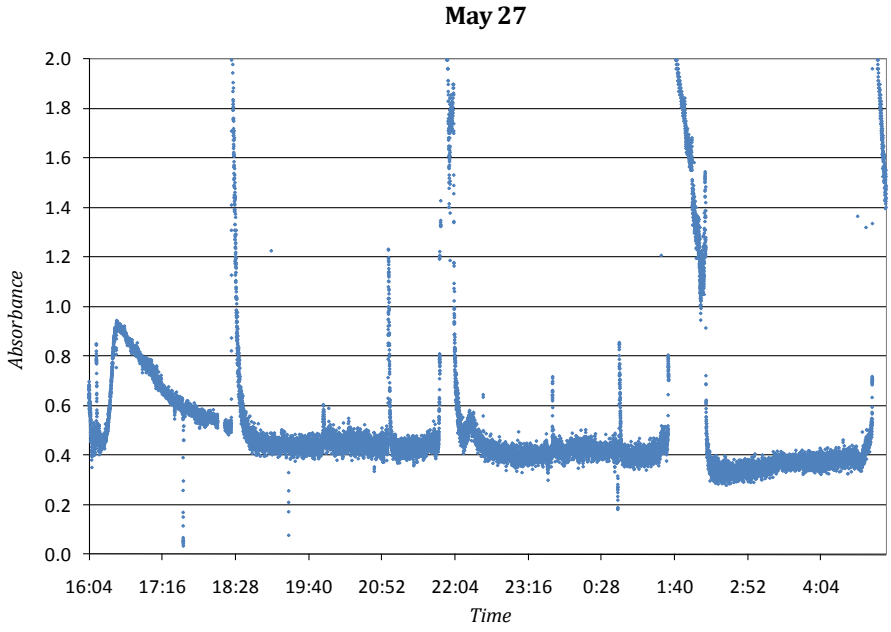


Figure 22: Absorbance (SXS2_srvy3)

**Table 13: SXS2_srvy3 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| MilliQ | 0.8766 | 0.0686 | 0.1953 | | 5.12 | | 0.0326 |
| Std 1 | 1.1487 | 0.0556 | 0.3472 | | (Std1 Avg) | | *Slope 1:* |
| Std 2 | 1.3187 | 0.2153 | 0.2776 | | | | 0.0337 |
| Std 3 | 1.9657 | 0.1335 | 0.2427 | | | | *Slope 2:* |
| Std 4 | 2.5933 | 0.1356 | 2.5933 | | | | 0.0461 |
| *Average* | | 1.4681 | | | | | |

**Internal Lag time:** ≈ 7 minutes

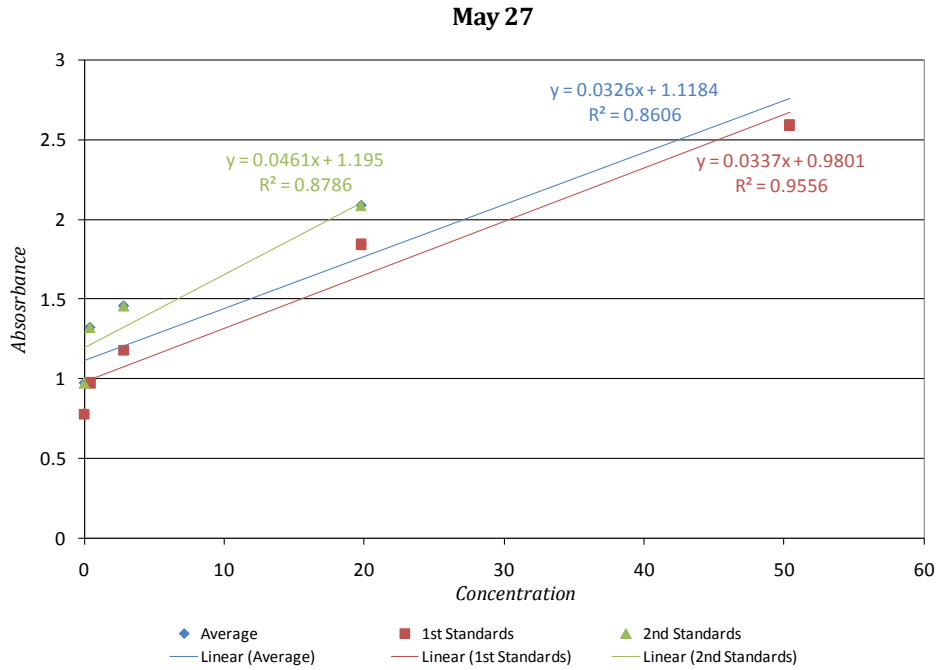


Figure 23: SXS2_srvy3 standards

**Table 14: SXS2_srvy3 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| MilliQ | 0 | 5/27/09 | 15:03 | 0.7789 | 0.03940 |
| Std 2 | 2.81 | 5/27/09 | 15:20 | 1.1799 | 0.06014 |
| Std 3 | 19.8 | 5/27/09 | 15:45 | 1.8443 | 0.19711 |
| Std 4 | 50.41 | 5/27/09 | 15:55 | 2.5933 | 0.13557 |
| Std 1 | 0.4 | 5/27/09 | 15:34 | 0.9751 | 0.05648 |
| MilliQ | 0 | 5/28/09 | 6:32 | 0.9742 | 0.09781 |
| Std 1 | 0.4 | 5/28/09 | 6:58 | 1.3223 | 0.05471 |
| Std 2 | 2.81 | 5/28/09 | 7:07 | 1.4575 | 0.37047 |
| Std 3 | 19.8 | 5/28/09 | 7:15 | 2.0870 | 0.06989 |

**Table 15: SXS2_srvy3 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Concentration* | *Date run* |
|---|---|---|---|---|---|---|---|
| 5/27/09 | 15:55 | SXS Cons. Std | 1.0488 | | 0.05746 | 32.17 | 5/27/09 |
| 5/27/09 | 18:40 | #34 | | | | | |
| 5/27/09 | 20:17 | #31 | 1.3632 | | 0.0123 | 74.86 | 6/22/09 |
| 5/27/09 | 21:28 | #28 | 1.2414 | | 0.0382 | 67.01 | 6/22/09 |
| 5/27/09 | 21:43 | SXS Cons. Std | | | | | **no plateau |
| 5/27/09 | 23:55 | #27 | | | | | |
| 5/28/09 | 2:55 | #38 | 1.1223 | | 0.0119 | 59.32 | 6/22/09 |
| 5/28/09 | 4:43 | #48 | | | | | |

**Table 16: SXS2_srvy3 notes**

| | | |
|---|---|---|
| 5/27/09 | 14:05 | reagents flowing |
| 5/27/09 | 14:42 | standards |
| 5/27/09 | 15:55 | SXS Consistency Std |
| 5/27/09 | 16:07 | TFF |
| 5/27/09 | 18:15 | labview error |
| 5/27/09 | 18:19 | program restart |
| 5/27/09 | 19:48 | unfiltered line |
| 5/27/09 | 20:52 | TFF |
| 5/27/09 | 21:43 | SXS Consistency Std |
| 5/27/09 | 21:58 | TFF |
| 5/27/09 | 23:35 | unfiltered line |
| 5/28/09 | 0:40 | TFF |
| 5/28/09 | 1:27 | lab standards |
| 5/28/09 | 2:05 | TFF |
| 5/28/09 | 4:48 | standards |

#### 4.3.1.1.5 May 28—Patch day 4 (SXS2_srvy4)

May 28 was the fourth day of surveying the tracer patch during SXS2. The run showed very little variation in concentration which may be partially attributable to the deterioration of the bubbles throughout the day (the bubble deterioration may have been caused by aging pump tubing for bubble injection). NASS-5 was also run twice as a benchmark for the day.

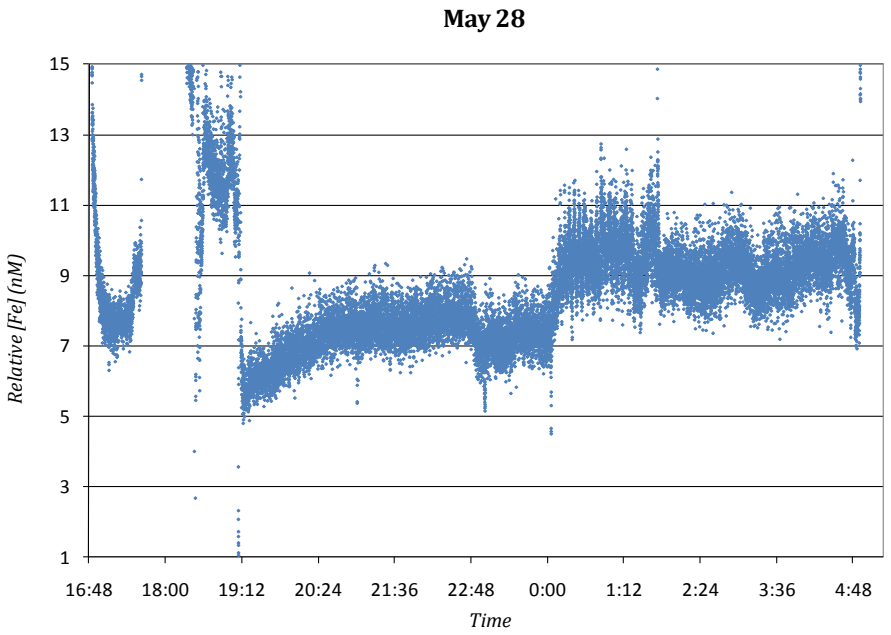


Figure 24: Relative [Fe] (SXS2_srvy4)

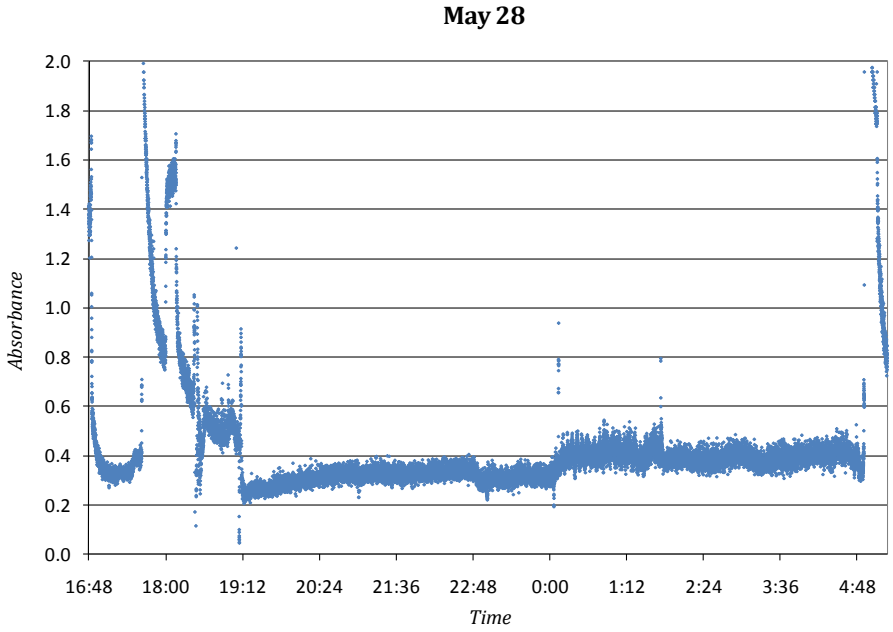


Figure 25: Absorbance (SXS2_srvy4)

**Table 17: SXS2_srvy4 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| MilliQ | 0.9210 | 0.05428 | -0.149 | | 3.92 | | 0.0417 |
| Std 1 | 1.2679 | 0.05031 | 0.031 | | *(Std1 Avg)* | | *Slope 1:* |
| Std 2 | 1.0476 | 0.04141 | -0.523 | | | | 0.0389 |
| Std 3 | 1.9796 | 0.05297 | -0.021 | | | | *Slope 2:* |
| Std 4 | 2.1170 | 0.07288 | -2.003 | | | | 0.0511 |
| *Average* | | 0.05437 | | | | | |

**Internal Lag time:** ≈ 7 minutes

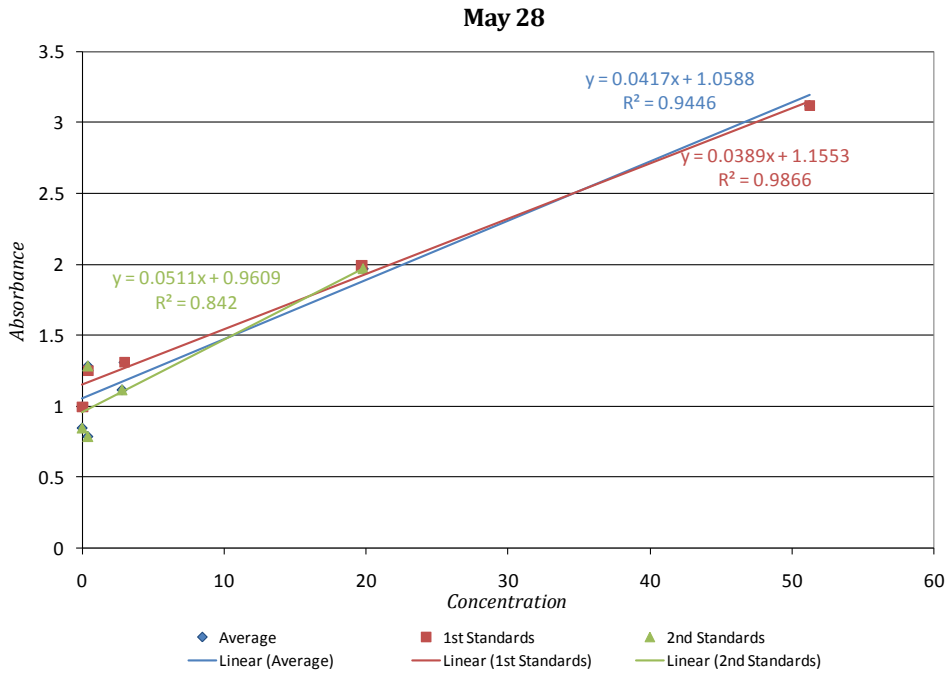


Figure 26: SXS2_srvy4 standards

**Table 18: SXS2_srvy4 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| MilliQ | 0 | 5/28/09 | 15:47 | 0.9954 | 0.08548 |
| Std 1 | 0.41 | 5/28/09 | 16:08 | 1.2524 | 0.05451 |
| Std 2 | 2.95 | 5/28/09 | 16:16 | 1.3089 | 0.06036 |
| Std 3 | 19.67 | 5/28/09 | 16:39 | 1.9899 | 0.06076 |
| Std 4 | 51.24 | 5/28/09 | 16:47 | 3.1185 | 0.09286 |
| Std 1 | 0.4 | 5/29/09 | 6:40 | 1.2834 | 0.04611 |
| Std 3 | 19.8 | 5/29/09 | 6:58 | 1.9692 | 0.04518 |
| Std 4 | 2.81 | 5/29/09 | 7:19 | 1.1154 | 0.05290 |
| Std 2 | 0.4 | 5/29/09 | 7:36 | 0.7863 | 0.02247 |
| MilliQ | 0 | 5/29/09 | 8:31 | 0.8466 | 0.02308 |

**Table 19: SXS2_srvy4 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Concentration* | *Date run* |
|---|---|---|---|---|---|---|---|
| 5/28/09 | 17:08 | #40 | | | | | |
| 5/28/09 | 18:50 | NASS-5 | 1.2315 | | 0.07870 | 4.21 | 5/28/2009 |
| 5/29/09 | 4:46 | #44 | | | | | |
| 5/29/09 | 5:50 | NASS-5 | 1.9605 | | 0.07301 | 21.99 | 5/29/2009 |

**Table 20: SXS2_srvy4 notes**

| | | |
|---|---|---|
| 5/28/09 | 14:25 | begin standards |
| 5/28/09 | 16:44 | begin TFF flow |
| 5/28/09 | 22:49 | bubbles deteriorate; need to replace tubing |
| 5/29/09 | 0:01 | unfiltered line |
| 5/29/09 | 1:36 | TFF |
| 5/29/09 | 5:10 | bulk seawater |
| 5/29/09 | 5:50 | standards |

#### 4.3.1.1.6 May 29—Patch day 5 (SXS2_srvy5)

May 29 was the final patch tracing day for SXS2. The system was run with little interruption except for a supersucker problem about 22:43. The system was switched to the unfiltered line between 00:36 and 3:50 but otherwise ran uneventfully on the TFF.

Variations in iron were measured throughout the transect, particularly at the end of the day. The dual slow increases of iron (one on either side of the supersucker problem at 22:43) are interesting to note. They could indicate some sort of iron accumulation issue either in our system or in the supersucker.

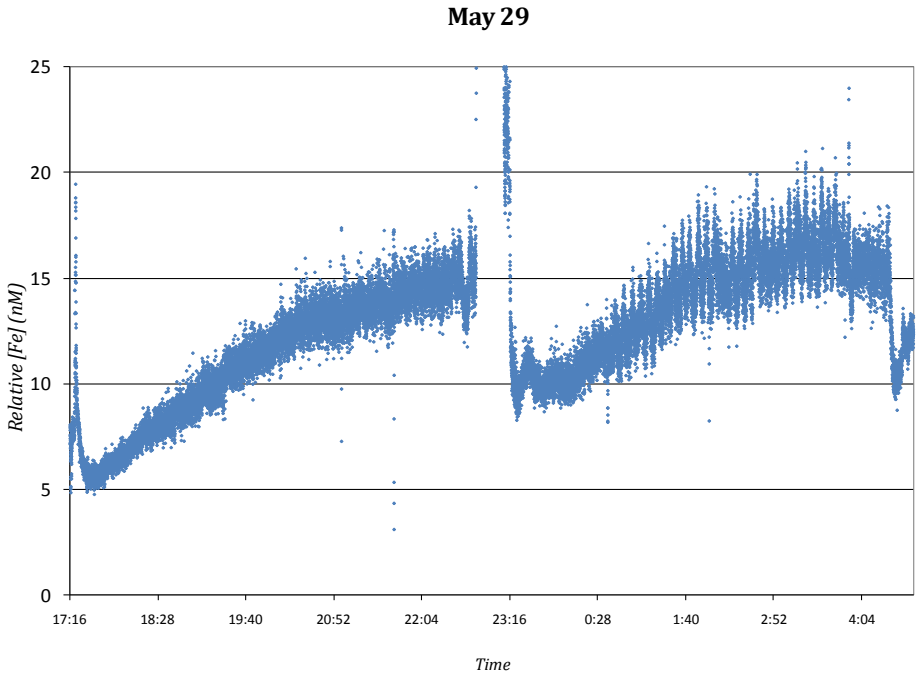


Figure 27: Relative [Fe] (SXS2_srvy5)

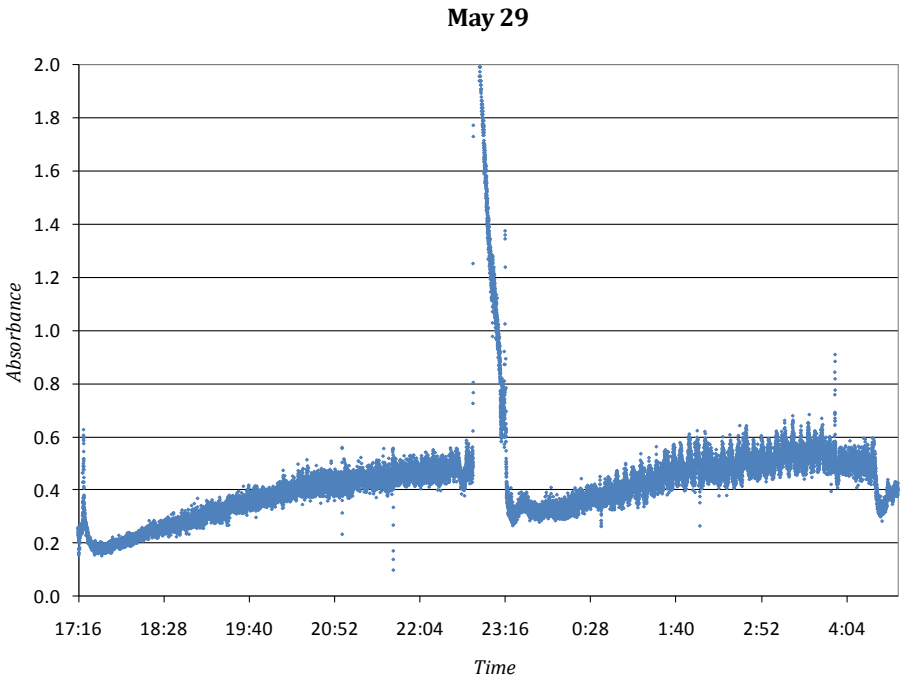


Figure 28: Absorbance (SXS2_srvy5)

**Table 21: SXS2_srvy5 summary**

| | *Abs* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| MilliQ | 0.6322 | 0.0225 | n/a | | 2.21 | | 0.0323 |
| Std 1 | 0.7435 | 0.2151 | 0.1945 | | *(Std1 Avg)* | | *Slope 1:* |
| Std 2 | 0.7720 | 0.0254 | 0.1851 | | | | 0.0328 |
| Std 3 | 1.5516 | 0.0461 | 0.0500 | | | | *Slope 2:* |
| Std 4 | 2.3104 | 0.0576 | 0.1496 | | | | 0.031 |
| *Average* | | 0.0365 | | | | | |

**Internal Lag time:** ≈ 5 minutes

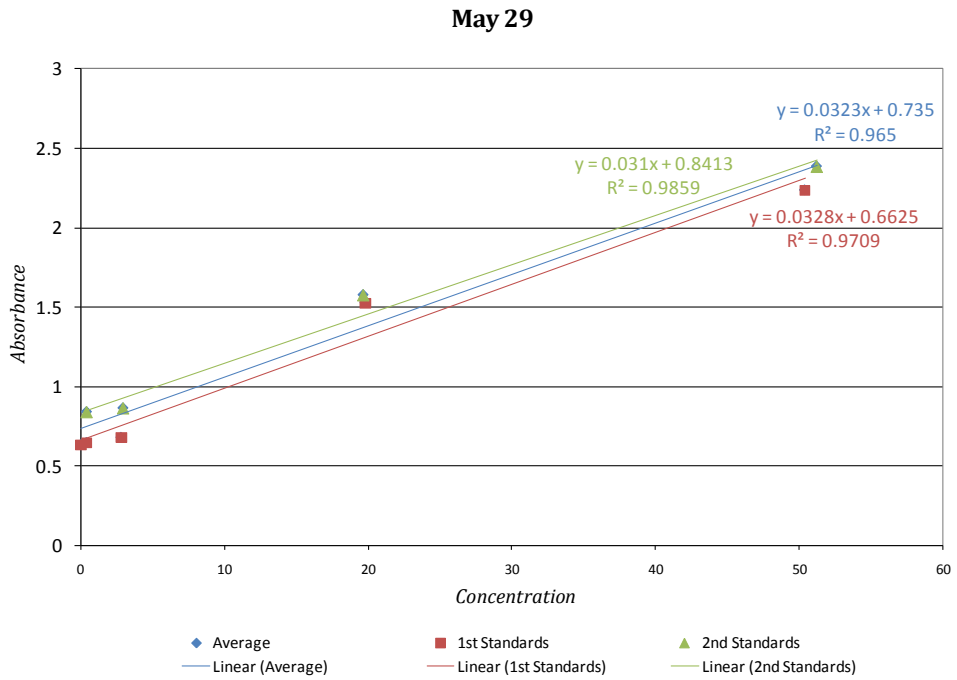


Figure 29: SXS2_srvy5 standards

**Table 22: SXS2_srvy5 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| Std 1 | 0.4 | 5/29/09 | 16:18 | 0.6463 | 0.02022 |
| Std 2 | 2.81 | 5/29/09 | 16:29 | 0.6795 | 0.01827 |
| Std 3 | 19.8 | 5/29/09 | 16:42 | 1.5266 | 0.04547 |
| Std 4 | 50.41 | 5/29/09 | 16:52 | 2.2356 | 0.06035 |
| MilliQ | 0 | 5/29/09 | 17:10 | 0.6322 | 0.02251 |
| Std 4 | 51.24 | 5/30/09 | 7:10 | 2.3852 | 0.05492 |
| Std 3 | 19.67 | 5/30/09 | 7:21 | 1.5766 | 0.04682 |
| Std 2 | 2.95 | 5/30/09 | 7:44 | 0.8646 | 0.03249 |
| Std 1 | 0.41 | 5/30/09 | 8:10 | 0.8407 | 0.02743 |

**Table 23: SXS2_srvy5 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Concentration* | *Date run* |
|---|---|---|---|---|---|---|---|
| 5/30/09 | 4:38 | Fe Check, surface | | | | | |

**Table 24: SXS2_srvy5 notes**

| | | |
|---|---|---|
| 5/29/09 | 15:53 | begin standards |
| 5/29/09 | 17:16 | TFF |
| 5/29/09 | 22:43 | bulk seawater |
| 5/29/09 | 23:11 | TFF |
| 5/30/09 | 0:36 | unfiltered line |
| 5/30/09 | 3:50 | TFF |
| 5/30/09 | 4:43 | bulk seawater |
| 5/30/09 | 6:59 | begin standards |

#### 4.3.1.1.7 May 30--45°N Transect (SXS2_xsct2)

The May 30th data is a transect of 45°N from the 31m isobath to the 250m isobaths. This transect shows encouraging changes in the iron concentration that match the movements of the supersucker in the water column. NASS-5 was run twice as a benchmark during this run.

