Assessment of the St. Marys River Biological Water Quality, Primary Productivity, and Pollutant Load – Phase I Monitoring

COASTAL INCENTIVE GRANT
FINAL REPORT
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GDNR CYCLE IX
ST. MARYS PHASE I GATES
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This report, prepared by Katy Smith, Keith Gates and Phillip Flournoy under award # 27-31-RE337-202 from the Office of Ocean and Coastal Resource Management, National Oceanic and Atmospheric Administration, reflects statements, findings, conclusions, and recommendations of the author(s) and does not necessarily reflect the views of OCRM or NOAA.

Introduction

The University of Georgia Marine Extension Service (MAREX) has conducted ongoing water quality research in Georgia's major coastal rivers over the past eight years. The St. Marys River was the fourth among the five major rivers to be monitored for one year. The initial monitoring began with scouting of the river in October 2006 and continued with monthly monitoring through September 2007. A suite of information was collected to assess the water quality of the St. Marys River.

The long-term goals of the MAREX Coastal Water Quality Initiative are to: (1) provide coastal officials and residents with accurate and easily understood information and relationships that link water quality and land use; (2) present the information through intuitive real-time and predictive models that allow science-based decisions weighing current environmental conditions against predictive ecological changes given alternative growth and development scenarios; (3) provide land-use options on a watershed scale that lessen environmental impacts of an expanding coastal population through the NEMO (Nonpoint Source Education for Municipal Officials) and Smart and Green Growth programs funded by Georgia Sea Grant; and (4) provide technical tools to local officials and support staff needed to incorporate enhanced data into active and responsive coastal planning and management programs.

Site Selection

In October 2006, Marine Extension Service specialists conducted an initial survey of the St. Marys River. Depth, time, GPS, temperature, salinity, dissolved oxygen, and pH data were collected during the initial survey. From this information, 5 sites were selected to be monitored monthly (Figure 1). Station 1 was placed in the mouth of the St. Marys River alongside a range marker. Site 2 was located in the mouth of North River. Station 3 was positioned along tall sandy cliffs in a bend upstream on the St. Marys River. The site chosen for station 4 was an area just past the overhead I-95 bridge, and station 5 was positioned along side the pilings of the Highway 17 bridge. Monthly

monitoring took place for one year beginning in November 2006 and ending in September 2007. Table 1 highlights the date of each sampling event and the activities that took place on that particular day.

Sampling Methods

Field sampling was conducted from the 23-foot *R/V Sea Ox*. Sampling dates were chosen according to tidal stage using the WWW Tide and Current Predictor online (http://tbone.biol.sc.edu/tide/). The Kings Bay NSB, Kings Bay, Cumberland Sound, Georgia location was selected for tidal predictions. Sampling would begin on a chosen morning as close as possible to either a low or high tide, depending on the month.

Physical parameters including temperature, salinity, pH and dissolved oxygen, were measured using a Hydrolab Quanta®. Wind speed and direction and air temperature were recorded from a digital anemometer and current information was measured using a Model 2135 Flowmeter from General Oceanics, Inc. Light attenuation was measured using a research radiometer with a photodetector (International Light) and secchi depth was measured using a secchi disk.

Surface and bottom water samples were collected in various sampling containers for laboratory analysis of biological oxygen demand (BOD), total organic carbon (TOC), total nitrogen (TN), nutrients, chlorophyll-a, ATP, Enterococcus and fecal coliform bacteria, and total suspended solids (TSS). A Niskin-style sampling device attached to a davit on the side of the research vessel was used to collect bottom water at the chosen locations. Water was then dispensed into appropriate sample containers (ie. sterile bottles for bacterial testing) for each analysis. Water from the sampling device was transferred to an acid-washed polypropylene beaker for processing of nutrient and chlorophyll samples. Weather observations were recorded throughout the day at the various sites as well.

Nutrient Monitoring

Nutrient interactions were evaluated by measuring orthophosphate (PO_4^{3-}), nitrate (NO_3^-) and nitrite (NO_2^-), silicate (SiO_2), ammonia (NH_3), total dissolved phosphorous (TDP), total organic carbon (TOC) and total nitrogen (TN) concentrations. Orthophosphate, nitrate, nitrite, silicate and ammonia were measured using a Lachat QuikChem 8000 FIA+ auto analyzer (Hach Company). Prior to analysis, nutrient samples were filtered in the field through 0.45 um pore size polycarbonate filters using acid-washed filtration apparatus and transferred to acid-washed 125-mL polypropylene bottles. All nutrient samples, except those collected for silicate measurements, were stored frozen until time of analysis. Silicate samples were refrigerated in acid-washed 60-mL bottles. Filtered samples for TDP analysis were sent to Avery Laboratories in Savannah, Ga. to be properly digested and analyzed. Unfiltered water samples were collected for TOC and TN analyses. TOC and TN were measured by high temperature combustion on an Apollo 9000 TOC/TN analyzer (Tekmar Dohrmann).

Nutrient measurements were grouped into two to three-month intervals for the purposes of evaluating seasonal differences. November and December were designated as fall months, January through March as winter months, April to June as spring months and July to September as summer months. PO_4^{3-} ranged from 0.002 – 0.108 mg/L in the summer, 0.01 - 0.087 mg/L in the fall, 0.02 – 0.097 mg/L in the winter and 0.002 – 0.101 mg/L in the spring. NH_3 concentrations ranged from 0.017 – 0.129 mg N/L in the summer, 0.017 - 0.08 mg N/L in the fall, 0.007 – 0.099 mg N/L in the winter and 0.021 – 0.099 mg N/L in the spring. NO_3^- ranged from 0.015 – 0.110 mg N/L in the summer, 0.005 - 0.077 mg N/L in the fall, 0.013 – 0.061 mg N/L in the winter and 0.004 – 0.07 mg N/L in the spring. All of the minimum values exclude those results that were less than the method detection limits (MDL) for a particular analyte. Figure 2 shows average concentrations for orthophosphate, nitrate and ammonia for the entire sampling period. Nitrite concentrations are not represented graphically as these levels are so often less than the method detection limit. Silicate levels ranged from 0.687 mg/L in January 2007 at station 1 to 9.214 mg/L in February 2007 at station 5. Silicate concentrations were

generally higher upstream on the St. Marys River (Figure 3). TDP levels ranged from 0.02 mg P/L in July 2007 at station 3 to 0.160 mg P/L in December 2006 at station 2. Figure 4 displays average TDP concentrations from November 2006 to September 2007.

Carbon and Nitrogen were measured using an Apollo 9000 TOC/TN analyzer (Tekmar Dohrmann). Samples were collected in polypropylene containers and stored frozen until analysis. Total Nitrogen ranged from 0.20 to 1.12 mg/L, with an average of 0.47 mg/L, while Total Organic Carbon ranged from 2.60 to 62.85 mg/L, with an average of 14.75 mg/L (Figure 5). Total Organic Carbon concentrations increased up river and in general, TN followed the same trend.

Physical Measurements

Salinity levels varied monthly at the chosen locations according to the tidal stage during sampling and the amount of rain received prior to each sampling event. Salinity at the mouth of the river averaged 32.18 ppt on the surface and 32.71 ppt on the bottom. The average, maximum and minimum salinity levels observed at each station are represented in Table 2. The overall maximum salinity observed was 36.40 ppt at station 1 in November 2006 and the overall minimum salinity observed was 0.33 ppt at station 5 in August 2007. Figure 6 displays monthly salinity levels at the five St. Marys River locations.

Temperature, dissolved oxygen and pH were also recorded at each site from a hand-held Hydrolab Quanta. As temperature and dissolved oxygen (DO) are inversely correlated, the lowest levels of dissolved oxygen occurring at the time of year when the water temperature is highest. The minimum DO recorded during the year was 2.06 mg/L at station 5 on 4 September 2007. Figure 7 displays average temperature, salinity, pH and dissolved oxygen on the St. Marys River from November 2006 to September 2007. The pH ranged from 5.51 to 9.91, with an overall average of 7.35.

Total suspended solids were measured by filtering samples onto pre-weighed Type A/E filters and calculating the difference in dry weight before and after filtration (Clesceri, 1992). Minimum and maximum TSS values for the sampling period were 1.88 mg/L occurring in February 2007 at station 5 and 191.53 mg/L occurring in September 2007 at station 2. Figure 8 shows average suspended solids measured during each month of monitoring.

Turbidity was measured in nephelometric turbidity units (NTU) using a digital turbidimeter (HF Scientific). Turbidity ranged from 2.6 to 41.6 NTU, with an average of 11.1 NTU overall. Average turbidity levels from November 2006 to September 2007 are displayed in Figure 9. Secchi depth, measured by lowering a black and white secchi disk into the water and recording the depth at which the disk was no longer visible, ranged from 25 cm at station 5 in September 2007 to 166 cm at station 1 in August 2007.

Bacterial Indicators

In general, Enterococci populations were low in the St. Marys River, rarely exceeding EPA's most probable number (MPN) limit of 104 Enterococci per 100 mL for a single sample grab in coastal recreational waters. In September 2007, a maximum of 395 Enterococci per 100 mL was observed. This sampling event was preceded by rainfall, which may have led to the higher levels of bacteria due to runoff from upstream areas. Enterococci populations per 100 mL observed over the sampling period (Table 3) ranged from an MPN of 2 to 395 CFUs (colony forming units). Fecal coliform bacteria were also tested each month in the St. Marys River. The MPN per 100 mL for fecal coliform bacteria ranged from 1 to 300 during the sampling period. Table 4 shows minimum and maximum fecal coliform values, as well as averages, for the November 2006 to September 2007 sampling period. Figure 10 shows average Enterococci and fecal coliform bacteria measured during the St. Marys River study.

Current Measurements

Current measurements were recorded from a Model 2135 Flowmeter (General Oceanics, Inc.) each month on the surface and bottom at each of the five stations. In addition, a 13-hour current study was conducted on 13 September 2007. The site chosen for the current study was a public dock near the downtown St. Marys boat launch. Surface and bottom water current velocity measurements were recorded every half-hour (Figure 11). A Hydrolab Quanta was used to collect salinity, temperature, dissolved oxygen and pH measurements on the surface and bottom as well. Wind speed, direction and air temperature were recorded during each interval. During the current study, the Light and Dark Bottle Oxygen Method was used to measure primary productivity over a 12-hour period. These results are discussed in the section below entitled 'Primary Productivity.'

The highest observed surface and bottom current speeds measured during the current study were 0.488 m/s on the surface and 0.325 m/s on the bottom. High tide occurred around 10:53 at Kings Bay NSB, Kings Bay, Cumberland Sound, Georgia, with low tide at approximately 16:48. Salinity observations, displayed in Figure 12, show the maximum for the day occurring at 12:30 at the dock where the study took place. At 13:00, a drop in surface water salinity was observed, followed by a steady increase until the surface and bottom water salinity reached nearly the same concentration. This observation displays the initial stratification that occurs upon the turn of the tide, followed by steady mixing of the water column as the tide continues to ebb. From the same graph, one can see that the bottom water salinity decreases more gradually as the heavier salt water remains in the lower portion of the water column.

Primary Productivity

The Light and Dark Bottle Oxygen Method (Clesceri, 1992) was used to measure primary productivity at the chosen current study location on September 13, 2007. One set of light and dark bottles was positioned at the surface of this station. A second set of dark bottles is normally positioned at the bottom of the photic or euphotic zone which is defined as the depth at which surface illumination is reduced to 1% of ambient sun light.

A research radiometer with a photodetector (International Light) was used to measure light attenuation from the surface to the depth defined as the bottom of the photic zone. For this station, the euphotic zone occurred in only 0.3 meters, which was not deep enough to position an additional set of bottles, and thus only a surface set of bottles was used. A bilge pump, attached to the end of a hose, was situated at the surface to draw water and fill three light and three dark bottles. Dissolved oxygen in an initial light and dark bottle was measured using a portable BOD meter (YSI). These initial bottles were then incubated alongside duplicate 'final' light and dark bottles. The incubation was achieved by placing the bottles on a set of six c-clamps centered on a steel rod. The rod was then tied off with a length of rope to the side of the dock and incubated just below the surface for 12 hours. At the end of the incubation period, dissolved oxygen was determined in the duplicate 'final' light and dark bottles to measure the change in dissolved oxygen over the 12-hour incubation period. Primary productivity measurements were then calculated. Productivity measurements are expressed in terms of carbon. Net photosynthesis measured 28.26 mg $C/m^3/h$, while respiration measured 15.86 mg $C/m^3/h$.