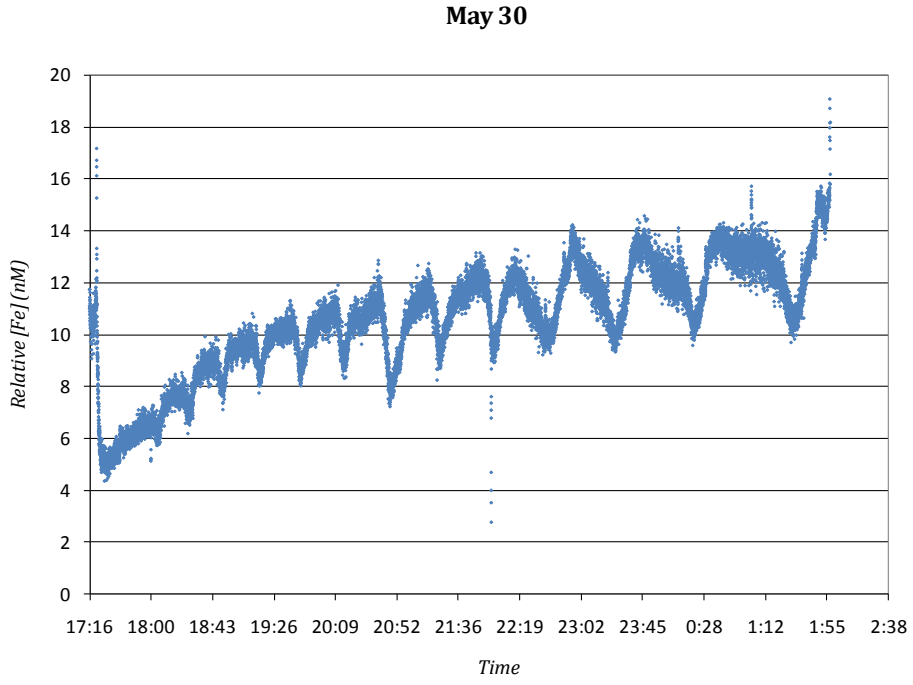


Figure 30: Relative [Fe] (SXS2_xsct2)

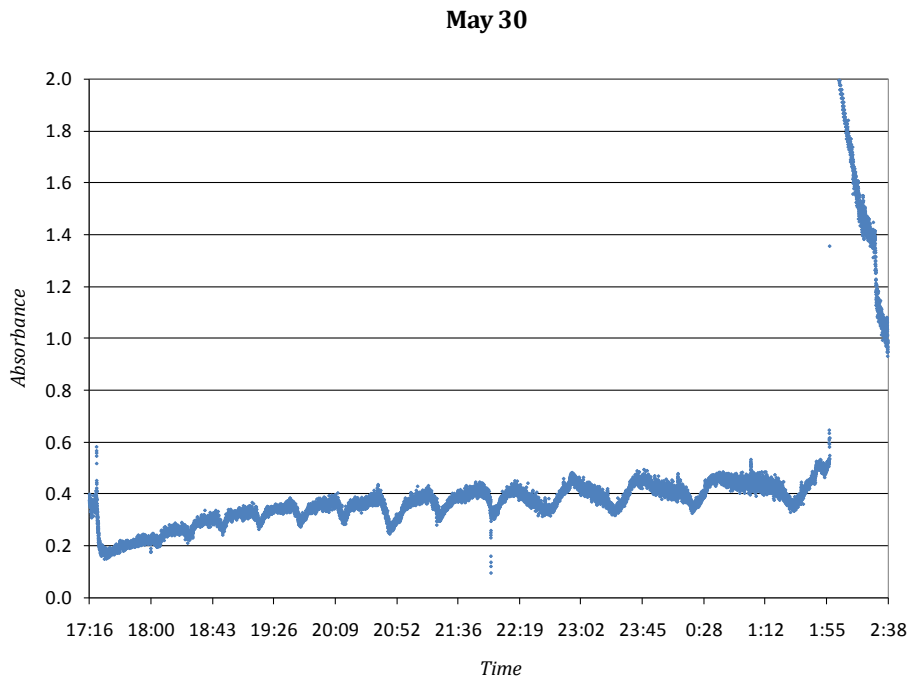


Figure 31: Absorbance (SXS2_xsct2)

**Table 25: SXS2_xsct2 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| MilliQ | 0.6003 | 0.0167 | -0.0681 | | 2.22 | | 0.0338 |
| Std 1 | 1.0015 | 0.0250 | 0.1136 | | *(Std1 Avg)* | | *Slope 1:* |
| Std 2 | 0.9992 | 0.0376 | 0.1817 | | | | 0.0305 |
| Std 3 | 1.7457 | 0.0532 | 0.1737 | | | | *Slope 2:* |
| Std 4 | 2.5225 | 0.0989 | 0.4041 | | | | 0.0372 |
| *Average* | | 0.0463 | | | | | |

**Internal Lag time:** ≈ 6 minutes

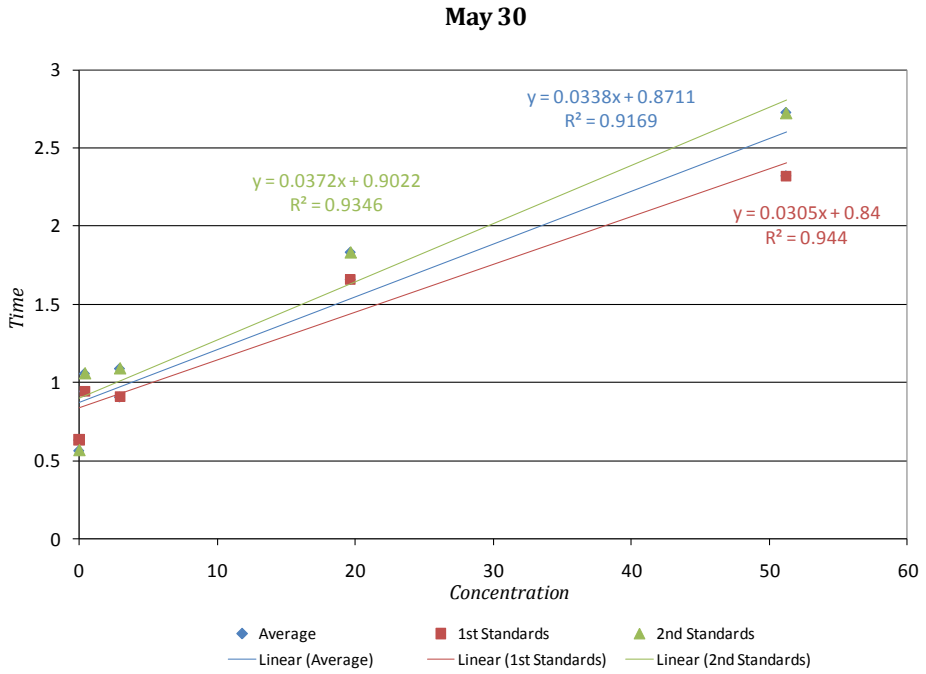


Figure 32: SXS2_xsct2 standards

**Table 26: SXS2_xsct2 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| MilliQ | 0 | 5/30/09 | 16:04 | 0.6343 | 0.01782 |
| 4 | 51.24 | 5/30/09 | 16:12 | 2.3204 | 0.05724 |
| 3 | 19.67 | 5/30/09 | 16:26 | 1.6588 | 0.05546 |
| 2 | 2.95 | 5/30/09 | 16:56 | 0.9083 | 0.04091 |
| 1 | 0.41 | 5/30/09 | 17:09 | 0.9447 | 0.03422 |
| 4 | 51.24 | 5/31/09 | 2:46 | 2.7245 | 0.14054 |
| 3 | 19.67 | 5/31/09 | 3:02 | 1.8325 | 0.05092 |
| 2 | 2.95 | 5/31/09 | 3:26 | 1.0900 | 0.03438 |
| 1 | 0.41 | 5/31/09 | 3:44 | 1.0583 | 0.01581 |
| MilliQ | 0 | 5/31/09 | 4:46 | 0.5662 | 0.01607 |

**Table 27: SXS2_xsct2 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Conc.* | *Date run* |
|---|---|---|---|---|---|---|---|
| 5/30/09 | 17:05 | NASS-5 | 0.8250 | n/a | 0.03673 | 1.09 | 5/20/09 |
| 5/31/09 | 3:31 | NASS-5 | 1.0686 | n/a | 0.02478 | 0.73 | 5/31/09 |

**Table 28: SXS2_xsct2 notes**

| | | |
|---|---|---|
| 5/30/09 | 15:38 | milliQ valve comparison |
| 5/30/09 | 16:03 | begin standards |
| 5/30/09 | 17:05 | NASS-5 |
| 5/30/09 | 17:16 | TFF |
| 5/31/09 | 1:51 | begin standards |
| 5/31/09 | 3:19 | NASS-5 |

#### 4.3.1.1.8 May 31—43.9°N Transect (SXS2_xsct3)

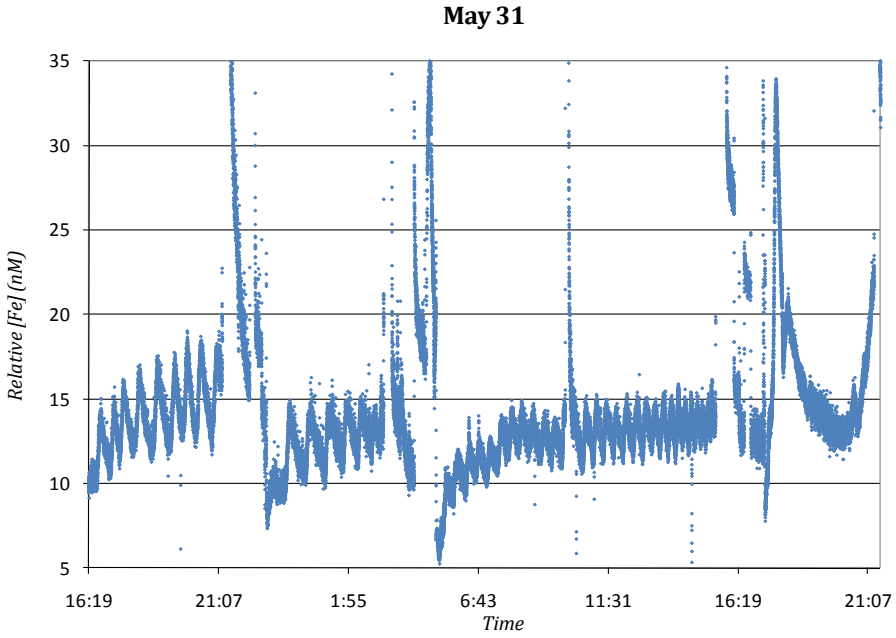


Figure 33: Relative [Fe] (SXS2_xsct3)

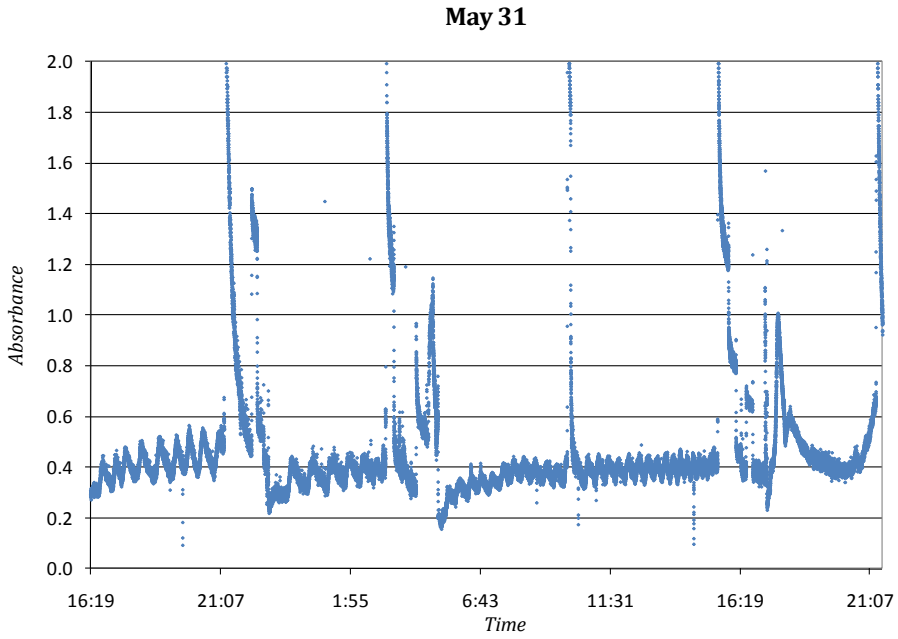


Figure 34: Absorbance (SXS2_xsct3)

**Table 29: SXS2_xsct3 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| MilliQ | n/a | n/a | | | 6.17 | | 0.0297 |
| Standard 1 | 0.9796 | 0.0611 | 0.8408 | | | | *Slope 1:* |
| Standard 3 | 1.1540 | 0.0421 | 0.7458 | | | | 0.0212 |
| Standard 4 | 2.5178 | 0.0869 | 1.2485 | | | | *Slope 2:* |
| *Average* | | 0.0634 | | | | | 0.0417 |
| | | | | | | | *Slope 3:* |
| | | | | | | | 0.0301 |
| | | | | | | | *Slope 4:* |
| | | | | | | | 0.0003 |

**Internal Lag time:** ≈ 5 minutes

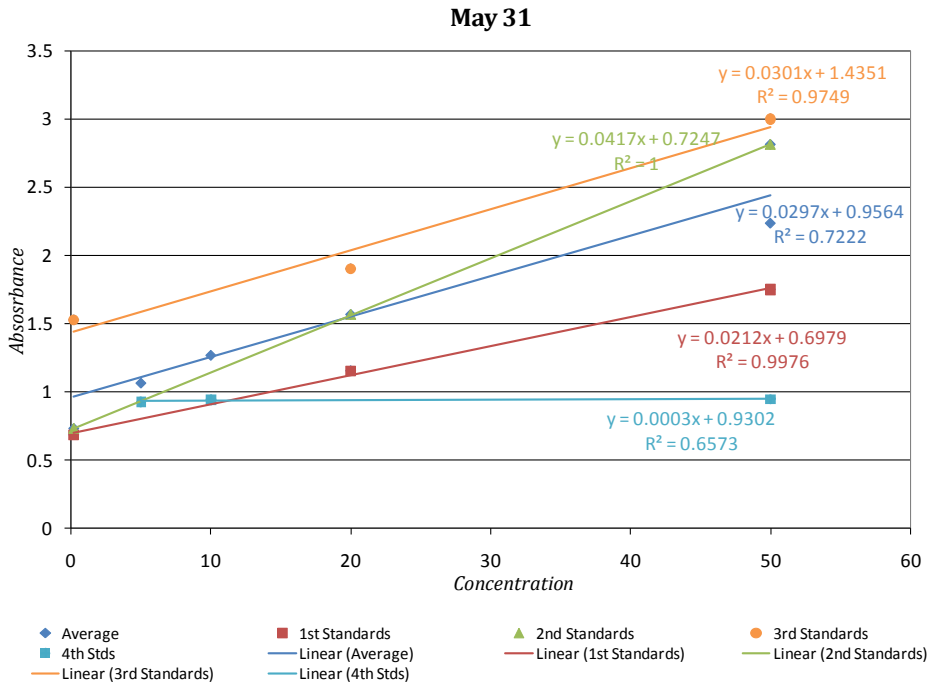


Figure 35: SXS2_xsct3 standards

**Table 30: SXS2_xsct3 standards**

| **Standards made onboard | | | | | |
|---|---|---|---|---|---|
| *Standard* | *Conc.* | *Date* | *Time* | *Absorbance* | *Stdev* |
| Std 3 | 20 | 5/31/2009 | 15:33 | 1.1528 | 0.04191 |
| Std 1 | 0.2 | 5/31/2009 | 15:44 | 0.6840 | 0.02932 |
| Std 4 | 50 | 5/31/2009 | 16:04 | 1.7480 | 0.12267 |
| Std 4 | 50 | 6/1/2009 | 3:25 | 2.8090 | 0.07139 |
| Std 1 | 0.2 | 6/1/2009 | 4:33 | 0.7298 | 0.13557 |
| Std 3 | 20 | 6/1/2009 | 5:01 | 1.5646 | 0.04382 |
| Std 4 | 50 | 6/1/2009 | 15:44 | 2.9965 | 0.06667 |
| Std 3 | 20 | 6/1/2009 | 16:02 | 1.8986 | 0.04062 |
| Std 1 | 0.2 | 6/1/2009 | 16:36 | 1.5248 | 0.01847 |
| consistency seawater + 5nM | 5 | 6/1/2009 | 22:14 | 1.0617 | 0.01931 |
| consistency seawater + 10nM | 10 | 6/1/2009 | 22:33 | 1.265 | 0.033044 |
| consistency seawater + 50nM | | 6/1/2009 | 22:42 | 2.2322 | 0.16475 |

**Table 31: SXS2_xsct3 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Conc.* | *Date run* |
|---|---|---|---|---|---|---|---|
| 5/31/2009 | 15:33 | NASS-5 | 0.60845 | n/a | 0.020408 | 18.66 | 5/31/2009 |
| 6/1/2009 | 3:24 | SXS Consis. Std. | 0.04054 | n/a | 0.04054 | 1.24 | 6/1/2009 |
| 5/31/2009 | 21:11 | TFF sample | 2.1839 | n/a | 0.0723 | 66.99 | 6/1/2009 |
| 6/1/2009 | 16:05 | NASS-5 | 1.0612 | n/a | 0.024388 | 32.55 | 6/1/2009 |
| 6/1/2009 | 16:26 | SXS Consis. Std. | 0.89321 | n/a | 0.045277 | 27.40 | 6/1/2009 |
| 6/1/2009 | 16:42 | SXS Consis. Std. | 0.84425 | n/a | 0.025607 | 25.90 | 6/1/2009 |
| 6/1/2009 | 22:42 | NASS-5 | 0.6881 | n/a | 0.021934 | 21.11 | 6/1/2009 |

**Table 32: SXS2_xsct3 notes**

| | | |
|---|---|---|
| 5/31/2009 | 14:35 | reagents flowing |
| 5/31/2009 | 15:02 | heaters weren't on |
| 5/31/2009 | 16:02 | TFF |
| 5/31/2009 | 21:05 | acidified MilliQ |
| 5/31/2009 | 22:48 | TFF |
| 6/1/2009 | 3:05 | standard, const. std.; reagent top off |
| 6/1/2009 | 5:04 | TFF |
| 6/1/2009 | 10:00 | brief switch to position 1, no signal |
| 6/1/2009 | 15:48 | standards |
| 6/1/2009 | 17:15 | TFF |
| 6/1/2009 | 18:45 | DPD top off |
| 6/1/2009 | 21:15 | standards |

#### *4.3.1.2 Discussion*

SXS 2 highlighted the need to resolve issues between the discrete samples and the inline data before SXS 3. It also raised concerns that the system may not be responding rapidly enough to chances in concentration. The bubble irregularities were believed to be the root cause of the slow response as well as creating unacceptable amounts of noise in the data.