Samples for chlorophyll analysis were collected in the St. Marys River using two different techniques. A Turner Designs 10-AU Field Fluorometer was used to measure in-vivo (living) chlorophyll-a on site. Water samples were also collected to measure in-vitro (extracted) chlorophyll-a concentrations. The extracted samples were filtered onto 0.7 um glass fiber filters (GF/F), placed in labeled petri dishes, wrapped in aluminum foil and stored frozen until analyzed. Chlorophyll was extracted from the collected samples by grinding the filters with 90% acetone and continuing the extraction in acetone at 4^oC for 24 hours (Clesceri, 1992). Sample absorbance is read in a spectrophotometer at several wavelengths of light, before acidification (750, 665 and 664 nm) and after acidification (750 and 665 nm). Chlorophyll-a concentrations are calculated based on absorbance values before and after acidification. Chlorophyll-a levels during the study ranged from 1.0 ug/L in February 2007 to 9.3 ug/L in December 2006. Total chlorophyll levels ranged from 0.9 ug/L in August 2007 to 14.8 ug/L in April 2007. Figure 13 shows

chlorophyll-a and total chlorophyll averages from November 2006 to September 2007 in the St. Marys River.

Adenosine triphosphate (ATP) is the measurement of energy released during metabolic processes. ATP, measured using Turner Designs' luminescent technology, was evaluated in the St. Marys River from November 2006 to September 2007. ATP measurements enable an indirect measurement of the number of small bacteria in a water sample. Based on a value of 5×10^{-16} g ATP per bacterium (Turner Designs Applications Note), the number of small bacteria in a water sample can be calculated using the ATP value. Figure 14 shows average ATP and calculated small bacteria levels in the St. Marys River. The overall average number of small bacteria per 50 ul of sample water was 317,523.

Biological Oxygen Demand was measured using the 5-day BOD test (Clesceri, 1992). Water from selected stations was collected in 2 liter polypropylene bottles, taking care not to introduce oxygen into the sample during collection. Samples were processed at full strength (1000 ml sample to 0 ml dilution water) and at half strength (500 ml sample to 500 ml dilution water). Nutrients were added and the initial dissolved oxygen was measured with a bench-top dissolved oxygen meter (YSI). The initial bottle and a duplicate bottle were incubated for 5 days at 20 degrees Celsius in the dark after which the dissolved oxygen was measured again. The difference in dissolved oxygen over the 5-day period measures the rate of oxygen uptake by microorganisms in the sample and is presented as a BOD value. A clean, clear body of water might show a BOD of less than 2 mg/L. Based on the full strength samples, the average BOD measured in the St. Marys River from November 2006 to September 2007 was 0.96 mg/L, with a range of 0.41 mg/L at station 5 during April 2007 to 2.16 mg/L at station 2 in February 2007. Figure 15 shows average BOD concentrations at each station on the St. Marys River.

Continuous Monitoring

A Hydrolab Datasonde 5x was used to collect temperature, salinity, dissolved oxygen and pH measurements every thirty minutes at several stations on the St. Marys River. The Datasonde 5x utilizes a new technology for dissolved oxygen measurements called luminescence. This technology improved data gathering in environments with heavy biological fouling. The continuous data, once collected, are downloaded from the instrument upon its return to the laboratory and the information is transferred to and stored in Microsoft Excel spreadsheets. These data provide a look at fluctuations in salinity and other physical factors over numerous tidal cycles (Figures 16 and 17). Data sets on the St. Marys River range from two weeks to a month.

Conclusions

The lower tidal portion of the St. Marys River, the area from the Highway 17 bridge to Cumberland Sound, was investigated during this one-year study. Originating in the Okefenokee Swamp, the St. Marys River contains tannins produced from decaying matter, thus making it a blackwater river. According to the St. Marys River Management Committee, "the river, with its extensive marsh system, relative lack of urban development and few pollution discharge points, has generally excellent water quality" (http://www.saintmarysriver.org/history.html). Bacterial levels observed from November 2006 to September 2007 were occasionally higher than the standards for recreational waters (MPN 104 per 100mL for Enterococci and MPN 200 per 100mL for fecal coliforms) and on average increased up river. The exact source(s) for the bacteria are unknown, but most likely occur from a combination of human and animal sources. Average carbon and nitrogen concentrations and average silicate levels showed up river increases as well. Alternatively, average chlorophyll levels decreased up river. Physical parameters measured during the study indicate a generally healthy river system. Dissolved oxygen levels fall to around 3 mg/L in late summer, but return to normal levels once the water temperatures cool down in the fall. Reduced oxygen levels in the summer are common in Georgia's estuaries. Biological oxygen demand and pH levels measured indicated a healthy estuarine system as well. Total suspended solids concentrations were generally low in the St. Marys River. According to the St. Johns River Water

Management Committee, "the biggest concern for the water quality of the St. Marys River and other coastal rivers is secondary impacts from development, such as chemical and pesticide runoff from lawns and streets, and leaking septic tanks" (http://www.sjrwmd.com/publications/pdfs/fs_stmarys.pdf).

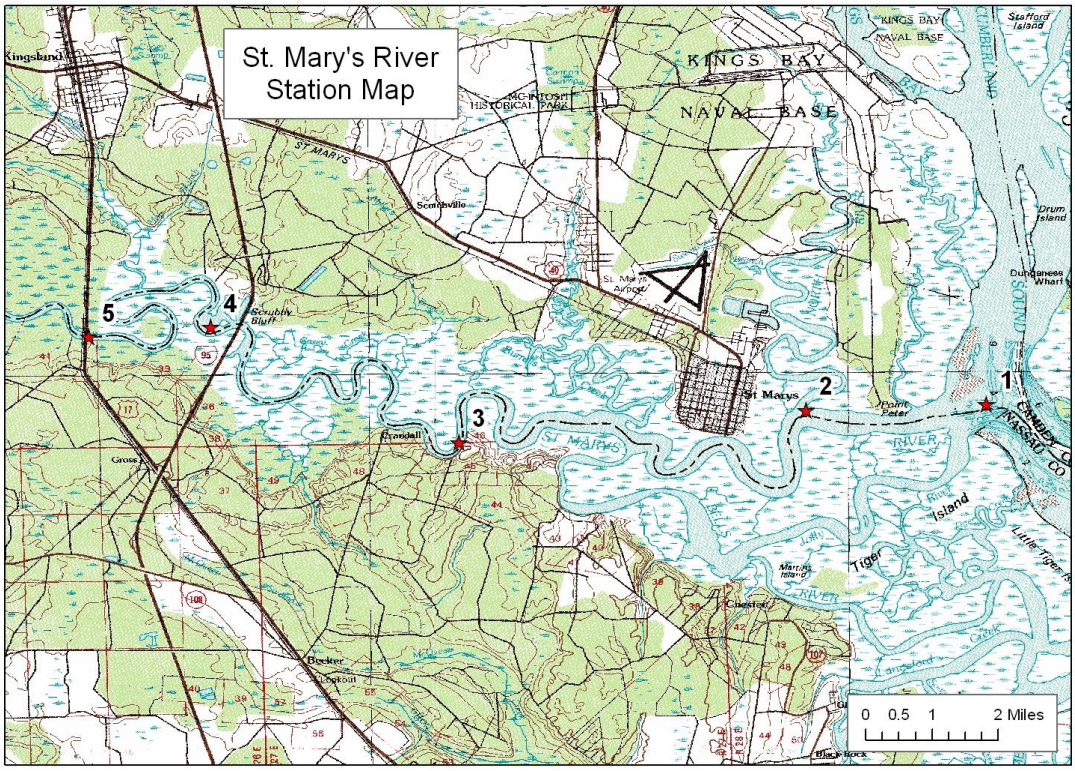

Figure 1. St. Marys River station locations for the 2006-2007 water quality monitoring study.

Table 1. Activities completed during each sampling event.

Date	Type	Description of Activities
10/3/06	**Location Scouting**	**Field measurements:** air temperature, wind speed and direction, GPS coordinates, water depth, surface and bottom water temperature, salinity, pH and dissolved oxygen.
11/14/06	**Sampling**	**Field measurements:** as listed above and including currents. **Laboratory samples collected:** Nutrient analyses (Nutrients)*, Total Organic Carbon (TOC), Total Nitrogen (TN), Chlorophyll-a (Chl-a), ATP, Microbiological analyses (Micro)**, Turbidity, Biological Oxygen Demand (BOD), and Total Suspended Solids (TSS).
12/5/06	**Sampling**	**Field measurements:** as listed above and including currents. **Laboratory samples collected:** Nutrients, TOC, TN, Chl-a, ATP, Micro, Turbidity, BOD, and TSS.
1/16/07	**Sampling**	**Field measurements:** as listed above and including currents. **Laboratory samples collected:** Nutrients, TOC, TN, Chl-a, ATP, Micro, Turbidity, BOD, and TSS.
2/13/07	**Sampling**	**Field measurements:** same as those conducted during scouting. **Laboratory samples collected:** Nutrients, TOC, TN, Chl-a, ATP, Micro, Turbidity, BOD, and TSS.
3/13/07	**Sampling**	**Field measurements:** same as those conducted during scouting. **Laboratory samples collected:** Nutrients, TOC, TN, Chl-a, ATP, Micro, Turbidity, BOD, and TSS.
4/10/07	**Sampling**	**Field measurements:** same as those conducted during scouting. **Laboratory samples collected:** Nutrients, TOC, TN, Chl-a, Micro, Turbidity, BOD, and TSS.
5/9/07	**Sampling**	**Field measurements:** same as those conducted during scouting. **Laboratory samples collected:** Nutrients, TOC, TN, Chl-a, Micro, Turbidity, BOD, and TSS.
6/5/07	**Sampling**	**Field measurements:** same as those conducted during scouting. **Laboratory samples collected:** Nutrients, TOC, TN, Chl-a, Micro, Turbidity, BOD, and TSS.
7/10/07	**Sampling**	**Field measurements:** same as those conducted during scouting; also currents and light attenuation. **Laboratory samples collected:** Nutrients, TOC, TN, Chl-a, ATP, Micro, Turbidity, BOD, and TSS.
8/7/07	**Sampling**	**Field measurements:** same as those conducted during scouting; also currents and light attenuation. **Laboratory samples collected:** Nutrients, TOC, TN, Chl-a, ATP, Micro, Turbidity, BOD, and TSS.
9/4/07	**Sampling**	**Field measurements:** same as those conducted during scouting; also currents and light attenuation. **Laboratory samples collected:** Nutrients, TOC, TN, Chl-a, ATP, Micro, Turbidity, BOD, and TSS.
9/13/07	**Current Study**	**Field measurements:** air temperature, wind speed and direction, GPS coordinates, water depth, surface and bottom water currents, temperature, salinity, pH and dissolved oxygen.

*Nutrient analyses included nitrate (NO_3), nitrite (NO_2), orthophosphate (PO_4^{3-}), ammonia (NH_4) and silicates (SiO_2).
**Microbiological analyses included the Multiple Tube Fermentation Technique for fecal coliforms, EPA Method 1600 Membrane Filtration for Enterococcus, and occasionally the A-1 Multiple Tube Technique for fecal coliforms conducted as an internal laboratory method comparison.