**Table 33: SXS 2 Summary**

| *Date* | *What?* | *Slope* | *R^2* | *Detection limit* |
|---|---|---|---|---|
| 23-May | 45N transect | 0.0466 | 0.999 | 0.92 |
| 25-May | Patch | 0.0237 | 0.997 | 5.07 |
| 26-May | Patch | 0.0302 | 0.940 | 4.46 |
| 27-May | Patch | 0.0326 | 0.861 | 5.12 |
| 28-May | Patch | 0.0427 | 0.945 | 3.92 |
| 29-May | Patch | 0.0323 | 0.965 | 2.21 |
| 30-May | 45N transect | 0.0338 | 0.917 | 2.22 |
| 31-May | 43.9N transect | .0297 | .722 | 6.17 |

#### 4.3.1.2.1 High Resolution Data SXS2

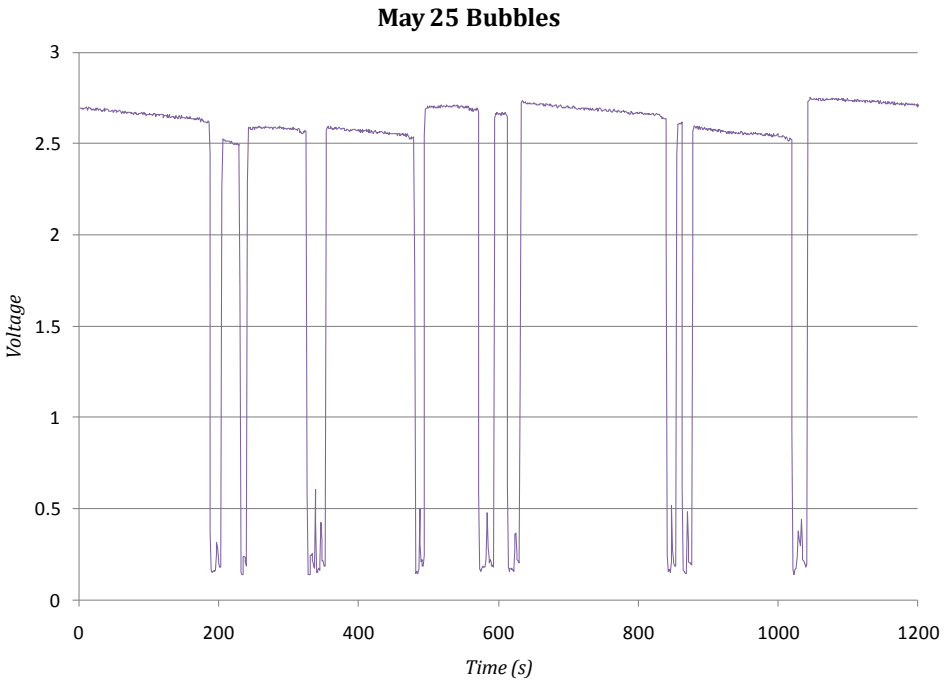


Figure 36: Early SXS2 bubble pattern (20 minutes)

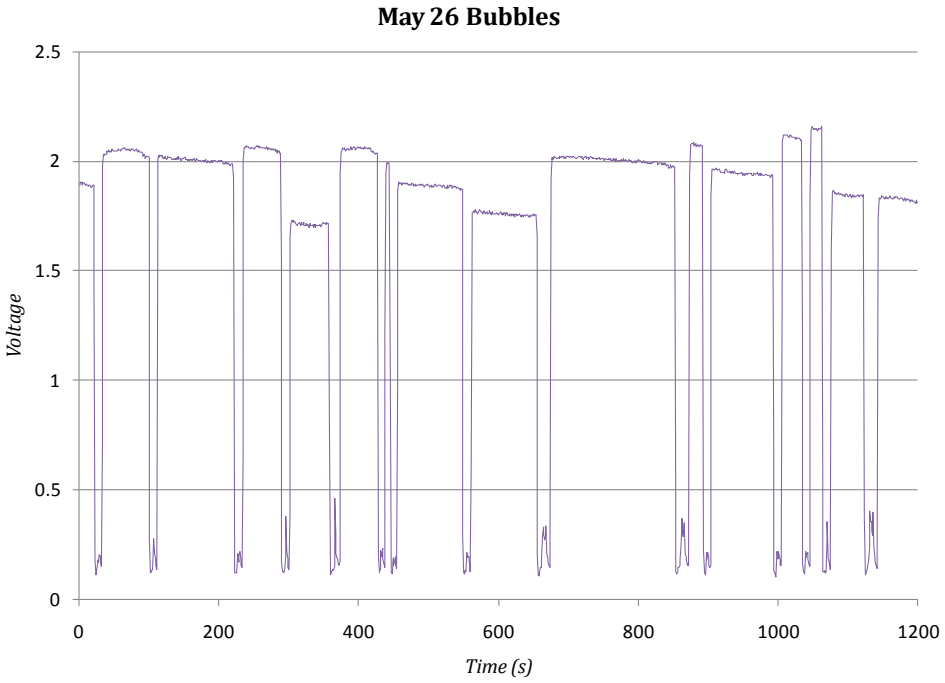


Figure 37: Mid-SXS2 bubble pattern (20 minutes)

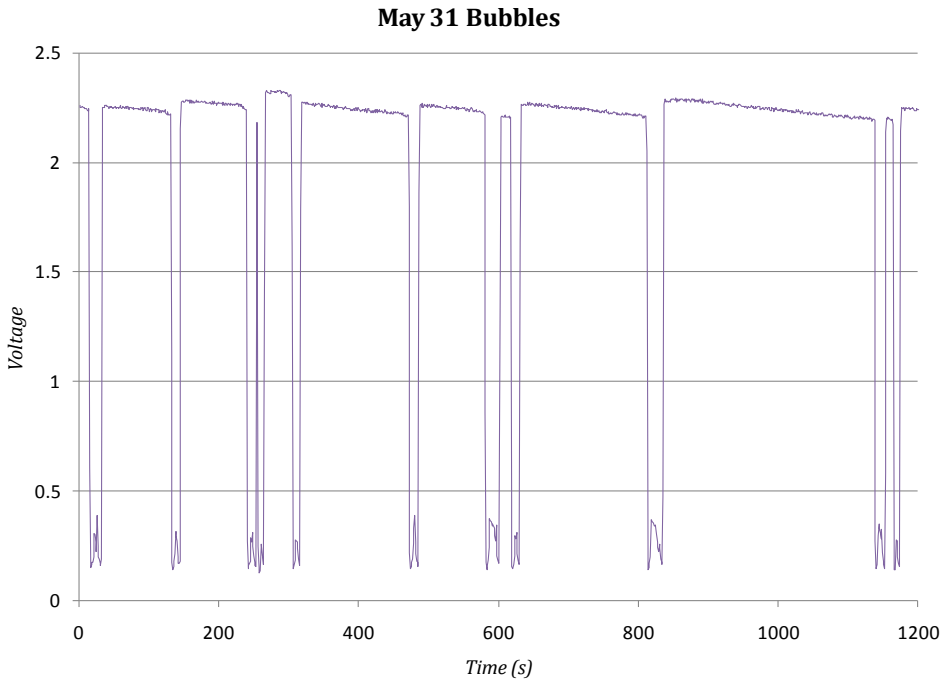


Figure 38: End SXS2 bubble pattern (20 minutes)

Above are three plots comparing the bubbles during SXS2. The plot of the May 26$^{th}$ (SXS2_srvy2) is perhaps most representative of the bubbles during this cruise. By the end of the cruise, the May 30 (SXS2_xsct2) and May 31 (SXS2_xsct3) bubbles were looking better, although not completely consistent. The improvements were largely due to improving the connections between glass tubing sections and eliminating some of the unnecessary acidification tubing.

#### 4.3.1.2.2 1 Hour Samples SXS2

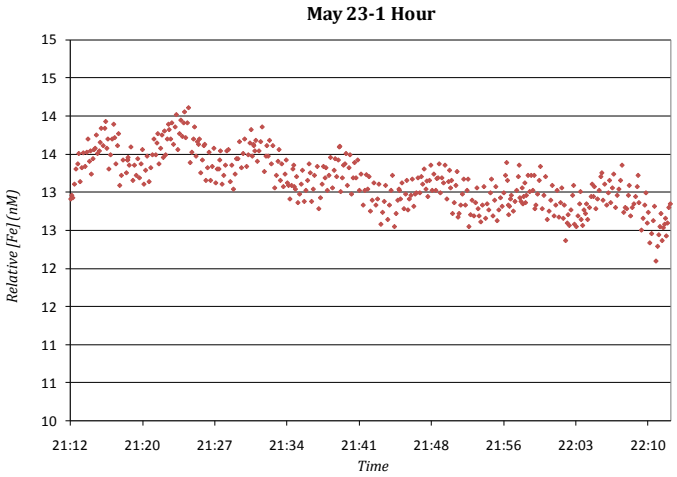


Figure 39: May 23 1 Hour Data

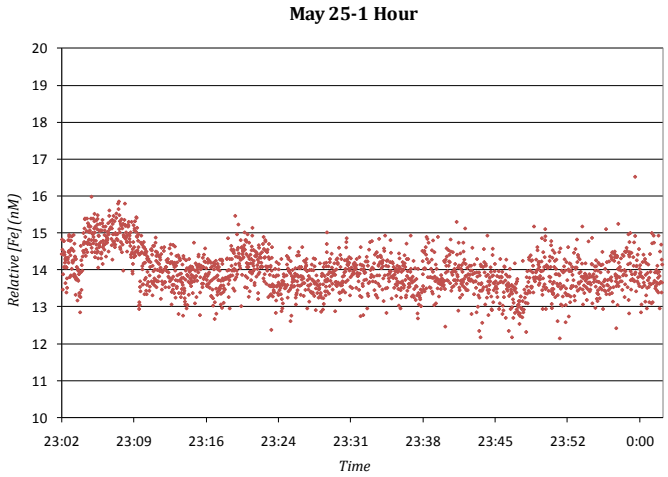


Figure 40: May 25 1 Hour Data

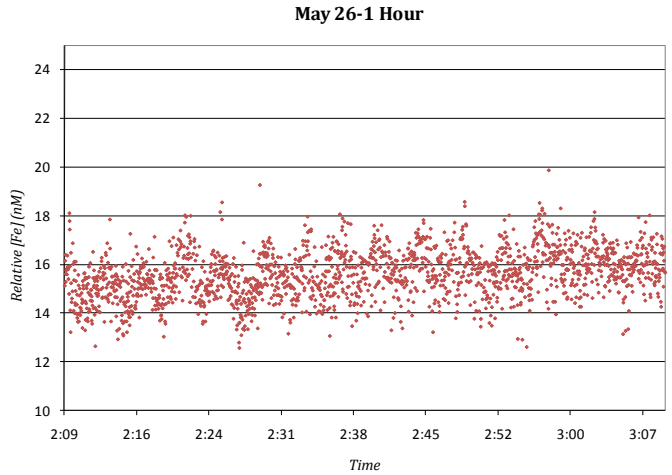


Figure 42: May 26 1 Hour Data

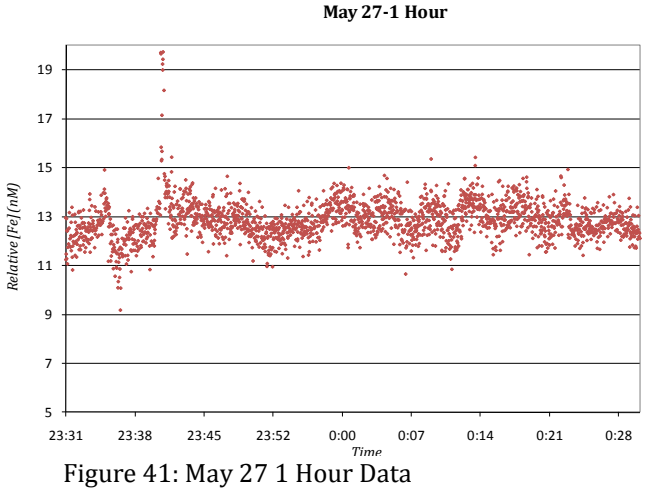


Figure 41: May 27 1 Hour Data

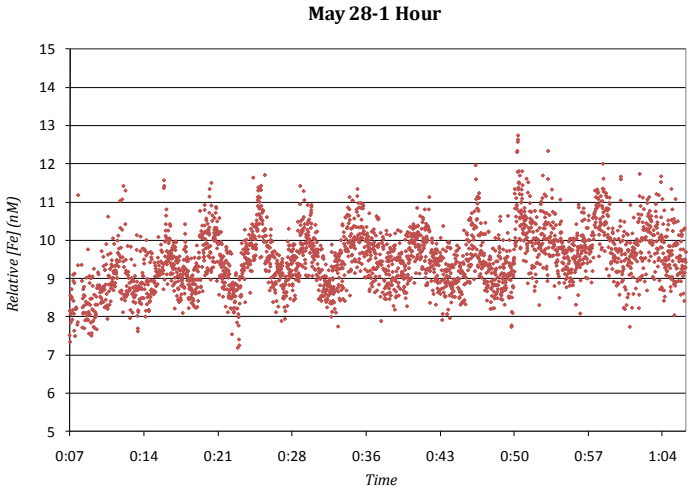


Figure 43: May 28 1 Hour Data

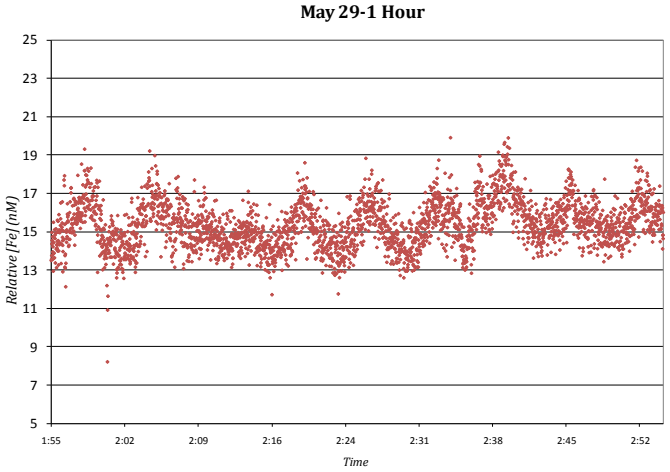


Figure 44: May 29 1 Hour Data

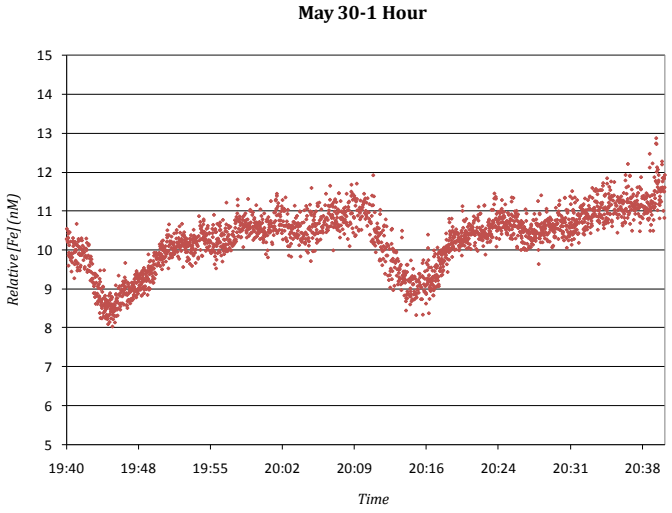


Figure 46: May 30 1 Hour Data

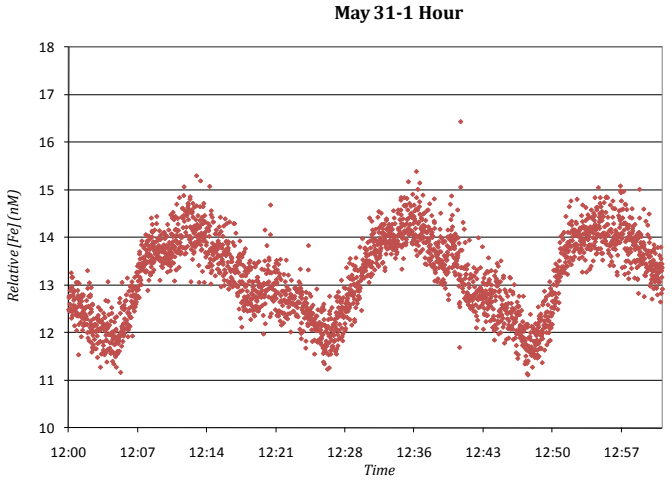


Figure 45: May 31 1 Hour Data

#### 4.3.1.2.3 Standard Voltages

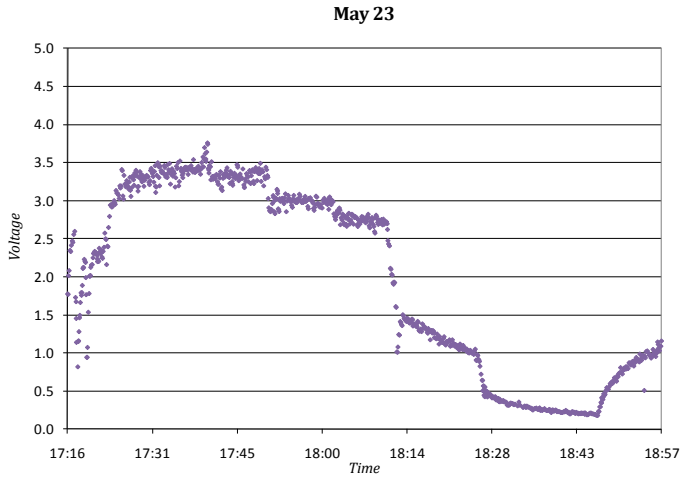


Figure 47: May 23 standards (2nd set)

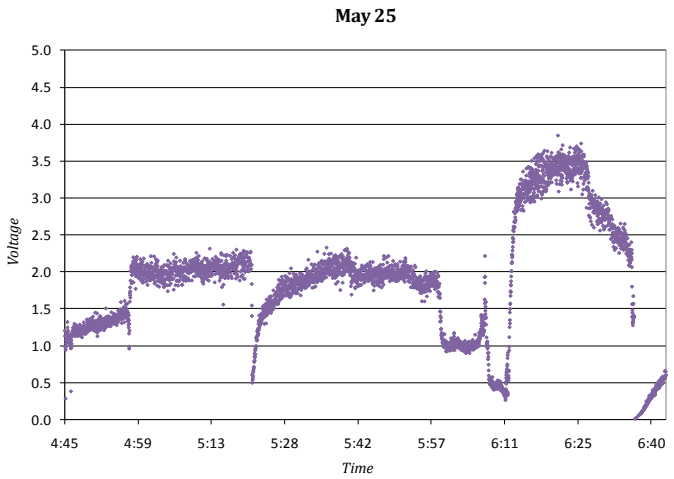


Figure 48: May 25 standards

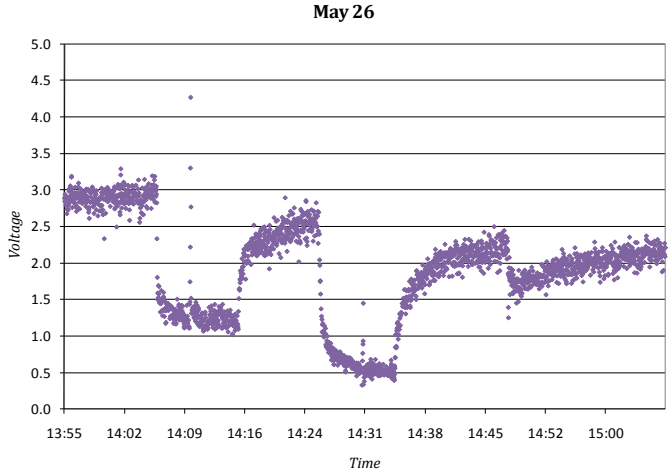


Figure 49: May 26 standards (1st set)

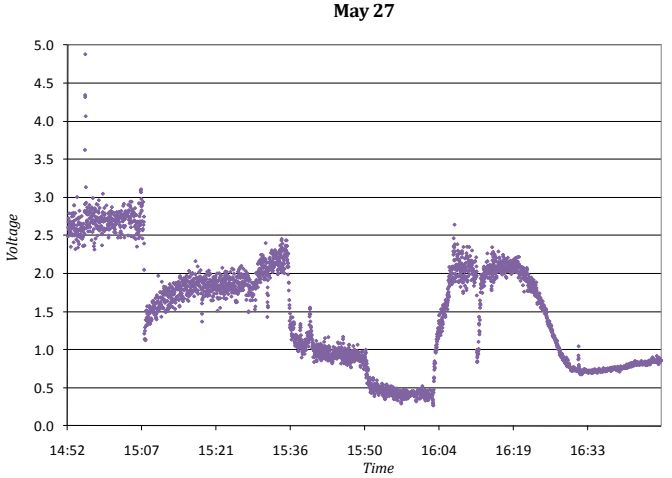


Figure 50: May 27 standards (1st set)

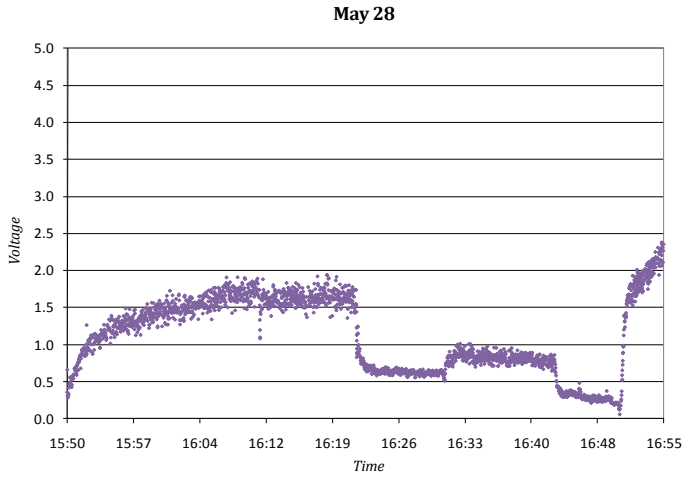


Figure 51: May 28 standards (2nd set)

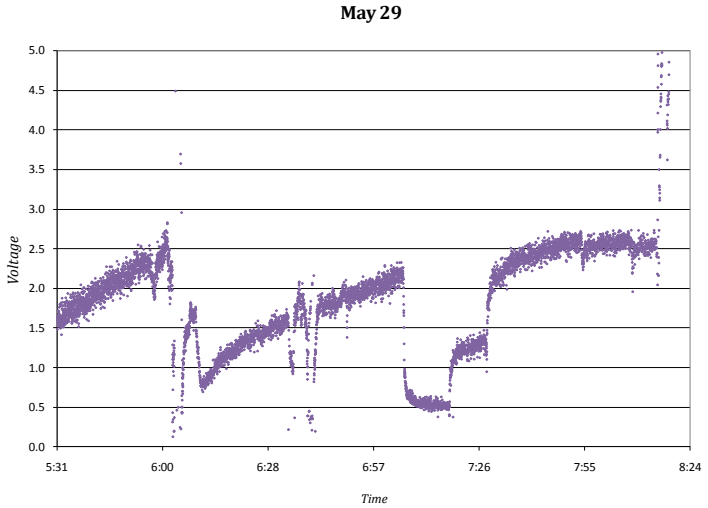


Figure 52: May 29 standards (1st set)

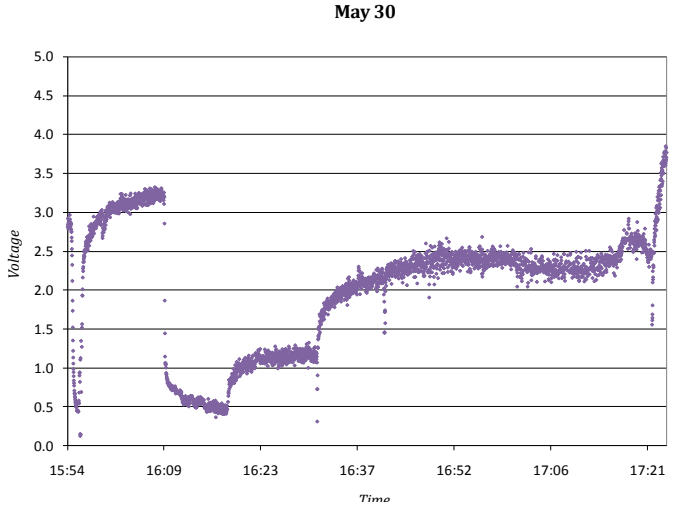


Figure 53: May 30 standards (1st set)

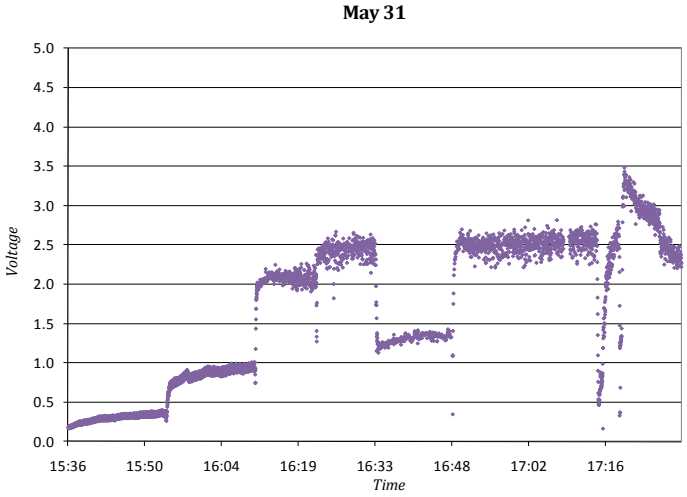


Figure 54: May 31 standards (3rd set)

### 4.3.2 SXS3 (August) Cruise

#### *4.3.2.1 Daily Results*

*Times given in the notes section reflect the time the change was expressed in the data.

##### 4.3.2.1.1 August 2—Patch tracing day 1 (SXS3_srvy1)

August 2, 2009 the first day of patch surveying during SXS3. A discrete sample (approximately 30 mL) was collected from the TFF from 21:46:42-21:49:25. This sample was immediately run unacidified (starting at 21:49:45 and measured at 22:25). The sample was then poured off into a new bottle, acidified, and then ran (starting 22:24:18 and measured 22:49). These two samples had drastically different absorbances. This measurement was ambiguous due to the small sample size as the system can take quite awhile to reequilibrate to discrete samples after running from the TFF and the voltage from the acidified sample was still trending upwards when the sample was gone (maximum measured voltage of the acidified sample was ~0.55V compared to a maximum voltage of ~1.1V for the unacidified sample).

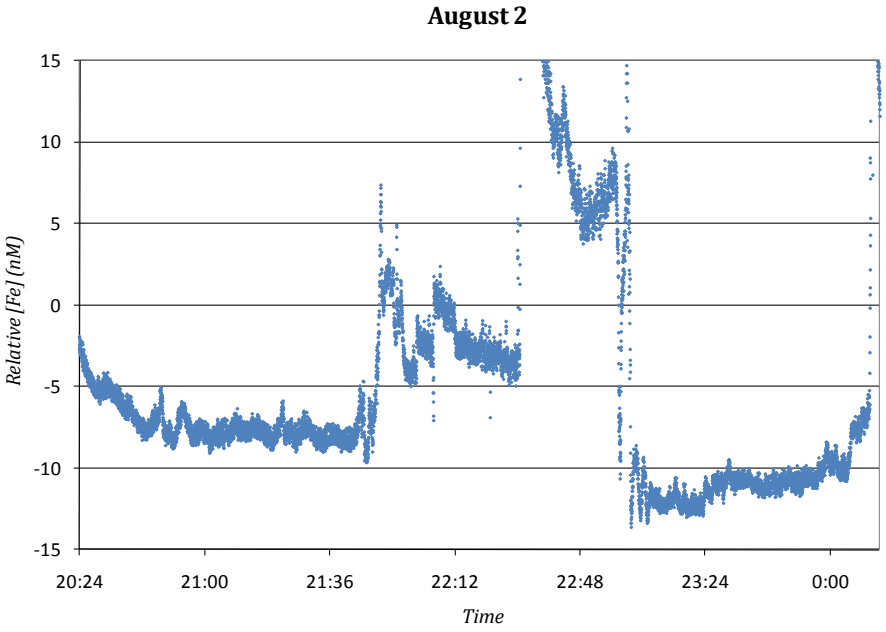


Figure 55: Relative [Fe] (SXS3_srvy1)

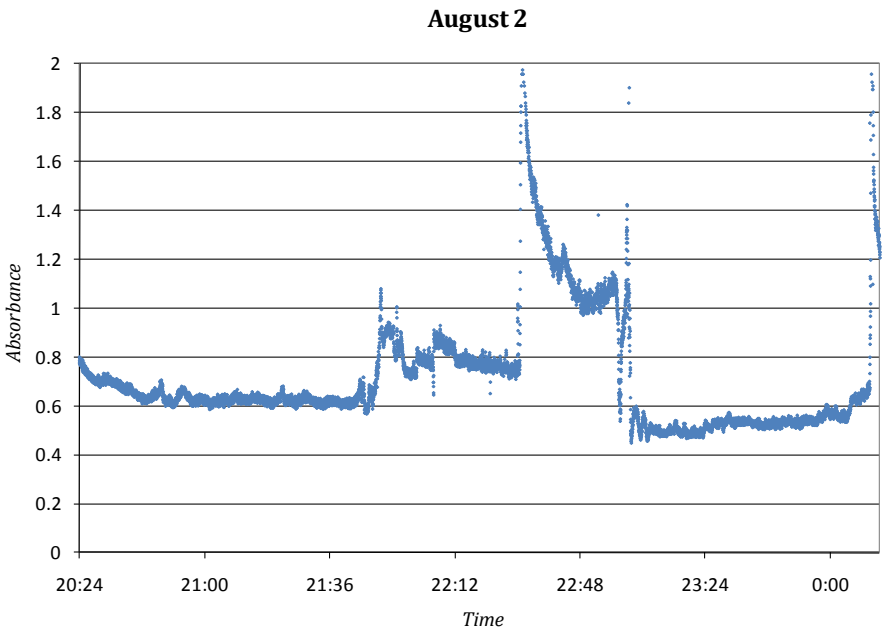


Figure 56: Absorbance (SXS3_srvy1)

**Table 34: SXS3_srvy1 summary**

| | *Absorbance* | *Stdev* | *Drift* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| Std 1 | 0.8218 | 0.0140 | n/a | | 1.39 | | 0.0301 |
| Std 2 | 0.9479 | 0.0167 | -0.0575 | | *(Std 1)* | | *Slope 1:* |
| Std 3 | 1.5102 | 0.0215 | 0.3921 | | | | 0.0233 |
| Std 4 | 2.2824 | 0.0342 | 0.5592 | | | | *Slope 2:* |
| *Average* | | 0.0227 | | | | | 0.0366 |

**Internal Lag time:** ≈ 4 minutes

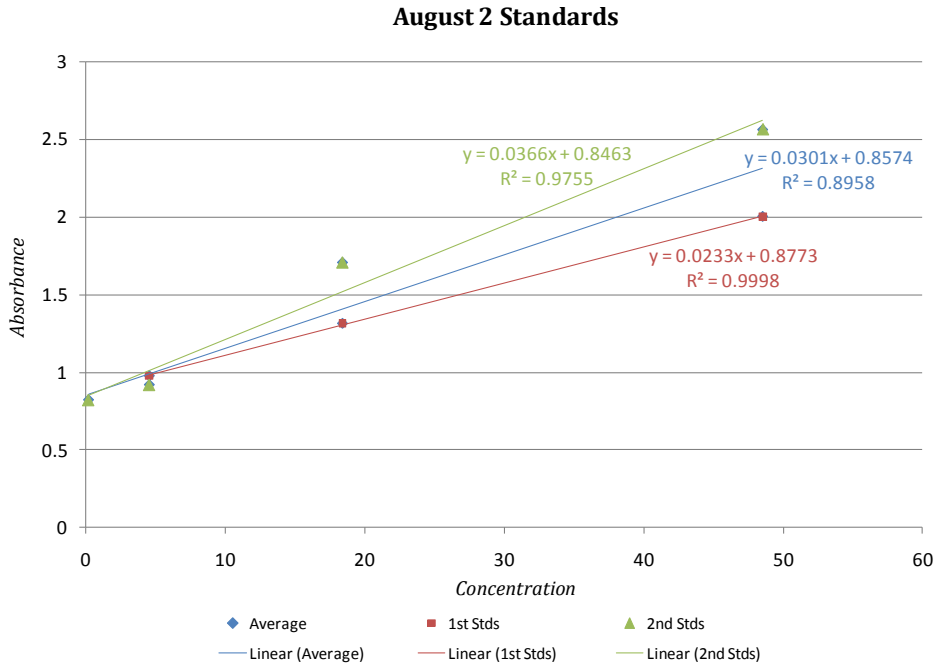


Figure 57: SXS3_srvy1 standards

**Table 35: SXS3_srvy1 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| Std 2 | 4.54 | 8/2/09 | 15:59 | 0.9767 | 0.01565 |
| Std 3 | 18.39 | 8/2/09 | 16:18 | 1.3141 | 0.01836 |
| Std 4 | 48.52 | 8/2/09 | 16:30 | 2.0028 | 0.02411 |
| Std 4 | 48.52 | 8/3/09 | 0:48 | 2.5620 | 0.04425 |
| Std 3 | 18.39 | 8/3/09 | 1:12 | 1.7062 | 0.02467 |
| Std 2 | 4.54 | 8/3/09 | 3:01 | 0.9191 | 0.01782 |
| Std 1 | 0.18 | 8/4/09 | 3:55 | 0.8218 | 0.01398 |

**Table 36: SXS3_srvy1 discrete samples**

| Date | Time | *Sample* | *Abs.* | *Blank Corr. Abs* | *Stdev* | *Conc.* | *Date run* |
|---|---|---|---|---|---|---|---|
| 8/2/09 | 22:25 | Discrete sample (unacidified) | 1.7375 | n/a | 0.04000 | 29.24 | |
| 8/2/09 | 22:49 | Discrete sample (acidified) | 2.3366 | n/a | 0.05338 | 49.14 | |

**Table 37: SXS3_srvy1 notes**

| | | |
|---|---|---|
| 8/2/2009 | 15:15 | Begin standards. Standards seem fairly quick but exhibited the same shallow slope seen throughout the cruise |
| 8/2/2009 | 17:23 | Acidified seawater. Lots of noise in this sample. Noise seemed to decrease throughout the cruise reaching a plateau during the August 8 data |
| 8/2/2009 | 20:09 | Changed buffer & took a sample from the TFF |
| 8/2/2009 | 21:57 | TFF sample—unacidified |
| 8/2/2009 | 22:51 | TFF sample—acidified in new bottle |
| 8/2/2009 | 23:02 | Return to SS flow |
| 8/3/2009 | 00:45 | Begin standards |
| 8/3/2009 | 04:37 | End standards |

#### 4.3.2.1.2 August 3—Patch tracing day 2 (SXS3_srvy2)

August 3 was the second day of the patch tracing during SXS3. The calculated absorbancies were quite high during this run, usually the absorbance ranges from 0-2 instead of the 2-12 seen here. This is probably due to samples taken during the day which cause disruptance to the flow of data.

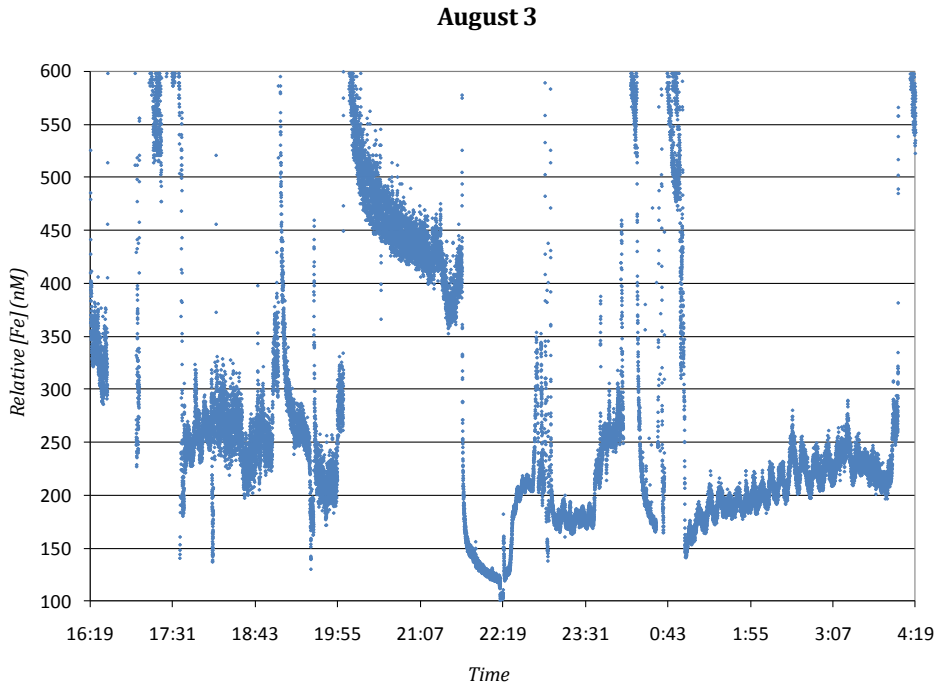


Figure 58: Relative [Fe] (SXS3_srvy2)

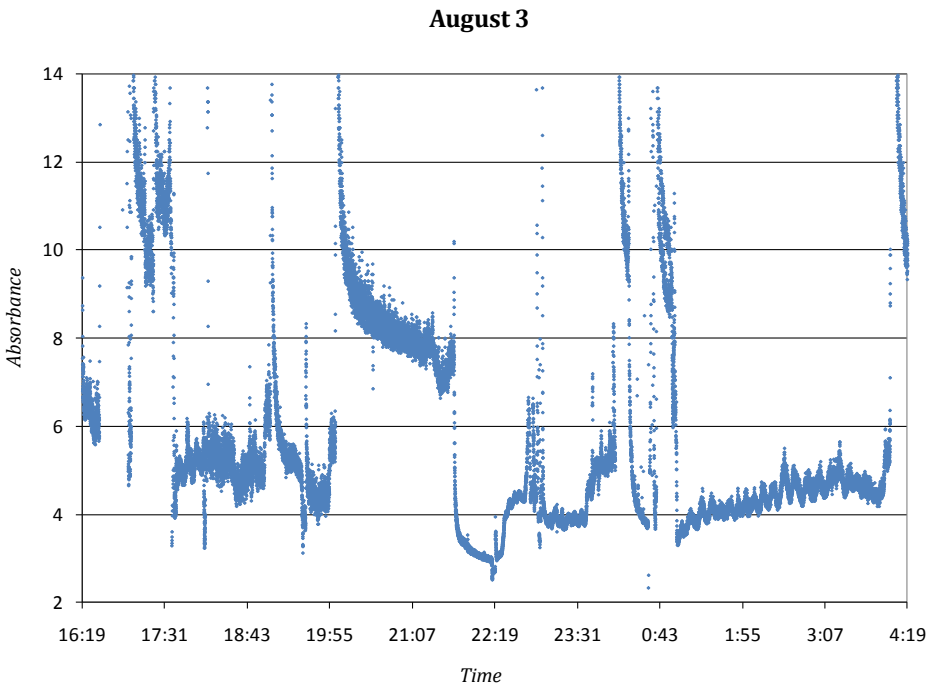


Figure 59: Absorbance (SXS3_srvy2)

**Table 38: SXS3_srvy2 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| Std 1 | 1.0460 | 0.0178 | -0.0340 | | 3.38 | | 0.0158 |
| Std 2 | 1.1340 | 0.0194 | -0.0095 | | *(Std1 Avg)* | | *Slope 1:* |
| Std 3 | 1.4348 | 0.0226 | 0.0629 | | | | 0.0081 |
| Std 4 | 1.8167 | 0.0264 | 0.6929 | | | | *Slope 2:* |
| *Average* | | 0.0215 | | | | | 0.0235 |

**Internal Lag time:** ≈ 5 minutes

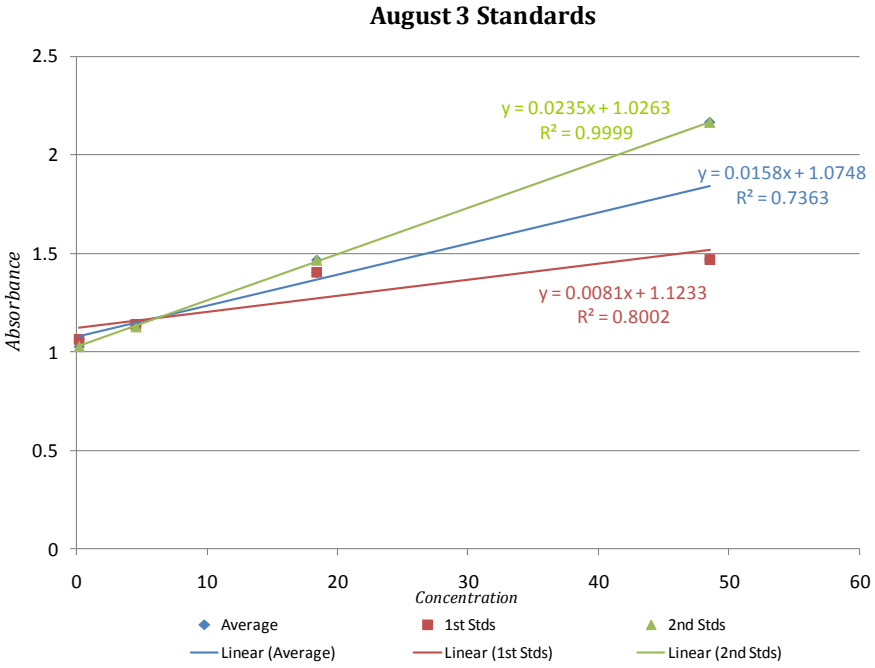


Figure 60: SXS3_srvy2 standards

**Table 39: SXS3_srvy2 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| Std 4 | 48.52 | 8/3/09 | 14:58 | 1.4702 | 0.02702 |
| Std 3 | 18.39 | 8/3/09 | 15:03 | 1.4033 | 0.02161 |
| Std 2 | 4.54 | 8/3/09 | 15:20 | 1.1387 | 0.02278 |
| Std 1 | 0.18 | 8/3/09 | 15:30 | 1.0630 | 0.02091 |
| Std 4 | 48.52 | 8/4/09 | 4:32 | 2.1631 | 0.02573 |
| Std 3 | 18.39 | 8/4/09 | 4:54 | 1.4662 | 0.02358 |
| Std 2 | 4.54 | 8/4/09 | 5:30 | 1.1292 | 0.01604 |
| Std 1 | 0.18 | 8/4/09 | 5:55 | 1.0290 | 0.01472 |

**Table 40: SXS3_srvy2 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Conc.* | *Date run* |
|---|---|---|---|---|---|---|---|
| 8/4/09 | 3:59 | #31 | 0.6855 | 0.6111 | 0.0066 | 77.97 | 9/14/09 |
| 8/3/09 | 17:15 | | 2.2886 | n/a | 0.0402 | | 8/3/09 |
| 8/3/09 | 17:30 | | 2.3878 | n/a | 0.0360 | | 8/3/09 |
| 8/3/09 | 23:52 | | 1.6395 | n/a | 0.0285 | | 8/3/09 |
| 8/4/09 | 0:50 | | 2.2446 | n/a | 0.0743 | | 8/3/09 |

**Table 41: SXS3_srvy2 notes**

| | | |
|---|---|---|
| 8/3/09 | 14:33 | begin standards |
| 8/3/09 | 15:35 | end standards |
| 8/3/09 | 16:32 | heater issues. Very hot; collected acidification line sample while cooling |
| 8/3/09 | 17:41 | acidification line test sample followed by double acidified acidification line sample |
| 8/3/09 | 18:38 | TFF |
| 8/3/09 | 18:58 | Surface TFF |
| 8/3/09 | 19:59 | bulk acidified seawater |
| 8/3/09 | 21:43 | milliQ |
| 8/3/09 | 22:54 | TFF |
| 8/3/09 | 23:38 | milliQ |
| 8/4/09 | 0:03 | begin acidification line tests |
| 8/4/09 | 0:59 | end acidification line tests; begin TFF |
| 8/4/09 | 4:03 | standards |

#### 4.3.2.1.3 August 4—Patch tracing day 3 (SXS3_srvy3)

August 4 was the third day of the patch survey for SXS3. The system was run alternating between the surface fish flow (known to be very low in iron) and the supersucker flow. A discrete sample was collected from the surface at about 21:59 and run unacidified. The sample was then poured into a new bottle, acidified, and ran on the system. The results, as usual, did not match.

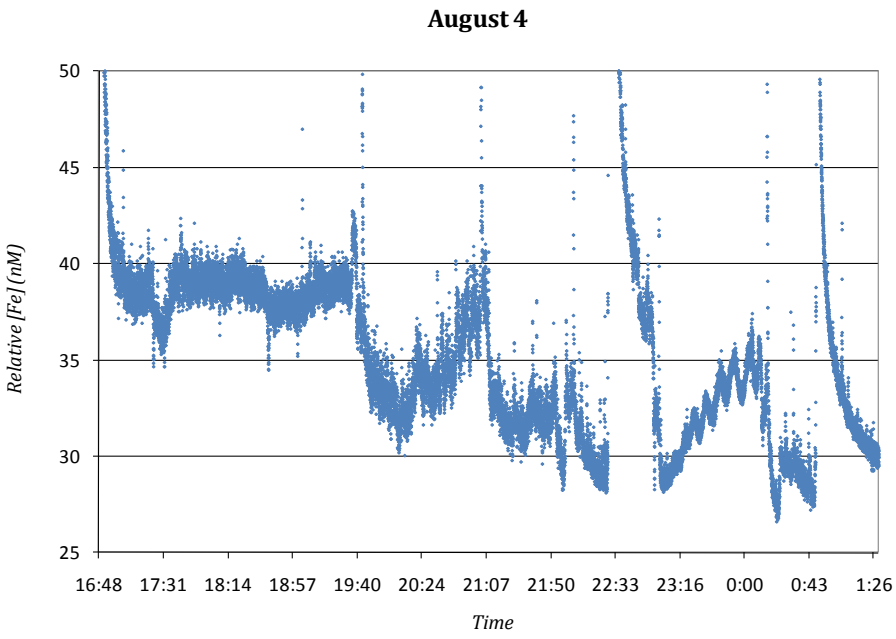


Figure 61: Relative [Fe] (SXS3_srvy3)

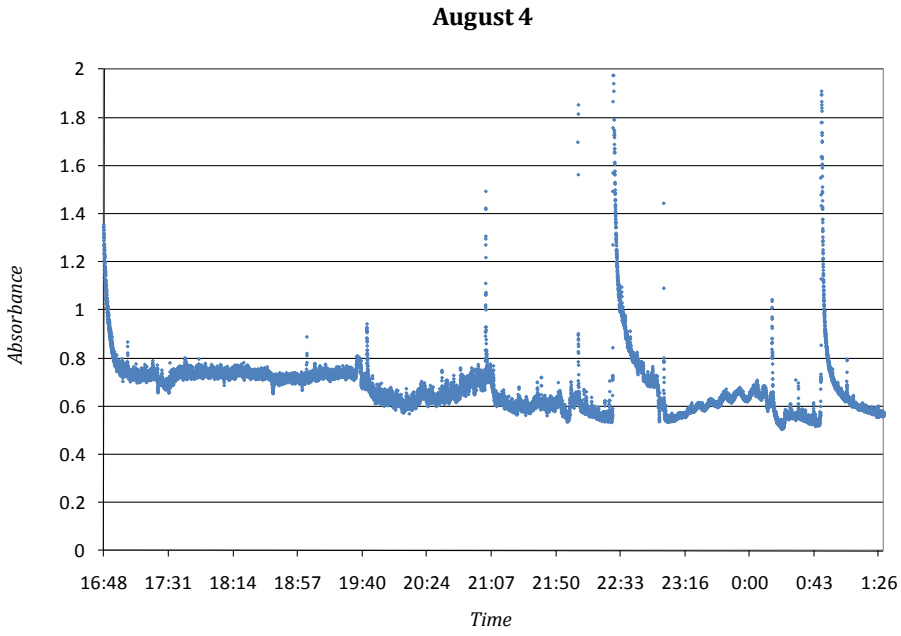


Figure 62: Absorbance (SXS3_srvy3)

**Table 42: SXS3_srvy3 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| Std 1 | 1.3553 | 0.0232 | -0.0164 | | 3.68 | | 0.0189 |
| Std 2 | 1.3191 | 0.0169 | -0.0098 | | *(Std1 Avg)* | | *Slope 1:* |
| Std 3 | 1.5517 | 0.0211 | -0.0038 | | | | 0.0198 |
| Std 4 | 2.2207 | 0.0396 | 0.0190 | | | | *Slope 2:* |
| *Average* | | 0.0252 | | | | | 0.018 |

**Internal Lag time:** ≈ 5 minutes

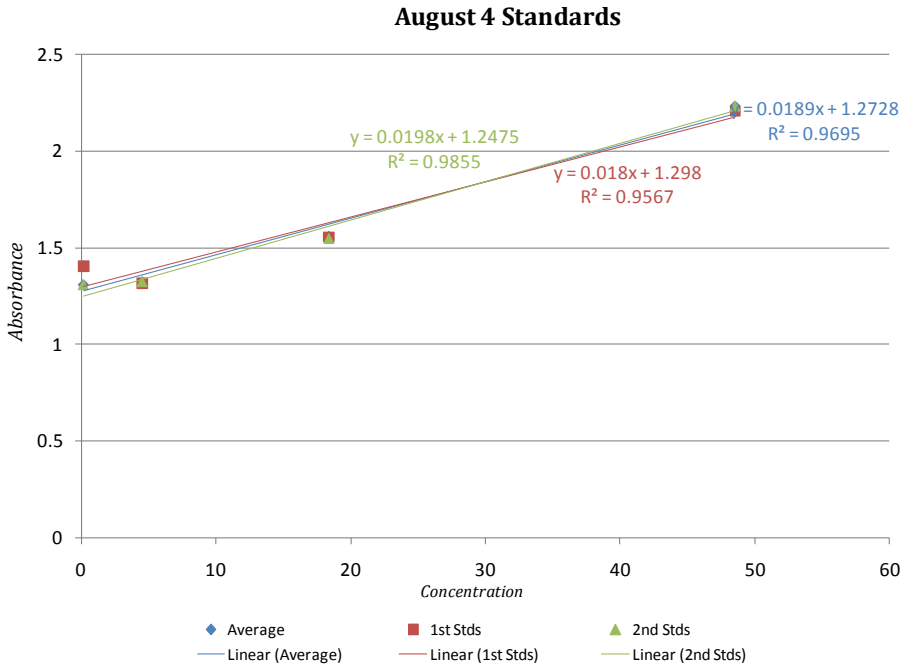


Figure 63: SXS3_srvy3 standards

**Table 43: SXS3_srvy3 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| Std 4 | 48.52 | 8/4/09 | 15:47 | 2.2066 | 0.03008 |
| Std 3 | 18.39 | 8/4/09 | 16:09 | 1.5572 | 0.02303 |
| Std 2 | 4.54 | 8/4/09 | 16:25 | 1.3163 | 0.02179 |
| Std 1 | 0.18 | 8/4/09 | 21:43 | 1.4044 | 0.03141 |
| Std 1 | 0.18 | 8/5/09 | 1:28 | 1.3062 | 0.01501 |
| Std 2 | 4.54 | 8/5/09 | 1:50 | 1.3218 | 0.01202 |
| Std 3 | 18.39 | 8/5/09 | 2:19 | 1.5462 | 0.01920 |
| Std 4 | 48.52 | 8/5/09 | 3:05 | 2.2347 | 0.04910 |

**Table 44: SXS3_srvy3 discrete samples**

| Date | Time | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Conc.* | *Date run* |
|---|---|---|---|---|---|---|---|
| 8/4/09 | 22:22 | surface sample (unacdified) | 1.2666 | n/a | 0.02051 | 67.02 | 8/4/09 |
| 8/4/09 | 22:50 | surface sample (acdified) | 1.6357 | n/a | 0.01681 | 86.54 | 8/4/09 |

**Table 45: SXS3_srvy3 notes**

| | | |
|---|---|---|
| 8/4/2009 | 15:06 | Began replacing tubing |
| 8/4/2009 | 15:25 | Finished replacing tubing |
| 8/4/2009 | 15:41 | Standards |
| 8/4/2009 | 16:47 | TFF |
| 8/4/2009 | 19:45 | Surface TFF |
| 8/4/2009 | 22:30 | Surface discrete sample collected |
| 8/5/2009 | 0:49 | Supersucker TFF |
| 8/5/2009 | 1:28 | Begin standards |

#### 4.3.2.1.4 August 5—Patch tracing day 4 (SXS3_srvy4)

August 5, 2009 was day four of the patch survey. The GCFA was run constantly with no discrete samples run during the day. A discrete sample was collected from the supersucker near the surface via the sink port and was very high in iron compared to in the inline samples even when taking into consideration the issues with NASS-5 when the sample was run in the lab on September 14, 2009.