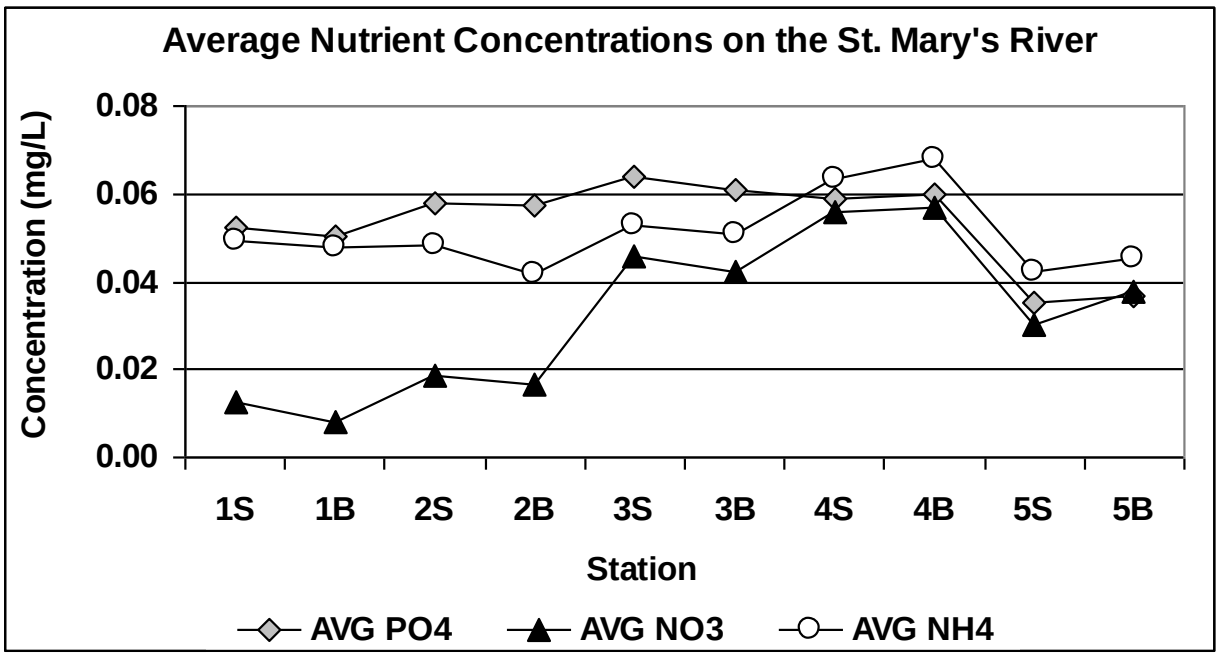

Figure 2. Average orthophosphate, nitrate and ammonia concentrations on the St. Marys River from November 2006 to September 2007.

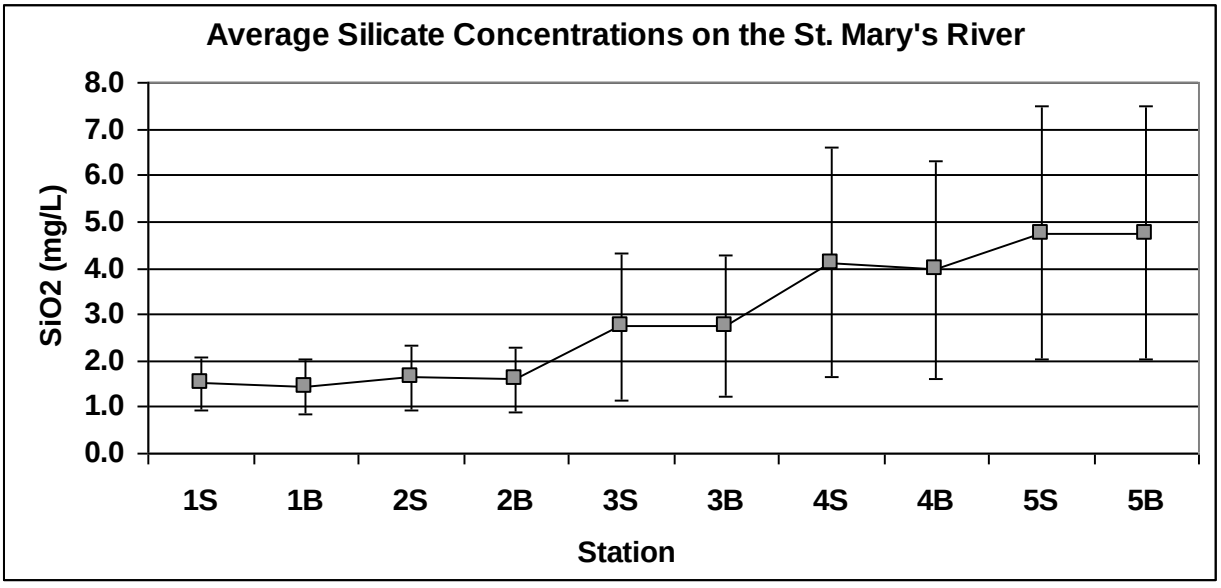

Figure 3. Average silicate concentrations on the St. Marys River from November 2006 to September 2007.