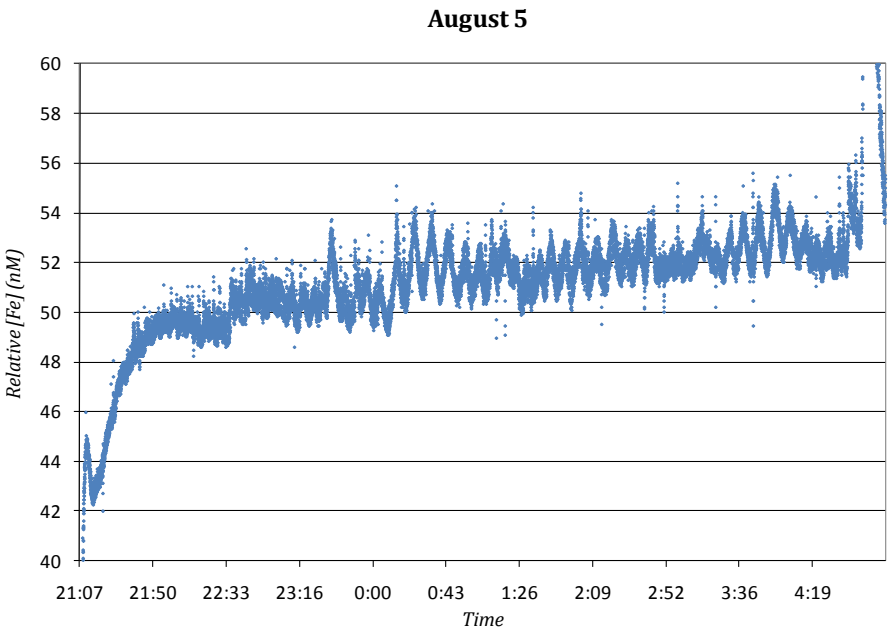


Figure 64: Relative [Fe] (SXS3_srvy4)

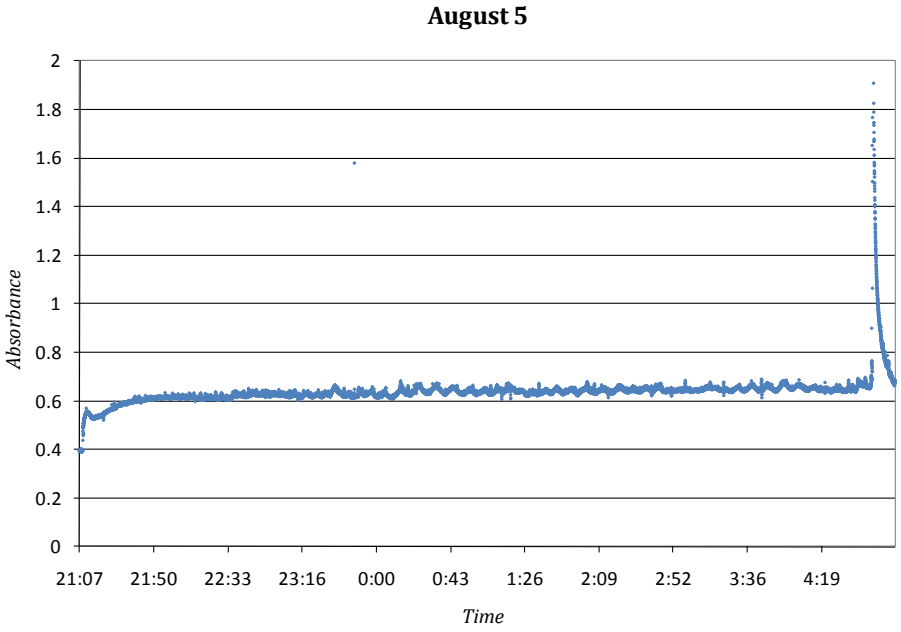


Figure 65: Absorbance (SXS3_srvy4)

**Table 46: SXS3_srvy4 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| Std 1 | 1.1741 | 0.0171 | 0.0171 | | 4.13 | | 0.0124 |
| Std 2 | 1.2196 | 0.0089 | 0.0035 | | *(Std1 Avg)* | | *Slope 1:* |
| Std 3 | 1.3694 | 0.0180 | 0.0097 | | | | 0.0142 |
| Std 4 | 1.7601 | 0.0137 | -0.0038 | | | | *Slope 2:* |
| *Average* | | 0.0144 | | | | | 0.0104 |

**Internal Lag time:** ≈ 5 minutes

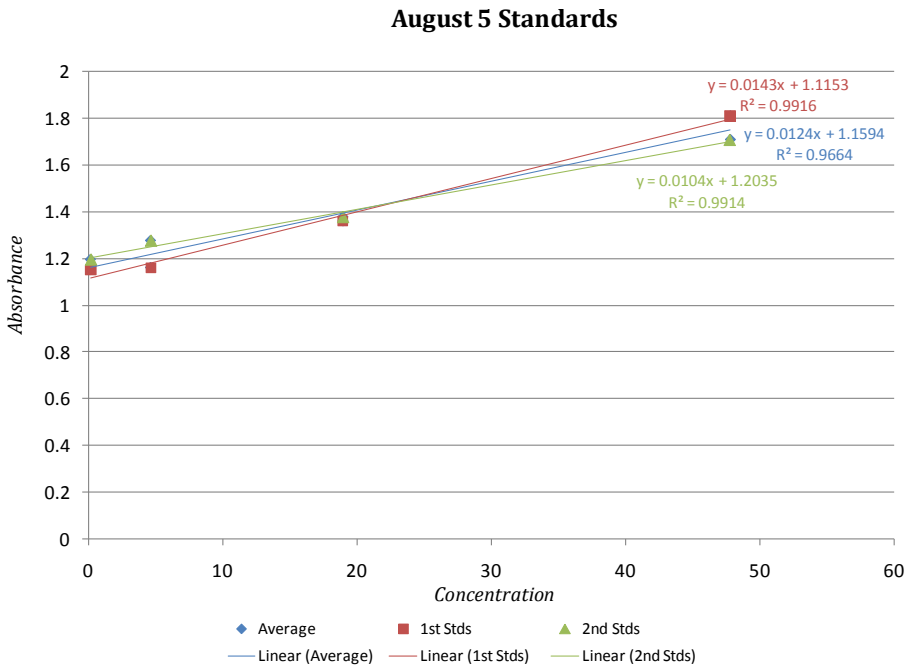


Figure 66: SXS3_srvy4 standards

**Table 47: SXS3_srvy4 standards**

| *Standard* | *Concentration* | *Date* | *Month* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| Std 1 | 0.18 | 8/5/09 | 17:32 | 1.1518 | 0.00852 |
| Std 2 | 4.65 | 8/5/09 | 17:43 | 1.1617 | 0.00716 |
| Std 3 | 18.97 | 8/5/09 | 18:03 | 1.3604 | 0.01316 |
| Std 4 | 47.8 | 8/5/09 | 18:20 | 1.8109 | 0.01563 |
| Std 2 | 4.65 | 8/6/09 | 5:37 | 1.2775 | 0.01064 |
| Std 1 | 0.18 | 8/6/09 | 5:57 | 1.1964 | 0.02558 |
| Std 3 | 18.97 | 8/6/09 | 6:13 | 1.3784 | 0.02291 |
| Std 4 | 47.8 | 8/6/09 | 6:27 | 1.7092 | 0.01180 |

**Table 48: SXS3_srvy 4 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Conc.* | *Date run* |
|---|---|---|---|---|---|---|---|
| 8/6/09 | 4:38 | #45 | 0.7294 | 0.6551 | 0.00843 | 83.19 | 9/14/09 |

**Table 49: SXS3_srvy4 notes**

| | | |
|---|---|---|
| 8/5/2009 | 17:04 | Begin standards |
| 8/5/2009 | 18:27 | End standards; begin milliQ |
| 8/5/2009 | 21:09 | End milliQ; begin TFF |
| 8/6/2009 | 4:46 | Begin standards |
| 8/6/2009 | 6:30 | End standards |

### 4.3.2.1.5 August 6—Patch tracing day 5 (SXS3_srvy5)

August 6, 2009 was the fifth day of following the patch during SXS3. The GCFA was run without interruption and a discrete TFF sample was taken at 15:14. This sample was acidified and run along with the standards at the end of the day.

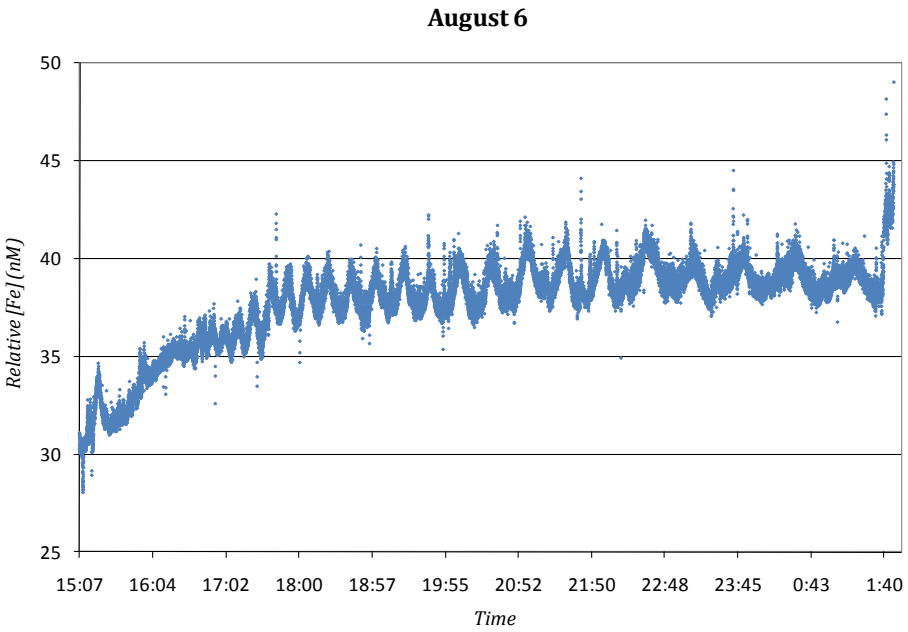


Figure 67: Relative [Fe] (SXS3_srvy5)

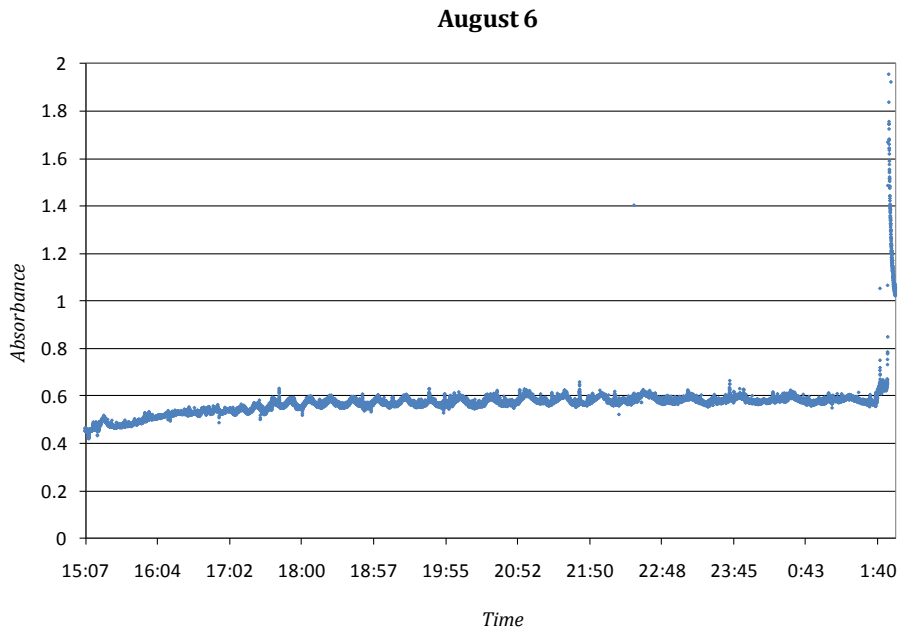


Figure 68: Absorbance (SXS3_srvy5)

**Table 50: SXS3_srvy5 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| MilliQ | 0.8104 | 0.0035 | n/a | | 1.91 | | 0.0149 |
| Std 1 | 1.0499 | 0.0095 | 0.1670 | | *(Std1 Avg)* | | *Slope 1:* |
| Std 2 | 1.1083 | 0.1771 | 0.2005 | | | | 0.0101 |
| Std 3 | 0.0153 | 0.0153 | 0.4356 | | | | *Slope 2:* |
| Std 4 | 0.0156 | 0.0156 | 0.6238 | | | | 0.0186 |
| *Average* | | 0.0487 | | | | | |

**Internal Lag time:** ≈ 5 minutes

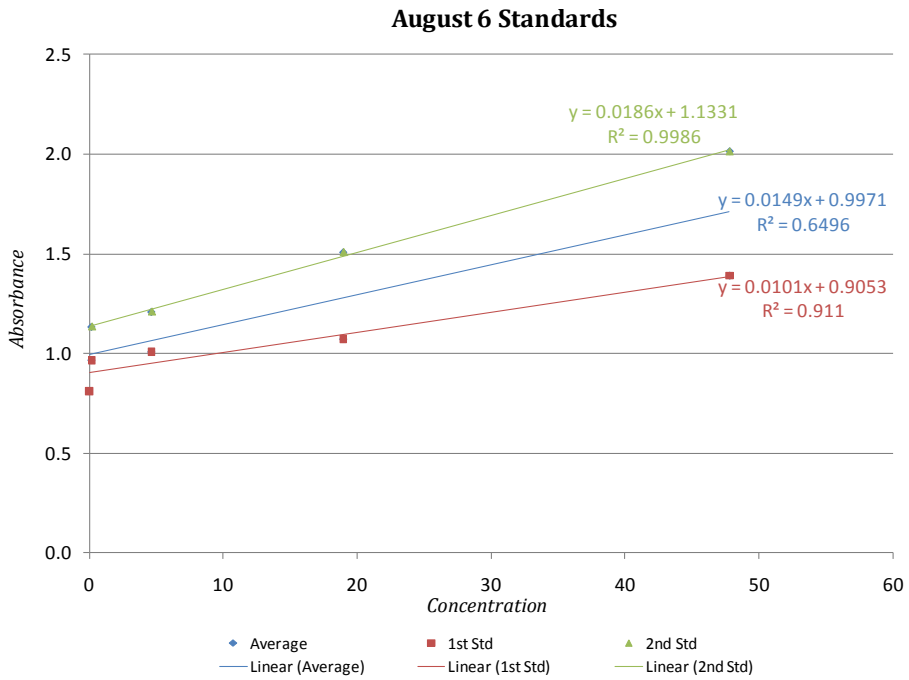


Figure 69: SXS3_srvy 5 standards

**Table 51: SXS3_srvy5 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| MilliQ | 0 | 8/6/09 | 13:50 | 0.8104 | 0.00355 |
| 1 | 0.18 | 8/6/09 | 14:07 | 0.9664 | 0.00879 |
| 2 | 4.65 | 8/6/09 | 14:32 | 1.0080 | 0.34019 |
| 3 | 18.97 | 8/6/09 | 14:43 | 1.0720 | 0.01162 |
| 4 | 47.8 | 8/6/09 | 14:54 | 1.3907 | 0.01126 |
| 4 | 47.8 | 8/7/09 | 2:08 | 2.0145 | 0.02003 |
| 3 | 18.97 | 8/7/09 | 2:43 | 1.5076 | 0.01894 |
| 2 | 4.65 | 8/7/09 | 3:15 | 1.2085 | 0.01401 |
| 1 | 0.18 | 8/7/09 | 3:29 | 1.1334 | 0.01021 |

**Table 52: SXS3_srvy5 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Conc.* | *Date run* |
|---|---|---|---|---|---|---|---|
| 8/6/09 | 15:14 | Acidified TFF sample | 1.5908 | n/a | 0.01682 | 106.77 | 8/7/09 |
| 8/7/09 | 1:47 | #51 | 0.8608 | 0.7864 | 0.00984 | 98.83 | 9/14/09 |

**Table 53: SXS3_srvy5 notes**

| | | |
|---|---|---|
| 8/6/09 | 13:51 | acidified milliQ |
| 8/6/09 | 14:12 | begin standards |
| 8/6/09 | 15:12 | TFF |
| 8/7/09 | 14:28 | TFF sample taken |
| 8/7/09 | 1:40 | begin standards |
| 8/7/09 | 3:32 | begin running TFF sample (collected 8/6 15:28) |

#### 4.3.2.1.6 August 7—45°N Transect (SXS3_xsct4)

The transect at 45°N was run uninterrupted. A sample (#61) was collected and run both unacidified and acidified at the end of the day. A plateau was never reached for the sample when it was acidified (only ~30mL were taken). Several other samples were collected, acidified, and analyzed in the lab.

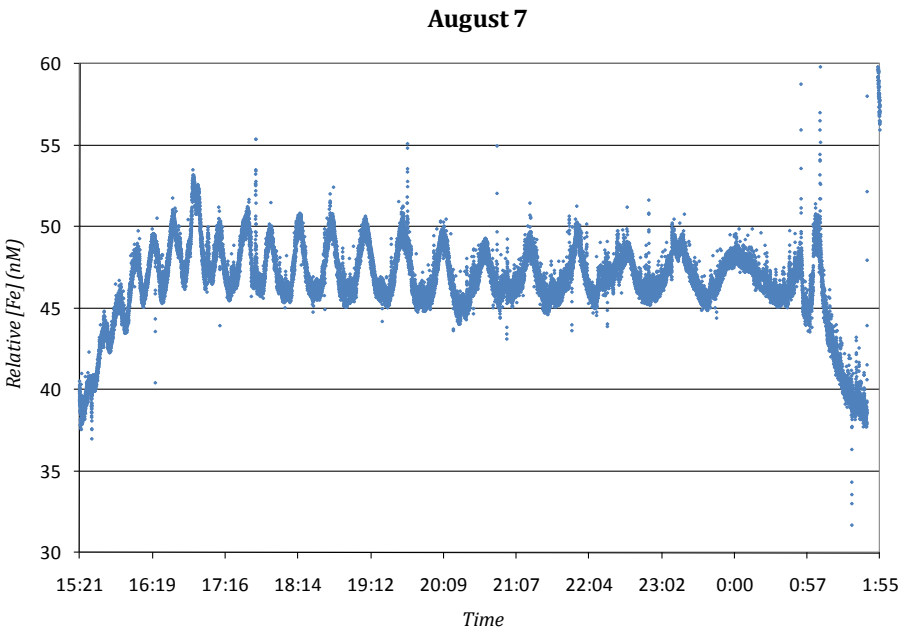


Figure 70: Relative [Fe] (SXS3_xsct4)

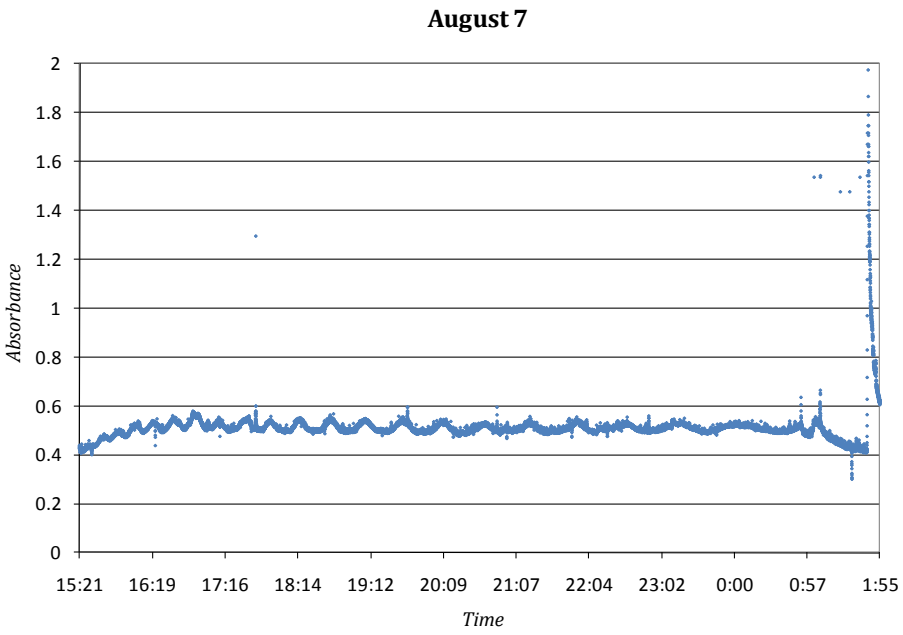


Figure 71: Absorbance

**Table 54: SXS3_xsct4 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| MilliQ | n/a | n/a | n/a | | 3.32 | | 0.0108 |
| Std 1 | 0.8838 | 0.0119 | 0.0020 | | *(Std1 Avg)* | | *Slope 1:* |
| Std 2 | 0.9665 | 0.0326 | 0.0448 | | | | 0.0103 |
| Std 3 | 1.0606 | 0.0176 | 0.0096 | | | | *Slope 2:* |
| Std 4 | 1.4153 | 0.0234 | 0.0101 | | | | 0.0114 |
| *Average* | | 0.0214 | | | | | |

**Internal Lag time:** ≈ 7 minutes

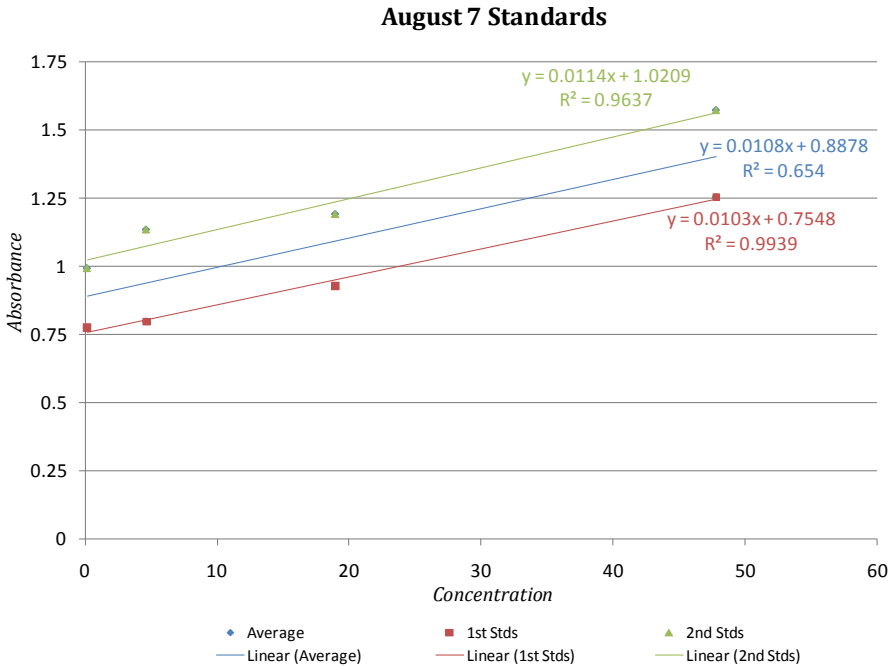


Figure 72: SXS3_xsct4 standards

**Table 55: SXS3_xsct4 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| Std 2 | 4.65 | 8/7/09 | 14:09 | 0.7973 | 0.01021 |
| Std 1 | 0.18 | 8/7/09 | 14:20 | 0.7745 | 0.01094 |
| Std 3 | 18.97 | 8/7/09 | 14:43 | 0.9282 | 0.01282 |
| Std 4 | 47.8 | 8/7/09 | 15:03 | 1.2551 | 0.01789 |
| Std 4 | 47.8 | 8/8/09 | 2:09 | 1.5756 | 0.02888 |
| Std 2 | 4.65 | 8/8/09 | 2:40 | 1.1357 | 0.05504 |
| Std 3 | 18.97 | 8/8/09 | 2:45 | 1.1930 | 0.02239 |
| Std 1 | 0.18 | 8/8/09 | 3:09 | 0.9932 | 0.01295 |

**Table 56: SXS3_xsct4 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Concentration* | *Date run* |
|---|---|---|---|---|---|---|---|
| 8/7/09 | 23:22 | #58 | 0.5629 | 0.4885 | 0.01328 | 63.37 | 9/14/09 |
| 8/8/09 | 1:25 | #59 | 0.9364 | 0.8621 | 0.72036 | 107.84 | 9/14/09 |
| 8/8/09 | 1:32 | #60 | 1.0983 | 1.0875 | 0.00652 | 161.12 | 9/15/09 |
| 8/8/09 | 1:38 | Fe #61, unacidified | 0.9819 | n/a | 0.02225 | 90.92 | 8/8/09 |
| 8/8/09 | | Fe #61, acidified no plateau | | | | | 8/8/09 |

**Table 57: SXS3_xsct4 notes**

| | | |
|---|---|---|
| 8/7/09 | 13:57 | begin standards |
| 8/7/09 | 15:11 | begin TFF |
| 8/8/09 | 1:08 | begin Fe #61 (unacidified) |
| 8/8/09 | 1:44 | begin Fe #61 (added acid to bottle) |
| 8/8/09 | 2:16 | standards |

#### 4.3.2.1.7 August 8—43.9°N Transect (SXS3_xsct5)

Transect 5 along 43.9°N was conducted on August 8-9, 2009. The data was collected relatively uninterrupted with a break at 8/9 3:06 when the supersucker flow was stopped. There was one other small problem with the GCFA at about 9/8 10:15 which was resolved and then standards were run. A discrete sample was also collected from the supersucker flow at 8/8 16:43 and the discrete sample was measured as having much higher iron than the inline sample. The source of this sample was not recorded, however it was most likely from the TFF but may possibly have been from the sink port.

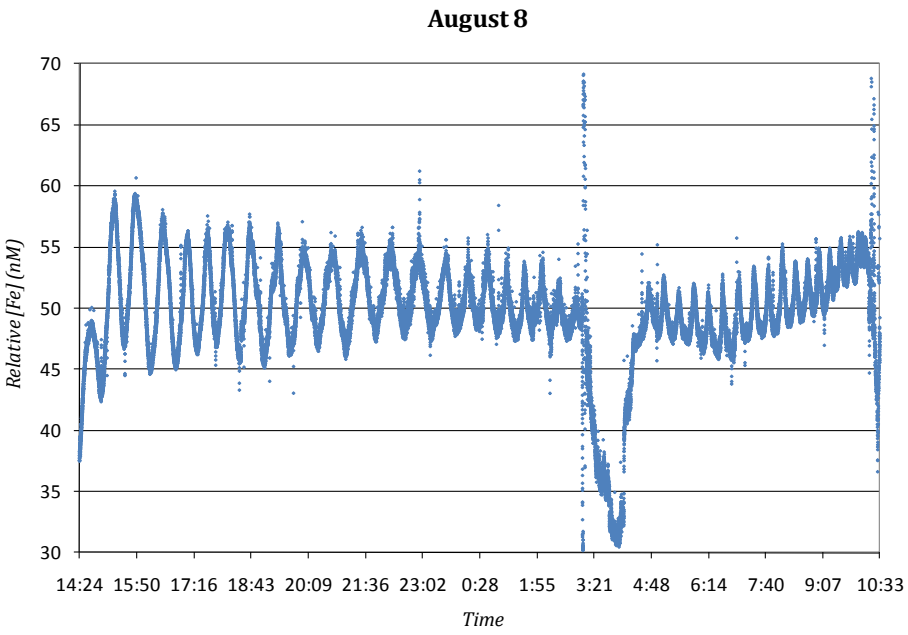


Figure 73: Relative [Fe] (SXS3_xsct5)

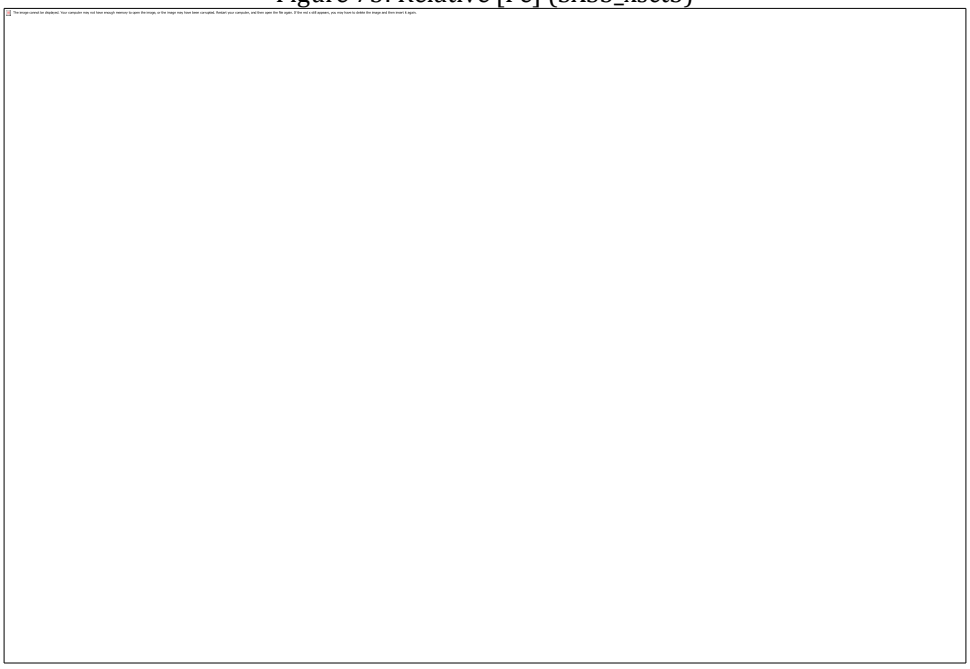

Figure 74: Absorbance (SXS3_xsct5)

**Table 58: SXS3_xsct5 summary**

| | *Absorb.* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| MilliQ | 1.0366 | 0.0130 | | | 2.45 | | 0.011 |
| Std 1 | 0.7465 | 0.0090 | -0.0252 | | *(Std1 Avg)* | | *Slope 1:* |
| Std 2 | 0.9845 | 0.0120 | 0.4728 | | | | 0.0072 |
| Std 3 | 1.0791 | 0.0165 | 0.4397 | | | | *Slope 2:* |
| Std 4 | 1.3873 | 0.0167 | 0.0052 | | | | 0.013 |
| *Average* | | 0.0135 | | | | | |

**Internal Lag time:** ≈ 5 minutes

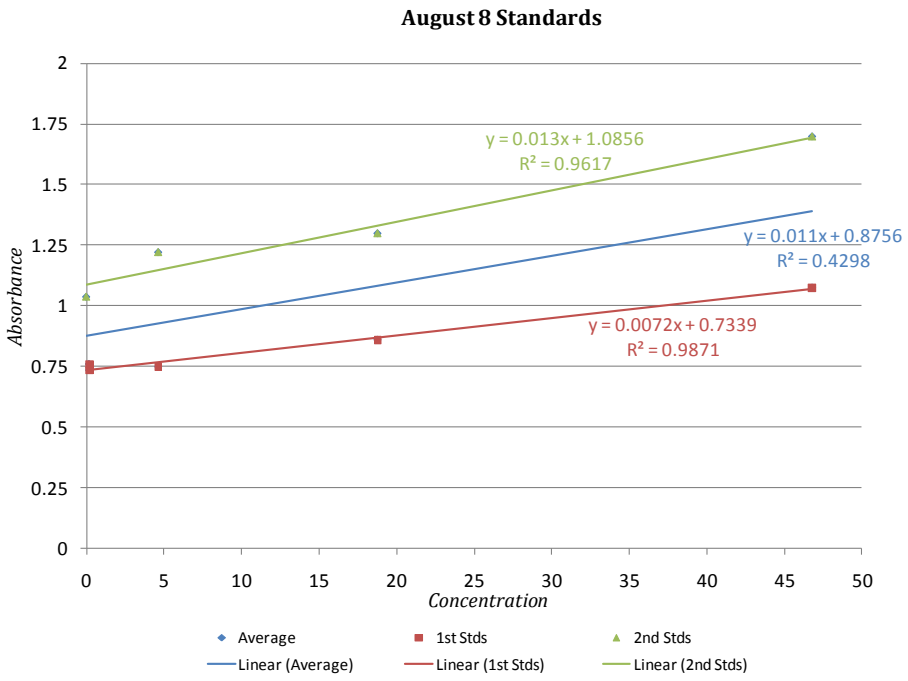


Figure 75: SXS3_xsct5 standards

**Table 59: SXS3_xsct5 standards**

| *Standard* | *Concentration* | *Date* | *Month* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| Std 1 | 0.18 | 8/8/09 | 13:23 | 0.7591 | 0.00710 |
| Std 1 | 0.19 | 8/8/09 | 13:36 | 0.7340 | 0.01084 |
| Std 2 | 4.64 | 8/8/09 | 13:46 | 0.7481 | 0.00801 |
| Std 3 | 18.77 | 8/8/09 | 14:04 | 0.8593 | 0.01456 |
| Std 4 | 46.78 | 8/8/09 | 14:09 | 1.0748 | 0.01414 |
| Std 2 | 4.64 | 8/9/09 | 11:59 | 1.2209 | 0.01592 |
| Std 3 | 18.77 | 8/9/09 | 12:14 | 1.2990 | 0.01854 |
| Std 4 | 46.78 | 8/9/09 | 12:41 | 1.6997 | 0.01931 |
| MilliQ | 0 | 8/9009 | 12:51 | 1.0366 | 0.01299 |

**Table 60: SXS3_xsct5 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Conc.* | *Date run* |
|---|---|---|---|---|---|---|---|
| 8/8/09 | 16:53 | #83 | 1.0295 | 0.9551 | 0.00740 | 118.92 | 9/14/09 |

**Table 61: SXS3_xsct5 notes**

| | | |
|---|---|---|
| 8/8/09 | 13:00 | standards |
| 8/8/09 | 14:10 | Begin TFF flow |
| 8/9/09 | 2:15 | topped off DPD and hydrogen peroxide |
| 8/9/09 | 3:06 | Switched to surface fish TFF (SS problem) |
| 8/9/09 | 4:02 | Switched back to TFF |
| 8/9/09 | 10:16 | Sample line came off, fixed about 10:25 |
| 8/9/09 | 10:39 | acidified CSW seawater |
| 8/9/09 | 11:56 | fixed flow problem (bubble stuck in detector) |
| 8/9/09 | 11:34 | begin standards |

#### 4.3.2.1.8 August 9—Waldport Line (SXS3_xsect6)

The Waldport line was run on August 9-10, 2009. There were a couple small problems with the supersucker (switched to the surface fish TFF at 04:!5 and back to supersucker at 04:49) and with the GCFA (bubble in the flow cell at 6:13). When switching to standards at the end of the run an airblock was created in the sample line—milliQ was forced into the tubing with a syringe to clear. The signal resumed but it was rather noisy which was problematic for the final set of standards.

A series of discrete samples were also collected at the TFF. Some discrete samples were measured as being lower in concentration than the inline samples while others were measured as higher than their inline counterparts.

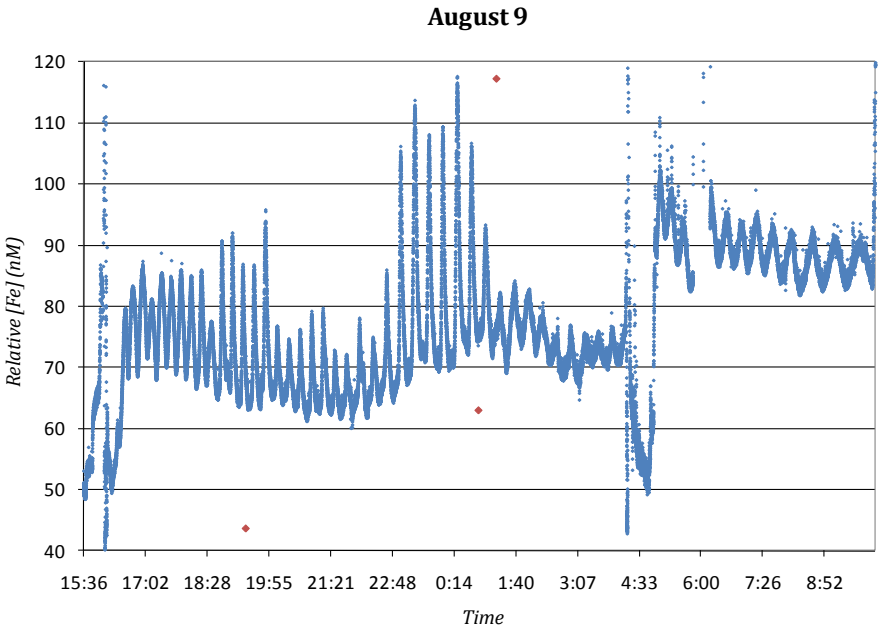


Figure 76: Relative [Fe] (SXS3_xsct6)

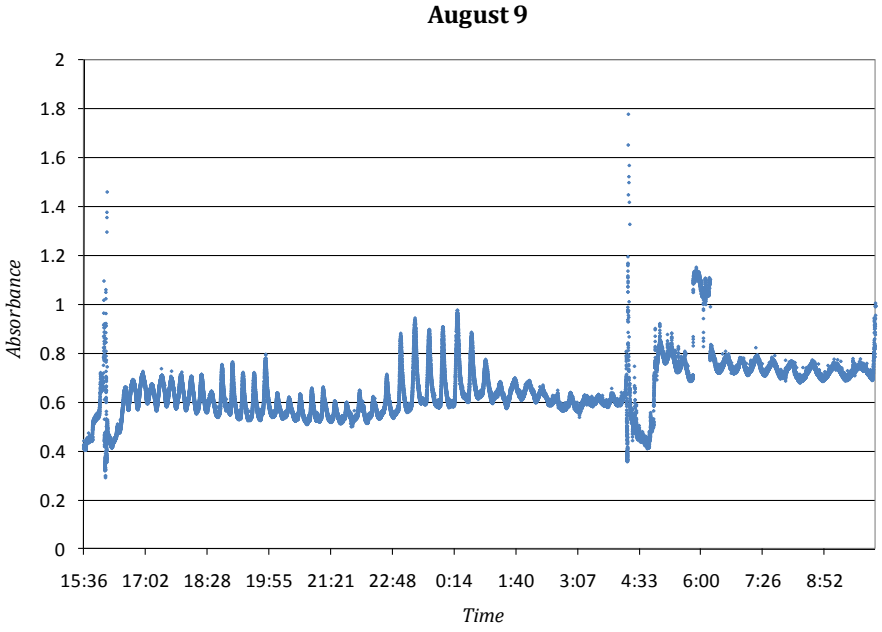


Figure 77: Absorbance (SXS3_xsct6)

**Table 62: SXS3_xsct6 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| MilliQ | 0.7256 | 0.0143 | -0.0391 | | 7.88 | | 0.0083 |
| Std 1 | 0.8621 | 0.0218 | -0.1920 | | *(Std1 Avg)* | | *Slope 1:* |
| Std 2 | 0.8270 | 0.0191 | -0.2599 | | | | 0.0082 |
| Std 3 | 0.9197 | 0.0215 | -0.1974 | | | | *Slope 2:* |
| Std 4 | 1.1854 | 0.0259 | -0.1344 | | | | 0.0084 |
| *Average* | | 0.0205 | | | | | |

**Internal Lag time:** ≈ 5 minutes

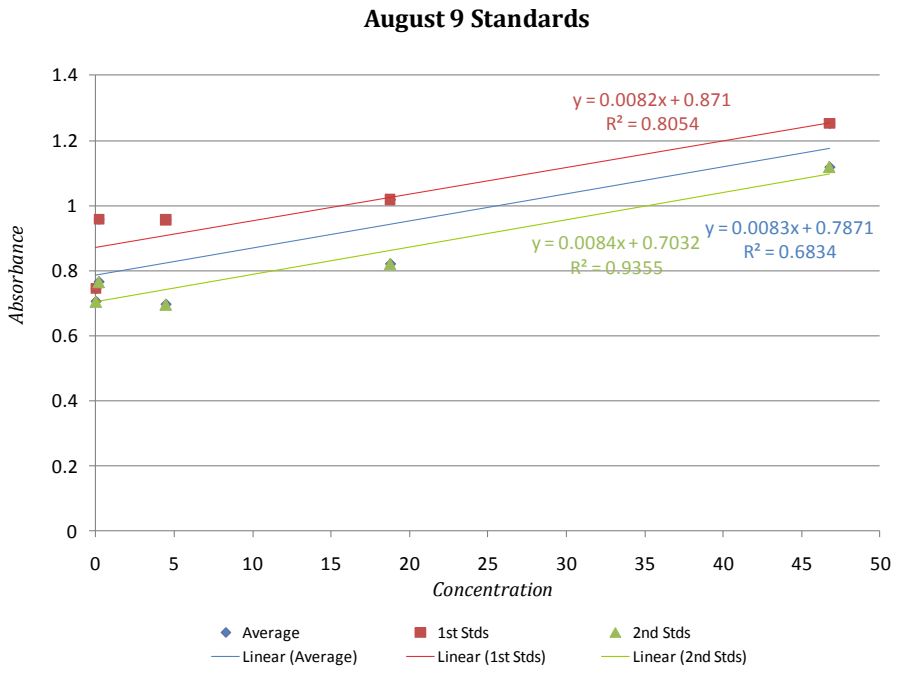


Figure 78: SXS3_xsct6 standards

**Table 63: SXS3_xsct6 standards**

| *Standard* | *Concentration* | *Date* | *Time* | *Absorbance* | *Stdev* |
|---|---|---|---|---|---|
| MilliQ | 0 | 8/9/2009 | 14:39 | 0.7451 | 0.00579 |
| Std 1 | 0.19 | 8/9/2009 | 15:17 | 0.9581 | 0.01284 |
| Std 2 | 4.46 | 8/9/2009 | 15:32 | 0.9569 | 0.01179 |
| Std 3 | 18.77 | 8/9/2009 | 15:41 | 1.0184 | 0.01276 |
| Std 4 | 46.78 | 8/9/2009 | 15:55 | 1.2526 | 0.01485 |
| MilliQ | 0 | 8/10/2009 | 11:28 | 0.7060 | 0.02276 |
| Std 1 | 0.19 | 8/10/2009 | 12:06 | 0.7661 | 0.03078 |
| Std 2 | 4.46 | 8/10/2009 | 12:17 | 0.6970 | 0.02644 |
| Std 3 | 18.77 | 8/10/2009 | 12:40 | 0.8210 | 0.03019 |
| Std 4 | 46.78 | 8/10/2009 | 12:57 | 1.1182 | 0.03699 |

**Table 64: SXS3_xsct6 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Concentration* | *Date run* |
|---|---|---|---|---|---|---|---|
| 8/9/09 | 19:23 | #91 | 0.3970 | 0.322644 | 0.010673 | 43.62 | 9/14/09 |
| 8/10/09 | 0:48 | #94 | 0.5595 | 0.485114 | 0.010914 | 62.96 | 9/14/09 |
| 8/10/09 | 1:10 | #95 | 1.1455 | 1.071144 | 0.012405 | 132.73 | 9/14/09 |
| 8/10/09 | 1:13 | #96 | 1.0155 | 0.941144 | 0.007313 | 117.25 | 9/15/09 |

**Table 65: SXS3_xsct6 notes**

| | | |
|---|---|---|
| 8/9/09 | 14:50 | begin standards |
| 8/9/09 | 16:16 | TFF |
| 8/10/09 | 4:20 | surface TFF |
| 8/10/09 | 5:48 | refilled buffer bottle |
| 8/10/09 | 6:06 | bubble in flow cell |
| 8/10/09 | 10:52 | standards |

#### 4.3.2.1.9 August 10—Newport Line (SXS3_xsect7)

The transect run on August 10-August 11 covered the Newport line going from west to east. This run went quite smoothly aside from some issues with the second set of standards.