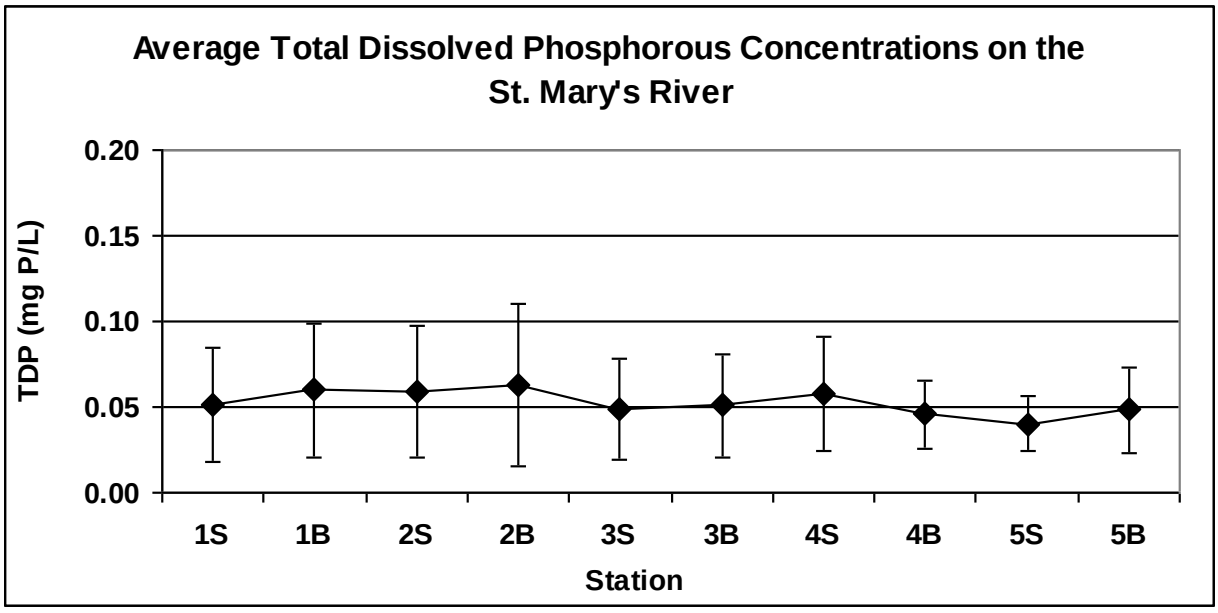

Figure 4. Average Total Dissolved Phosphorous concentrations from November 2006 to September 2007 on the St. Marys River.

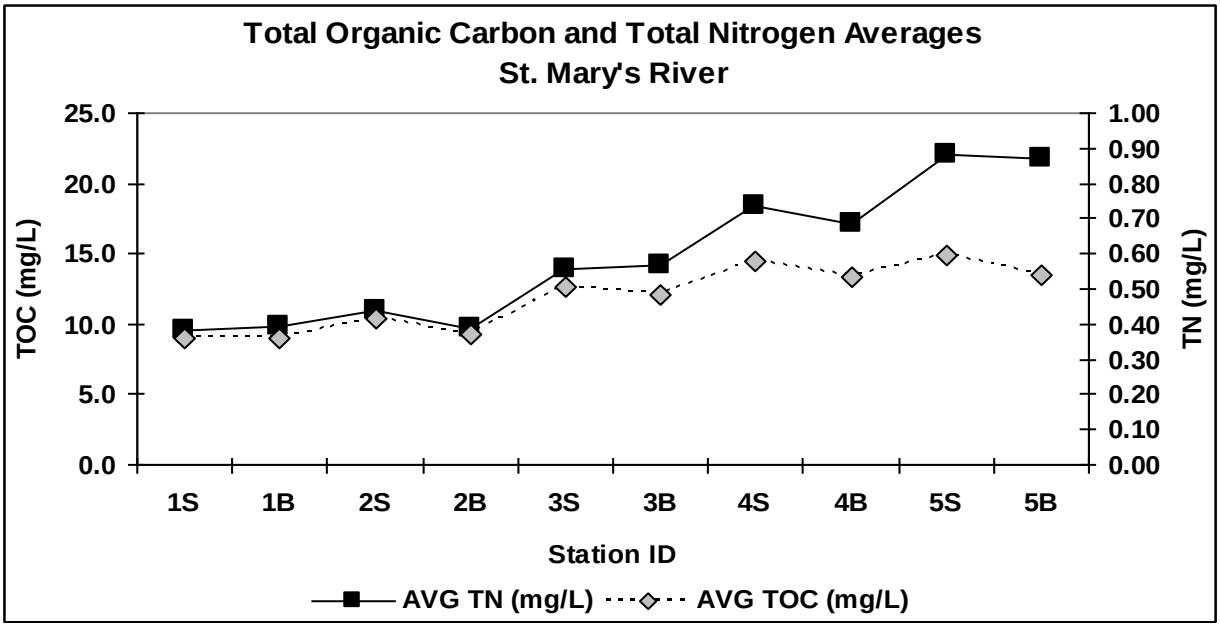

Figure 5. Average total organic carbon (TOC) and total nitrogen (TN) levels measured on the St. Marys River from November 2006 - September 2007.

Table 2. Average, maximum and minimum salinity levels at each station on the St. Marys River.

Station	Average (ppt)	Maximum (ppt)	Minimum (ppt)
1S	32.18	36.40	27.90
1B	32.71	36.38	30.12
2S	30.15	35.95	22.85
2B	30.26	35.14	23.25
3S	20.82	32.79	3.61
3B	20.61	32.07	3.88
4S	13.71	27.01	0.53
4B	14.13	26.45	0.52
5S	8.56	19.10	0.35
5B	8.66	18.71	0.33

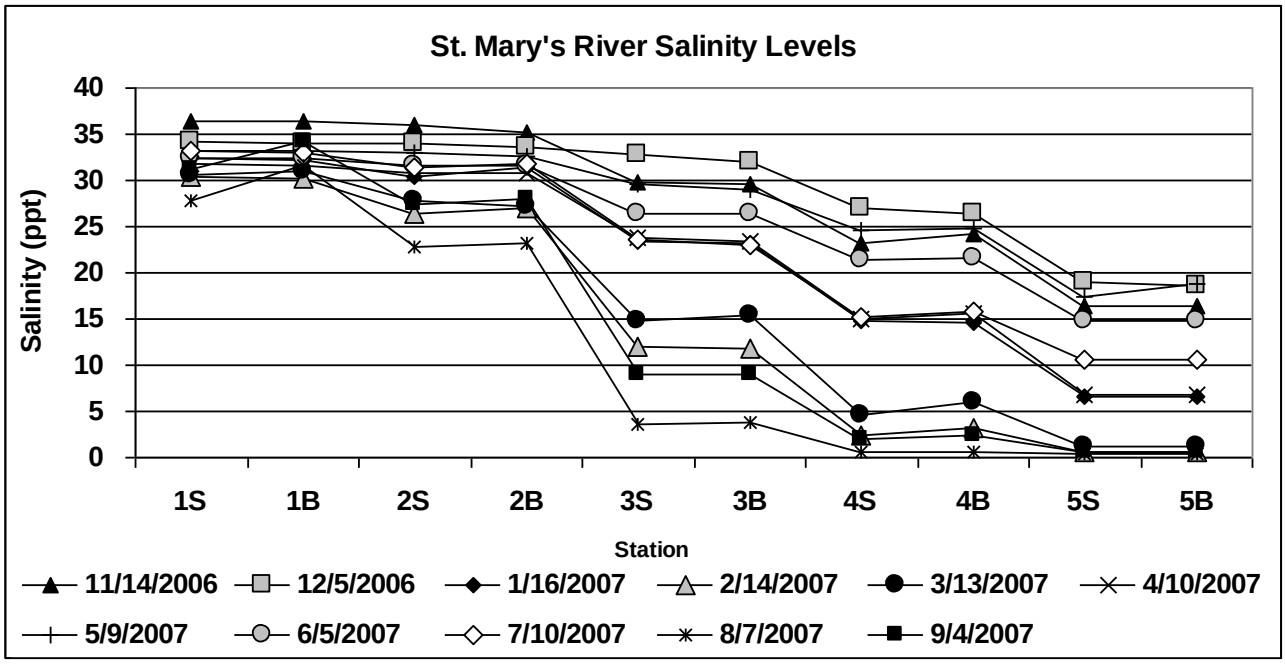

Figure 6. Salinity levels recorded monthly on the St. Marys River.

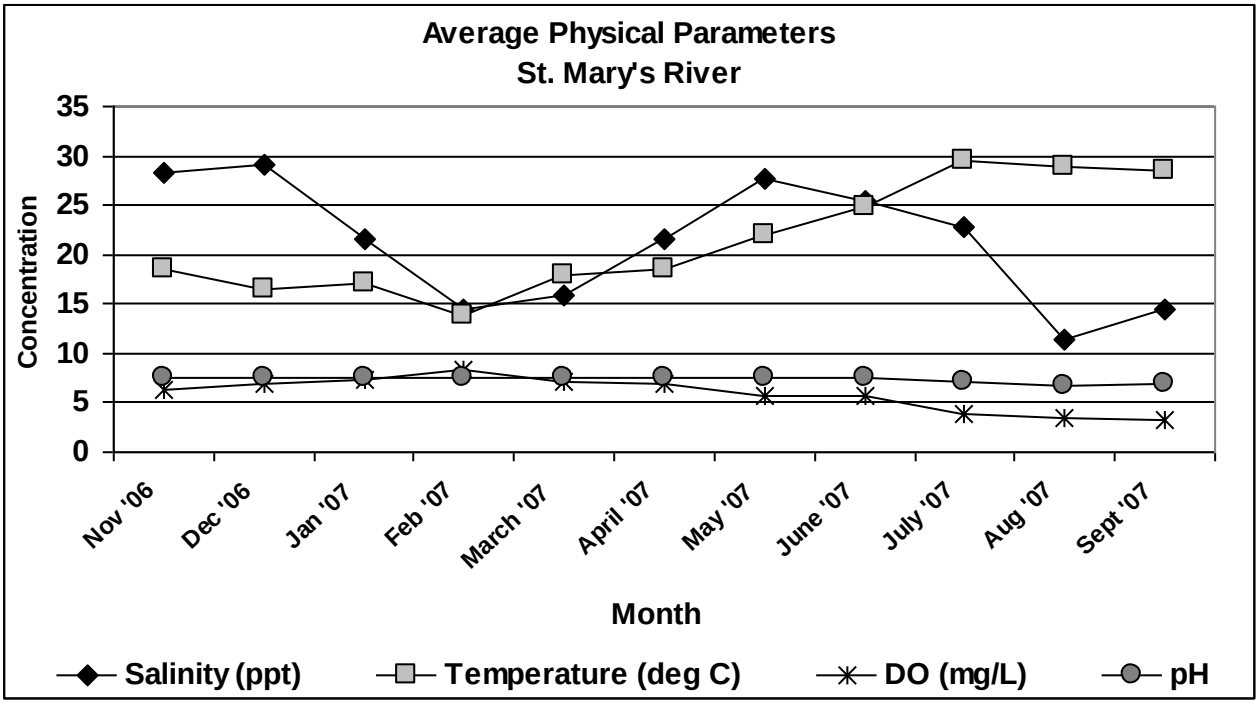

Figure 7. Average salinity, temperature, dissolved oxygen and pH on the St. Marys River from November 2006 to September 2007.

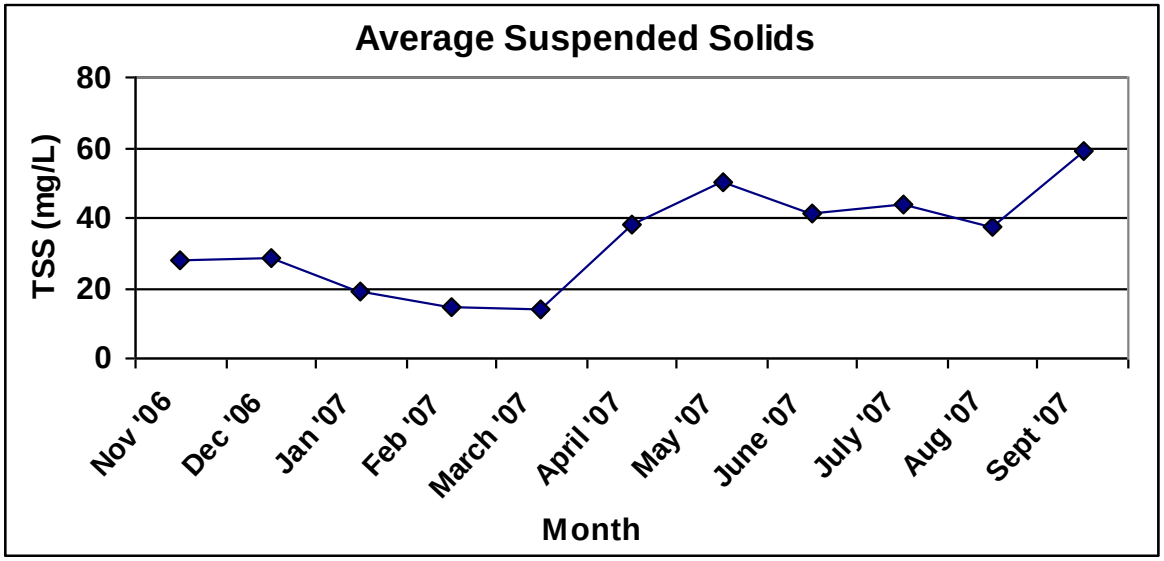

Figure 8. Average suspended solids measured in the St. Marys River from November 2006 to September 2007.