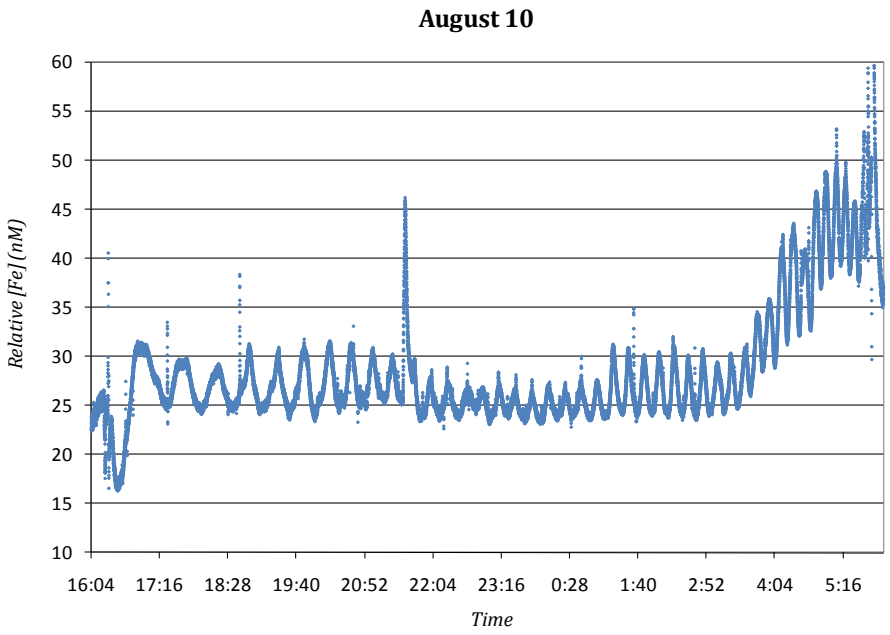


Figure 79: Relative [Fe] (SXS3_xsct7)

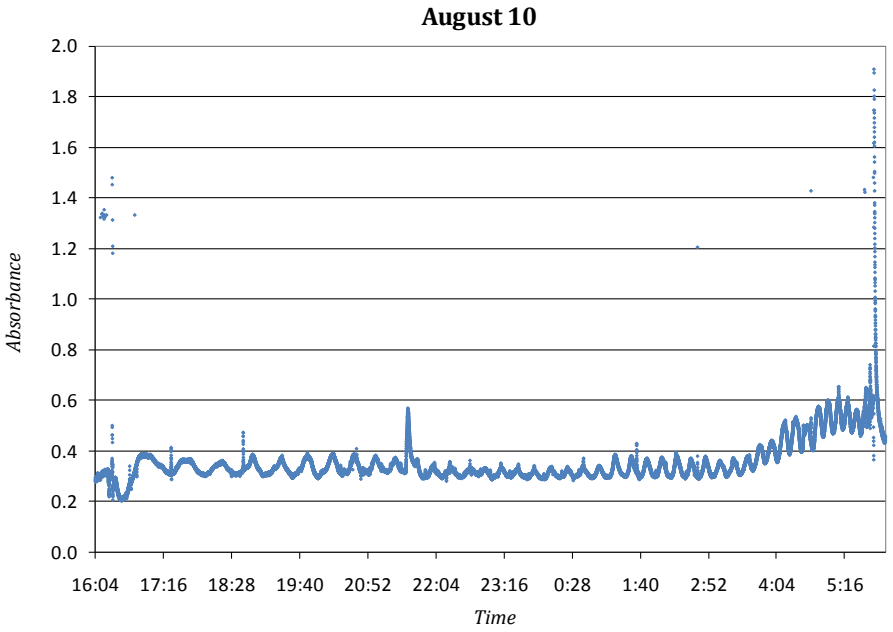


Figure 80: Absorbance (SXS3_xsct7)

**Table 66: SXS3_xsct7 summary**

| | *Absorbance* | *Stdev* | *Drift (Abs 2-Abs1)* | | *Detection Limit:* | | *Slope (avg)* |
|---|---|---|---|---|---|---|---|
| MilliQ | 0.2259 | 0.0094 | 0.1911 | | 2.29 | | 0.0123 |
| Std 1 | 0.4293 | 0.1568 | 0.3180 | | *(MilliQ Avg)* | | *Slope 1:* |
| Std 2 | 0.3903 | 0.0140 | 0.3096 | | | | 0.0135 |
| Std 3 | 0.6906 | 0.0060 | 0.7065 | | | | *Slope 2:* |
| Std 4 | | 0.0069 | 1.0438 | | | | 0.0111 |
| *Average* | | 0.0386 | | | | | |

**Internal Lag time:** ≈ 5 minutes

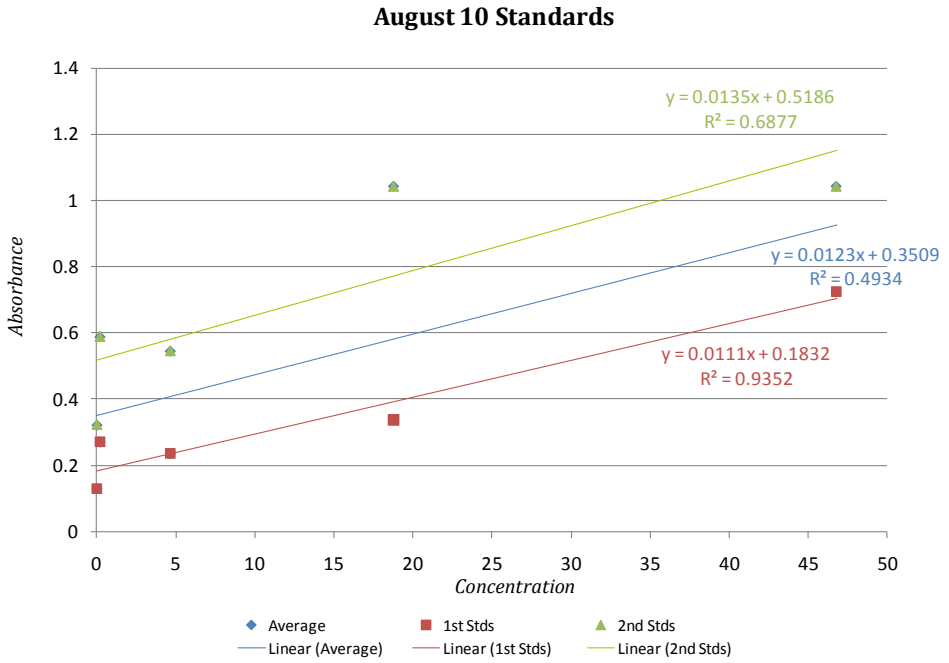


Figure 81: SXS3_xsct7 standards

**Table 67: SXS3_xsct7 standards**

| Standard | Concentration | Date | Time | Absorbance | Stdev |
|---|---|---|---|---|---|
| MilliQ | 0 | 8/10/09 | 15:03 | 0.1304 | 0.00825 |
| Std 1 | 0.19 | 8/10/09 | 15:14 | 0.2703 | 0.01273 |
| Std 2 | 4.64 | 8/10/09 | 15:25 | 0.2355 | 0.00942 |
| Std 3 | 18.77 | 8/10/09 | 15:45 | 0.3373 | 0.01196 |
| Std 4 | 46.78 | 8/10/09 | 16:17 | 0.7242 | 0.01371 |
| Std 4 | 46.78 | 8/11/09 | 6:03 | 1.0438 | 0 |
| Std 3 | 18.77 | 8/11/09 | 6:25 | 1.0438 | 0 |
| Std 2 | 4.64 | 8/11/09 | 6:40 | 0.5452 | 0.01849 |
| Std 1 | 0.19 | 8/11/09 | 6:44 | 0.5883 | 0.30089 |
| MilliQ | 0 | 8/11/09 | 6:57 | 0.3214 | 0.01055 |

**Table 68: SXS3_xsct7 discrete samples**

| *Date* | *Time* | *Sample* | *Abs* | *Blank Corr* | *Stdev* | *Conc.* | *Date run* |
|---|---|---|---|---|---|---|---|
| 8/11/09 | 5:47 | #115 | 1.7566 | 1.7458 | 0.00751 | 260.86 | 9/15/09 |
| 8/11/09 | 5:47 | #118 | 1.8233 | 1.8125 | 0.01519 | 270.97 | 9/15/09 |

**Table 69: SXS3_notes**

| | | |
|---|---|---|
| 8/10/09 | 14:56 | begin standards |
| 8/10/09 | 16:34 | TFF |
| 8/11/09 | 5:50 | standards |

### *4.3.2.2 Discussion*

#### 4.3.2.2.1 High Resolution Data SXS3

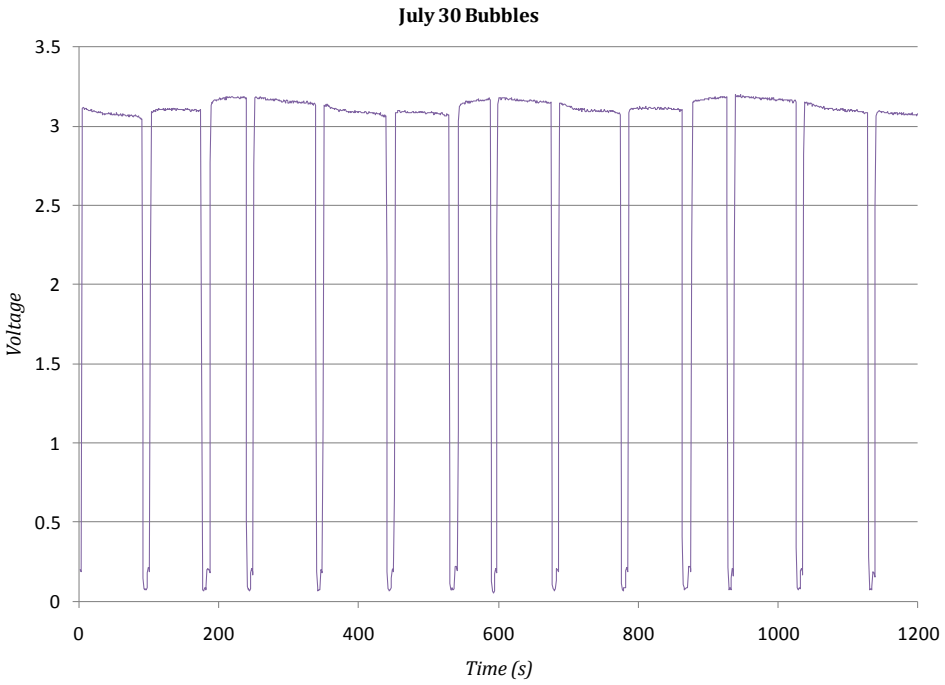


Figure 82: Early SXS3 bubble pattern (20 minutes)

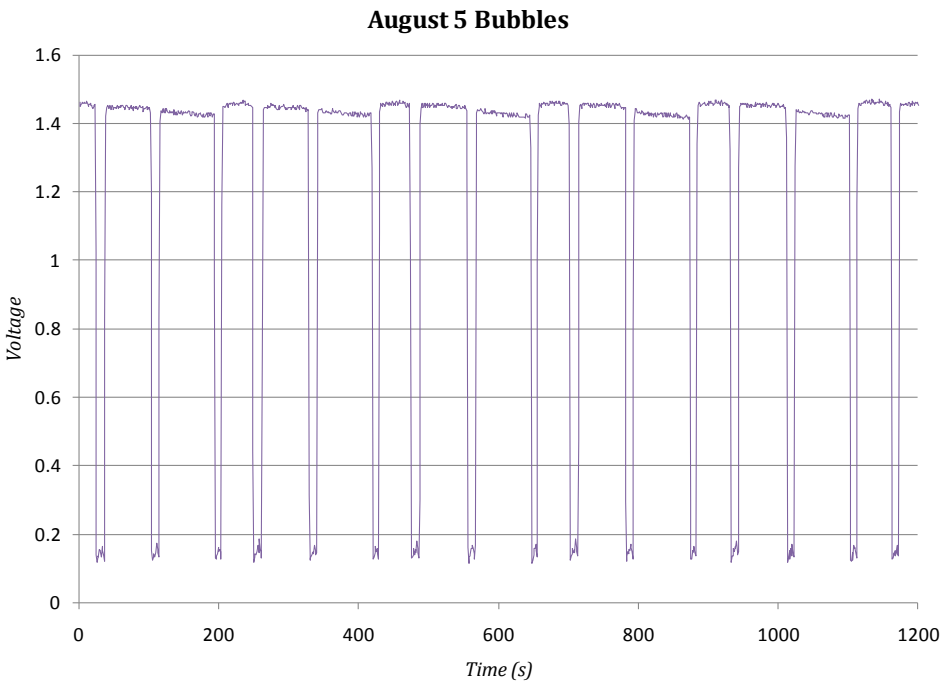


Figure 83: Mid-SXS3 bubble pattern (20 minutes)

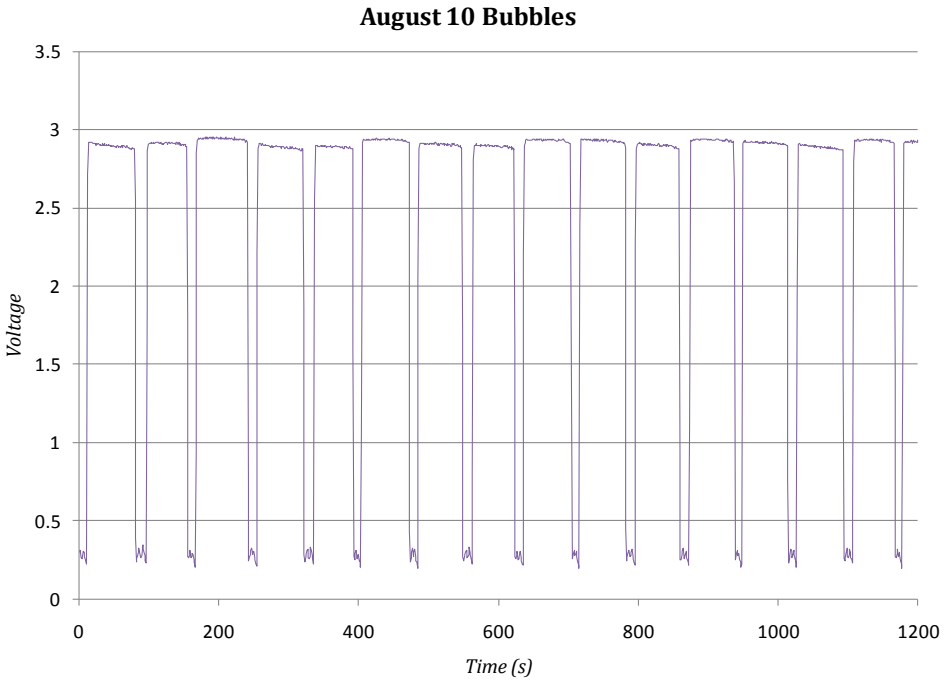


Figure 84: End SXS3 bubble pattern (20 minutes)

The changes in bubble patterns during the August cruise are different than during the May cruise. The rolling variation in the July 30 data is characteristic of early in the cruise. It began to dissipate (as in the August 5 data) and eventually subsided into the best bubble patterns seen on any of the SUCCES cruses as seen in the August 10 data.

#### 4.3.2.2.2 1 Hour Data SXS3

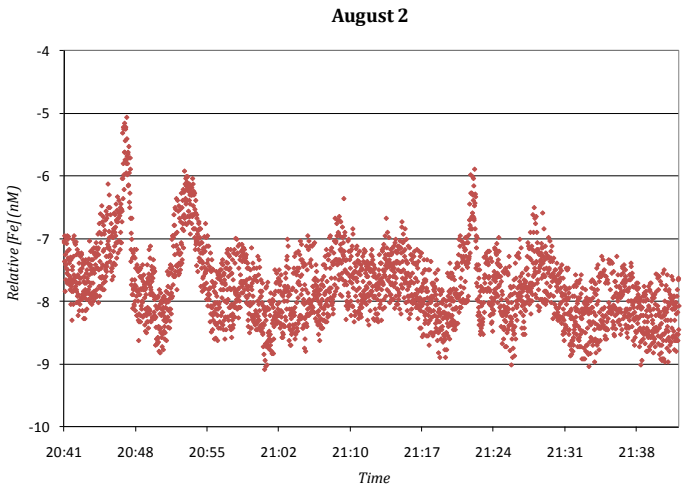


Figure 85: August 2, 1 Hour Data

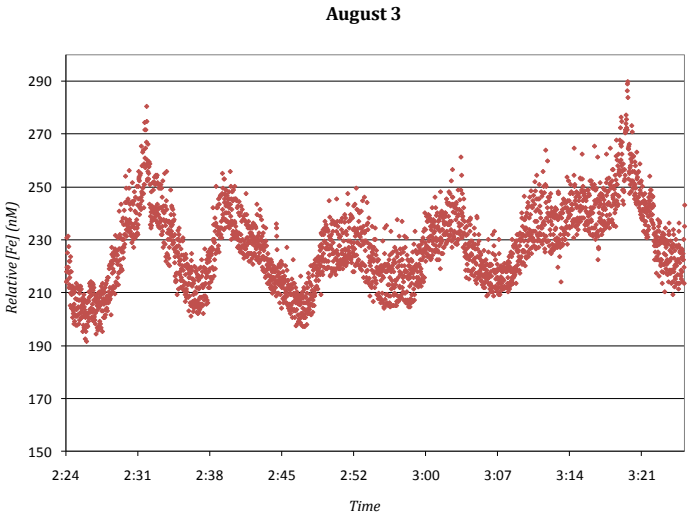


Figure 86: August 3, 1 Hour Data

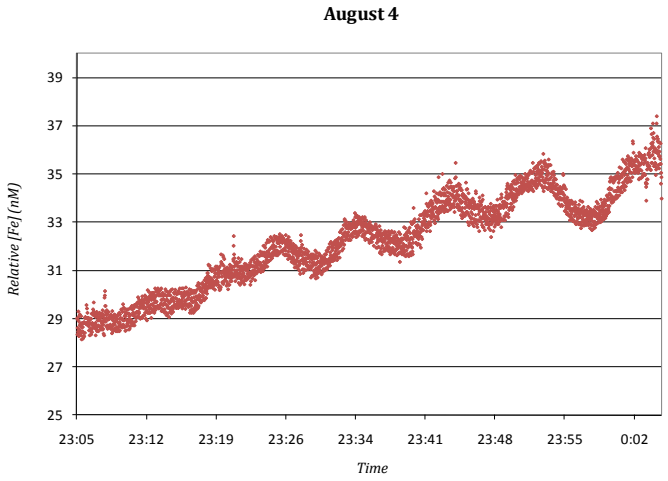


Figure 88: August 4, 1 Hour Data

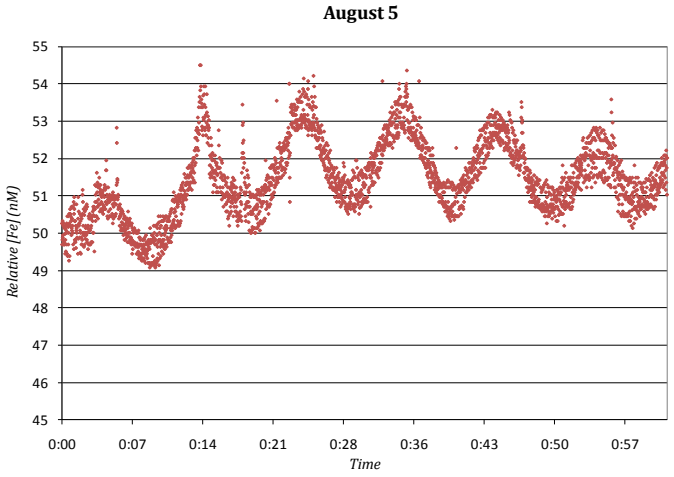


Figure 87: August 5, 1 Hour Data

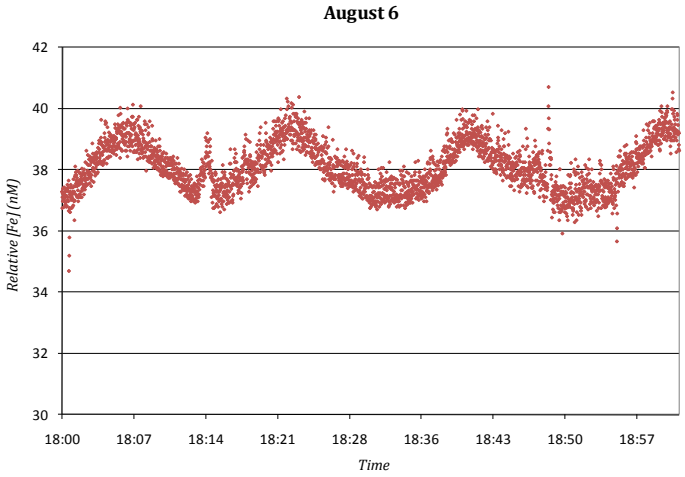


Figure 89: August 6, 1 Hour Data

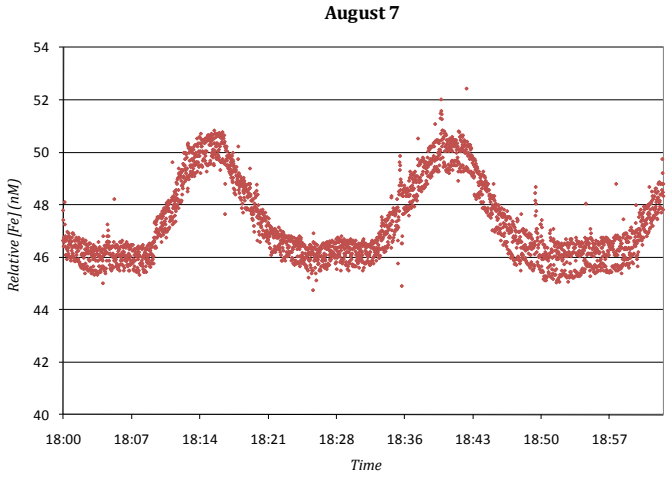


Figure 90: August 7, 1 Hour Data

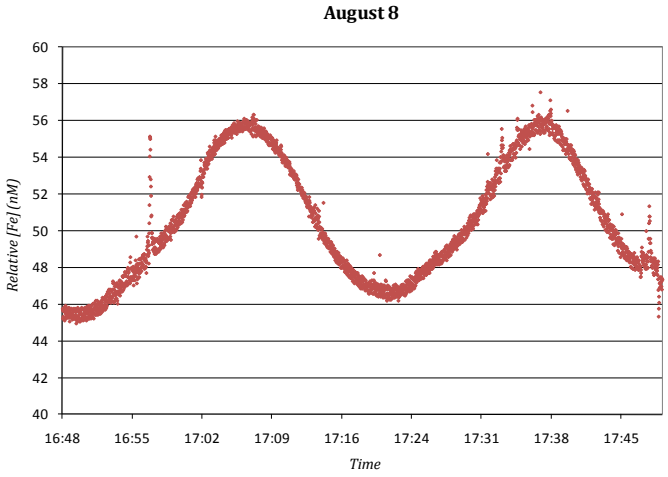


Figure 91: August 8, 1 Hour Data

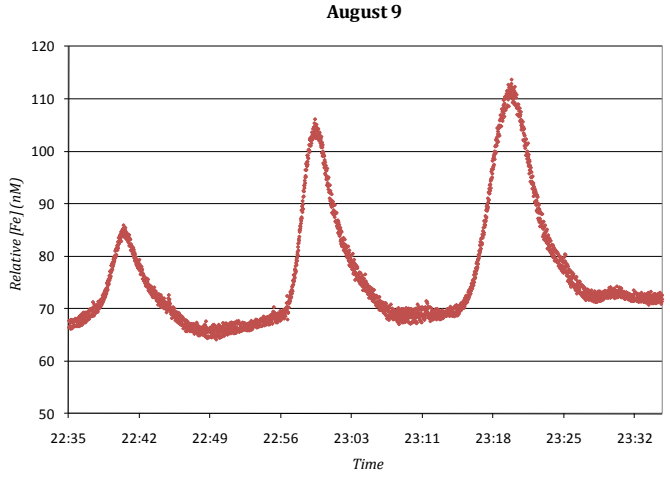


Figure 92: August 9, 1 Hour Data

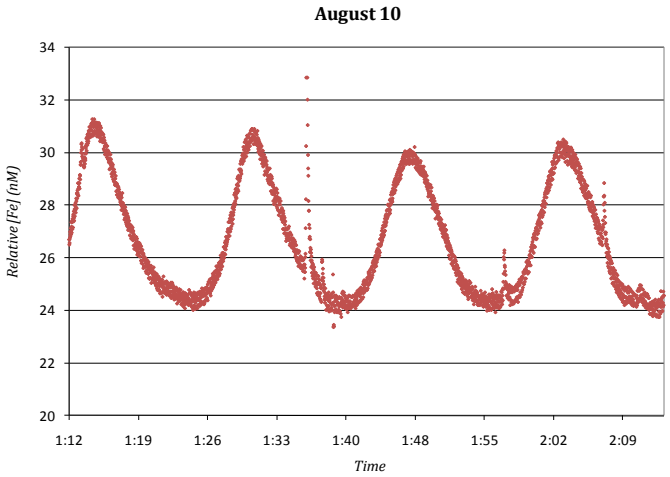


Figure 93: August 10, 1 Hour Data

#### 4.3.2.2.3 Standard Voltages

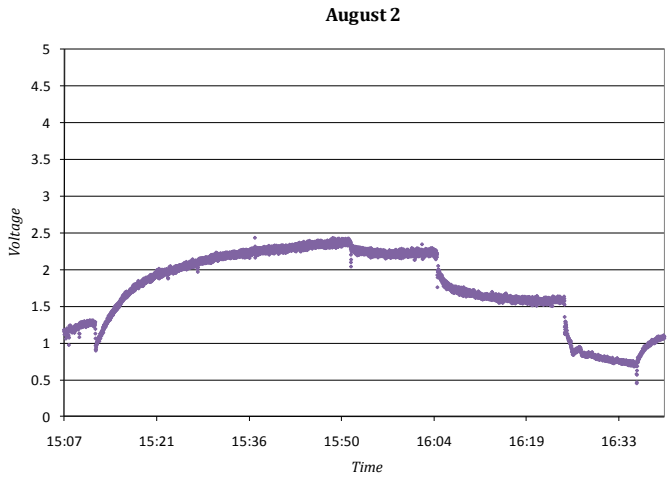


Figure 94: August 2 Standards (1st set)

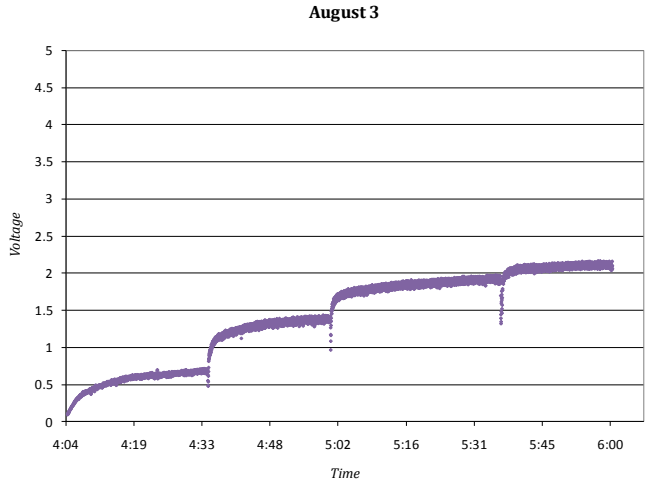


Figure 95: August 3 Standards (2nd set)

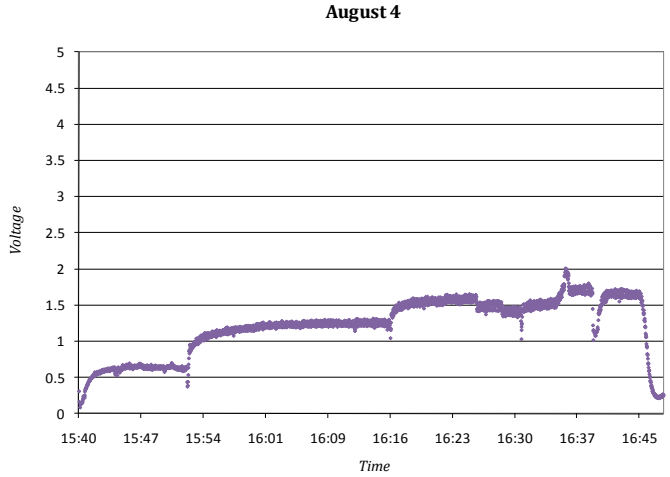


Figure 96: August 4 Standards (1st set)

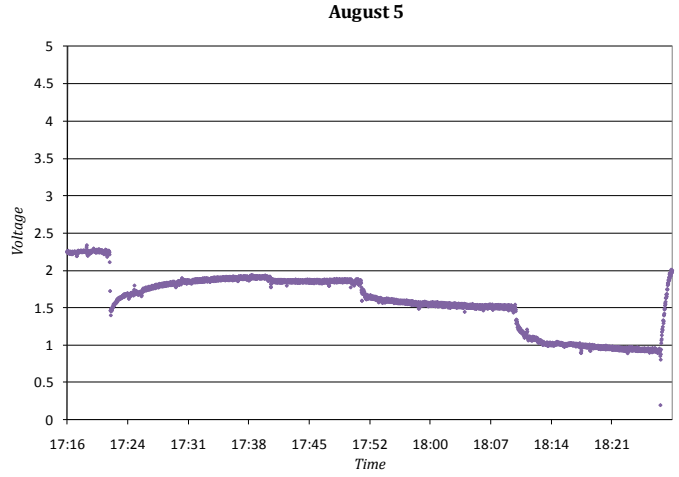


Figure 97: August 5 Standards (1st set)

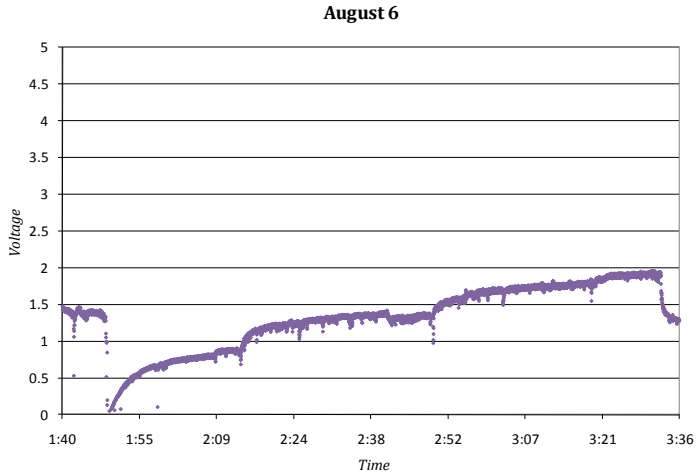


Figure 98: August 6 Standards (2nd set)

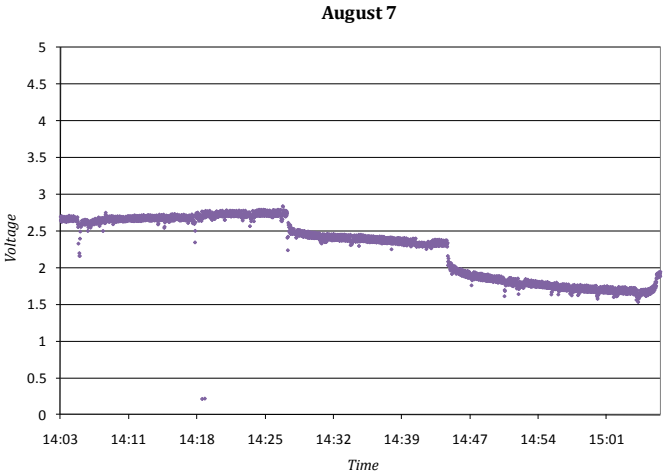


Figure 99: August 7 Standards (1st set)

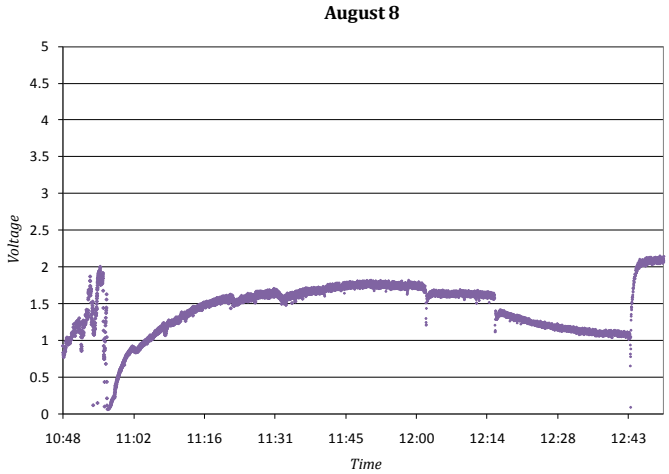


Figure 101: August 8 Standards (1st set)

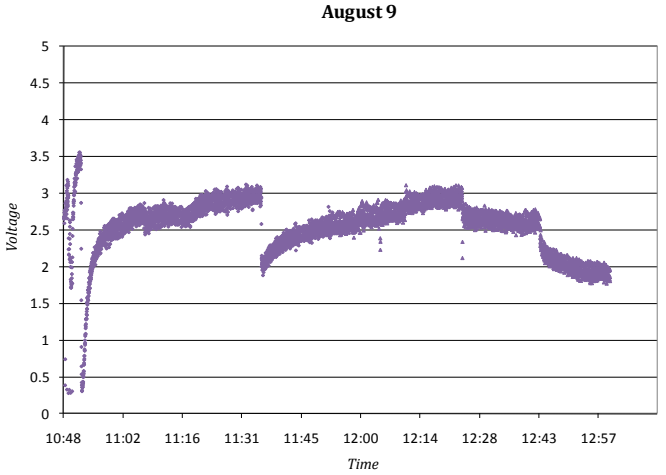


Figure 100: August 9 Standards (1st set)

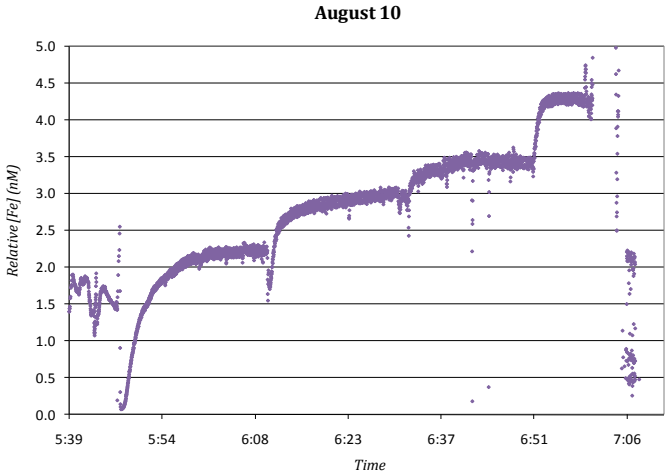


Figure 102: August 10 Standards (2nd set)

### 4.3.3 Cruise Data

**Table 70: Cruise data files**

| *Transect* | | *File* | *Descriptions* |
|---|---|---|---|
| **SXS2** | | | |
| May 23 | 45°N Transect *SXS2_xsct1* | May23.xlsx | May 23 summary of standards and discrete samples, charts of [Fe] and absorbance |
| | | May23data.csv | Processed data file from LabView |
| | | May23times.csv | Peak picking times used in Matlab |
| May 25 | Patch, Day 1 *SXS2_srvy1* | May25.xlsx | May 25 summary file |
| | | May25data.csv | Processed data file from LabView |
| | | May25times.csv | Peak picking times used in Matlab |
| May 26 | Patch, Day 2 *SXS2_srvy2* | May26.xlsx | May 26 summary file |
| | | May26data.csv | Processed data file from LabView |
| | | May26times.csv | Peak picking times used in Matlab |
| May 27 | Patch, Day 3 *SXS2_srvy3* | May27.xlsx | May 27 summary file |
| | | May27data.csv | Processed data from LabView |
| | | May27times.csv | Peak picking times used in Matlab |
| May 28 | Patch, Day 4 *SXS2_srvy4* | May28.xlsx | May 28 summary file |
| | | May28data.csv | Processed data from LabView |
| | | May28times.csv | Peak picking times used in Matlab |
| May 29 | Patch, Day 5 *SXS2_srvy5* | May29.xlsx | May 29 summary file |
| | | May29data.csv | Processed data from LabView |
| | | May29times.csv | Peak picking times used in Matlab |
| May 30 | 45°N Transect *SXS2_xsct2* | May30.xlsx | May 30 summary file |
| | | May30data.csv | Processed data from LabView |
| | | May30times.csv | Peak picking times used in Matlab |
| May 31 | 43.9°N Transect *SXS2_xsct3* | May31.xlsx | May 31 summary file |
| | | May31data.csv | Processed data from LabView |
| | | May31times.csv | Peak picking times used in Matlab |
| **SXS3** | | | |
| August 2 | Patch, Day 1 *SXS3_srvy1* | Aug2.xlsx | August 2 summary of standards and discrete samples, charts of [Fe] and absorbance |
| | | Aug2data.csv | Processed data file from LabView |
| | | Aug2times.csv | Peak picking times used in Matlab |
| August 3 | Patch, Day 2 *SXS3_srvy2* | Aug3.xlsx | August 3 summary file |
| | | Aug3data.csv | Processed data file from LabView |
| | | Aug3times.csv | Peak picking times used in Matlab |
| August 4 | Patch, Day 3 *SXS3_srvy3* | Aug4.xlsx | August 4 summary file |
| | | Aug4data.csv | Processed data file from LabView |
| | | Aug4times.csv | Peak picking times used in Matlab |

| | | | |
|---|---|---|---|
| August 5 | Patch, Day 4<br>*SXS3_srvy4* | Aug5.xlsx | August 5 summary file |
| | | Aug5data.csv | Processed data file from LabView |
| | | Aug5times.csv | Peak picking times used in Matlab |
| August 6 | Patch, Day 5<br>*SXS3_srvy5* | Aug6.xlsx | August 6 summary file |
| | | Aug6data.csv | Processed data file from LabView |
| | | Aug5times.csv | Peak picking times used in Matlab |
| August 7 | 45°N Transect<br>*SXS3_xsct4* | Aug7.xlsx | August 7 summary file |
| | | Aug7data.csv | Processed data file from LabView |
| | | Aug7times.csv | Peak picking times used in Matlab |
| August 8 | 43.9°N Transect<br>*SXS3_xsct5* | Aug8.xlsx | August 8 summary file |
| | | Aug8data.csv | Processed data file from LabView |
| | | Aug8times.csv | Peak picking times used in Matlab |
| August 9 | Waldport Line<br>*SXS3_xsct6* | Aug9.xlsx | August 9 summary file |
| | | Aug9data.csv | Processed data file from LabView |
| | | Aug9times.csv | Peak picking times used in Matlab |
| August 10 | Newport Line<br>*SXS3_xsct7* | Aug10.xlsx | August 10 summary file |
| | | Aug10data.csv | Processed data file from LabView |
| | | Aug10times.csv | Peak picking times used in Matlab |

# 5 Discussion

As it was deployed on SUCCES2 (May 2009) and SUCCES3 (August 2009) there were both failures and successes with the GCFA. The system was improved from the May cruise to the August cruise by focusing on the need to have uniformly sized bubbles that would proceed through the system without breaking or smearing. These improvements seemed to boost the system's ability to show changes in iron concentration.

The system still exhibits a high and widely varying detection limit. During the cruises, the detection limit varied from about 1.6 nM to as high as 5.1 nM. In the lab, the detection limit varied just as much (see chart).

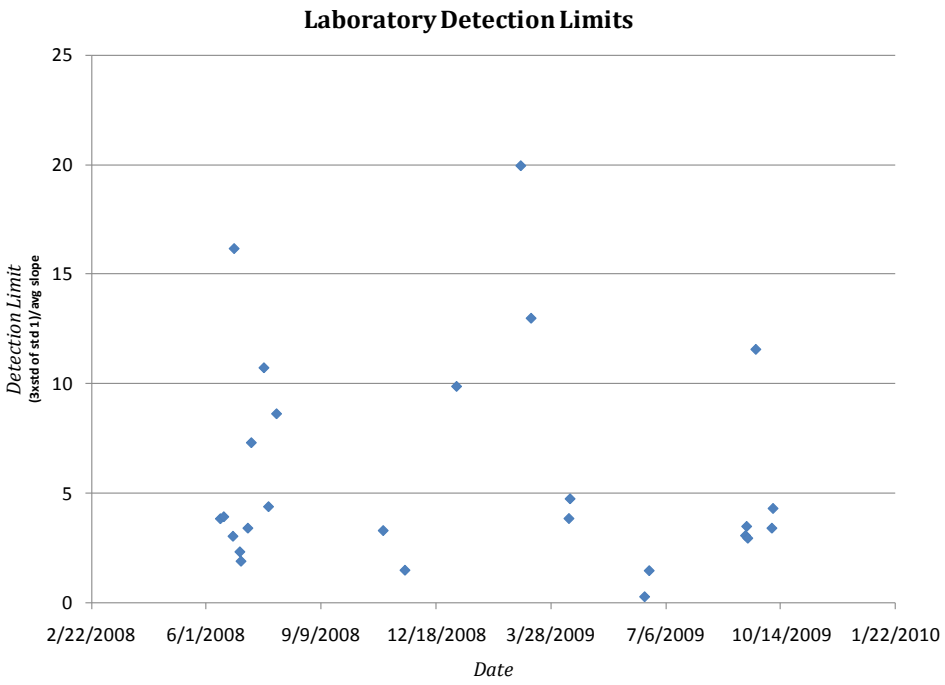


Figure 103: Laboratory detection limits

Issues with the detection limit may be attributable to the inability to achieve consistent bubbles. When the bubbles lack consistency, the reagents may not be mixed in the same proportion in each sample “packet” leading to different measurements in each one. This variation would boost the standard deviation from the mean and lead to a higher detection limit.

The system also has a response time issue that has not been completely quantified. Sometimes it appears that the system responds quite quickly to a change in concentration while others it seems to respond excruciatingly slowly. The pattern of response does not change, however. A change in concentration is characterized by a large and fast jump that accounts for as much as 70% of the total change in voltage. This initial change is followed by a much longer, slower, and lower magnitude “ramping up” or “ramping down” of voltage. The reasons for the slow response time have not been established. Iron could be "sticking" to the inside of the tubing although the concentration is seen as ramping down when going from a low standard to a high one. There is also the possibility that the glass tubing heightens the sticking issue. Glass tubing is often rejected in iron work as it is known to have a high iron background. For our work however, the glass tubing is crucial to maintaining consistent bubbles. The reason for this ramping may also not be thought of yet.

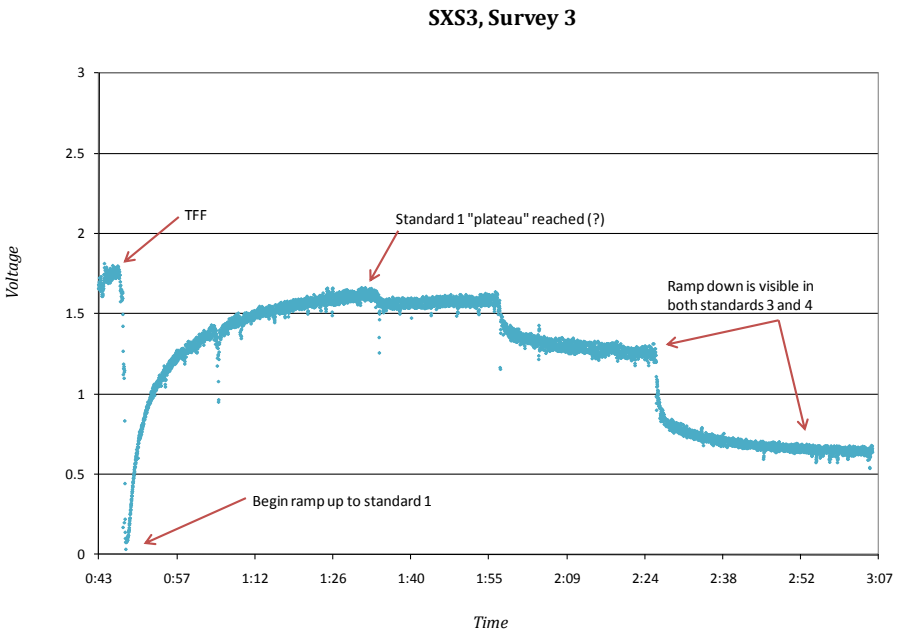


Figure 104: Standard ramping

The chart above illustrates the final set of standards on day 3 of surveying during SXS3. The "ramping down effect" is seen in the changes to the 3rd and 4th standards. Standard 4 particularly exemplifies the fast initial drop followed by a long and slow secondary change. The chart also illustrates a problem that may be connected to the response time issue. The system does not seem to transition well from water flowing from the TFF to the first standard. The long slow ramp up to standard 1's plateau limits our ability to run standards in the middle of the day because it takes up to an hour and a half. From the time the instrument first detected the beginning of standard 1 to the time it reached its plateau was almost 50 minutes.

On board the ship, the system appears to respond fast enough to catch a signal as the supersucker was moved from the bottom boundary layer to the surface. It was discovered, accidentally, that there is enough pressure from the TFF to push water over the peristaltic pump even when it is not operating. If the sample was pushed through the system at a higher rate than the standards or samples in the lab, this could possibly have had the effect of “sweeping” iron through the system before it had a chance to stick to anything.

The system also occasionally has problems accurately measuring the concentration of standard and internal reference materials. NASS-5 was more often than not measured at concentrations of about 10 nM when in reality it is about 3.7 nM. This is partially accounted for by the poor

detection limit but also points towards some other lingering issues with standards and general feasibility of the method.

The most damning problem may be the discrepancy between the discrete and inline samples. Several of these samples were run during the cruises at the end of a day's run or as part of the next day's standards and did not match up with their inline counterpart. The majority of the samples from SXS2 and SXS3 were run in the lab. While it was evident the system was having some problems when the discrete samples from SXS3 were run in lab (the NASS-5 concentration was off by as much as a factor of 5) the discrete samples did not remotely resemble the concentrations measured inline by the GCFA.

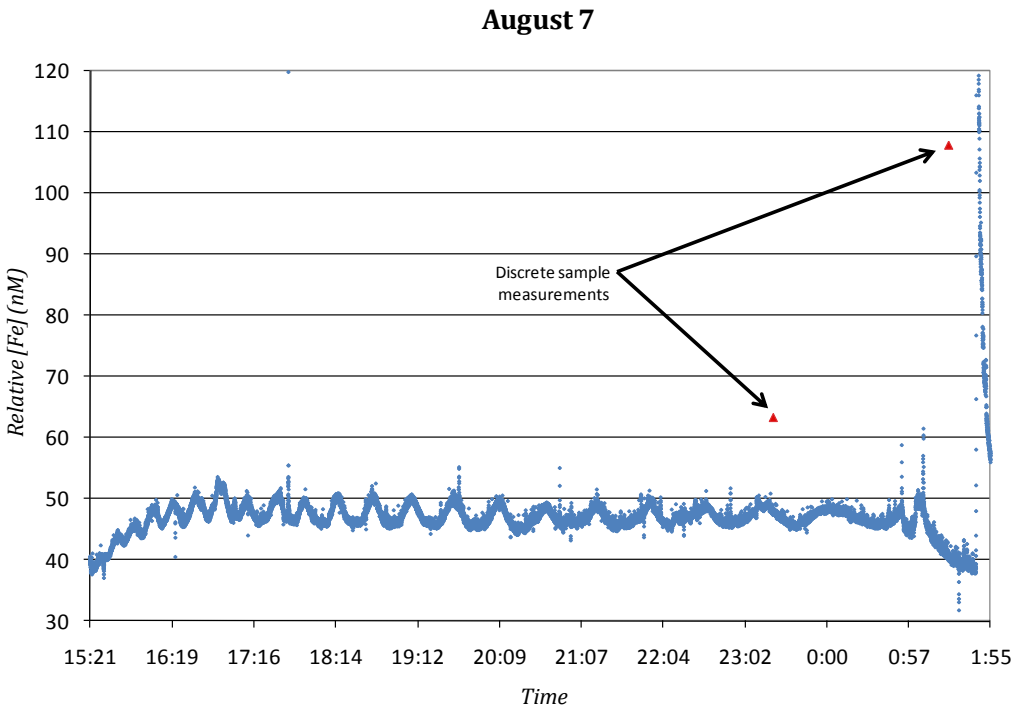


Figure 105: Inline vs discrete discrepancies

The data from the May cruise is not complete but the samples run from SXS2 do not appear to match their inline counterparts either. With inline acidification, temperature, and pH eliminated in the laboratory this requires a new way of looking at it to determine the issues. Perhaps the increased flow rates for sample cause the sample to be under-acidifed with respect to both concentration of HCl and time.

In order for the GSCFA to be deployed successfully the offsets between the discrete samples and the inline samples must be resolved. Additionally, work should be done to quantify and improve the response time as well as decreasing the detection limit.

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