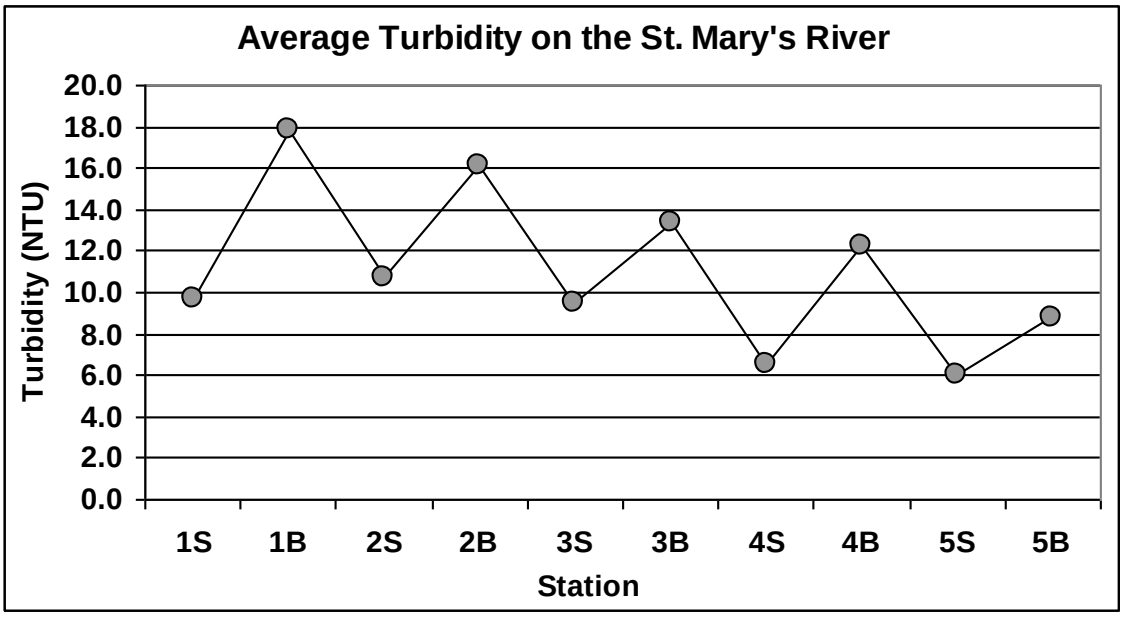

Figure 9. Average turbidity on the St. Marys River from November 2006 to September 2007. An "S" represents a surface sample and a "B" represents a bottom sample.

Table 3. Minimum and maximum MPN Enterococci counts recorded for each sampling event in the St. Marys River from November 2006 to September 2007.

Sampling Date	Minimum MPN Enterococci	Maximum MPN Enterococci
11/14/06	2	27
12/5/06	2	117
1/16/07	2	95
2/14/07	3	112
3/13/07	2	90
4/10/07	2	13
6/5/07	2	20
7/10/07	2	33
8/7/07	3	127
9/4/07	10	395
Overall	2	395

Table 4. Minimum, maximum and average fecal coliform bacteria measured at each St. Marys River station during the 2006 – 2007 sampling period.

Fecal Coliform Bacteria			
Sample	Minimum	Maximum	Average
1S	1	130	18
1B	2	300	36
2S	2	17	6
2B	2	30	9
3S	2	80	30
3B	2	70	25
4S	4	220	71
4B	8	300	92
5S	5	240	97
5B	13	220	73
Overall	1	300	46

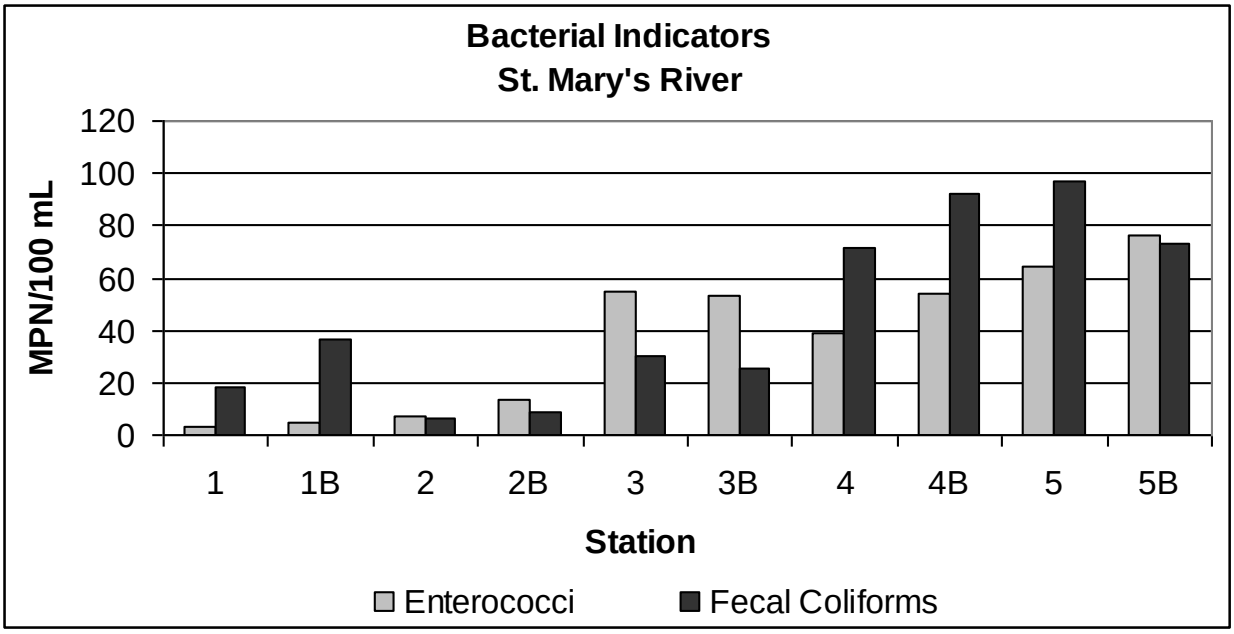

Figure 10. Average Enterococci and fecal coliform bacteria in the St. Marys River from November 2006 to September 2007.

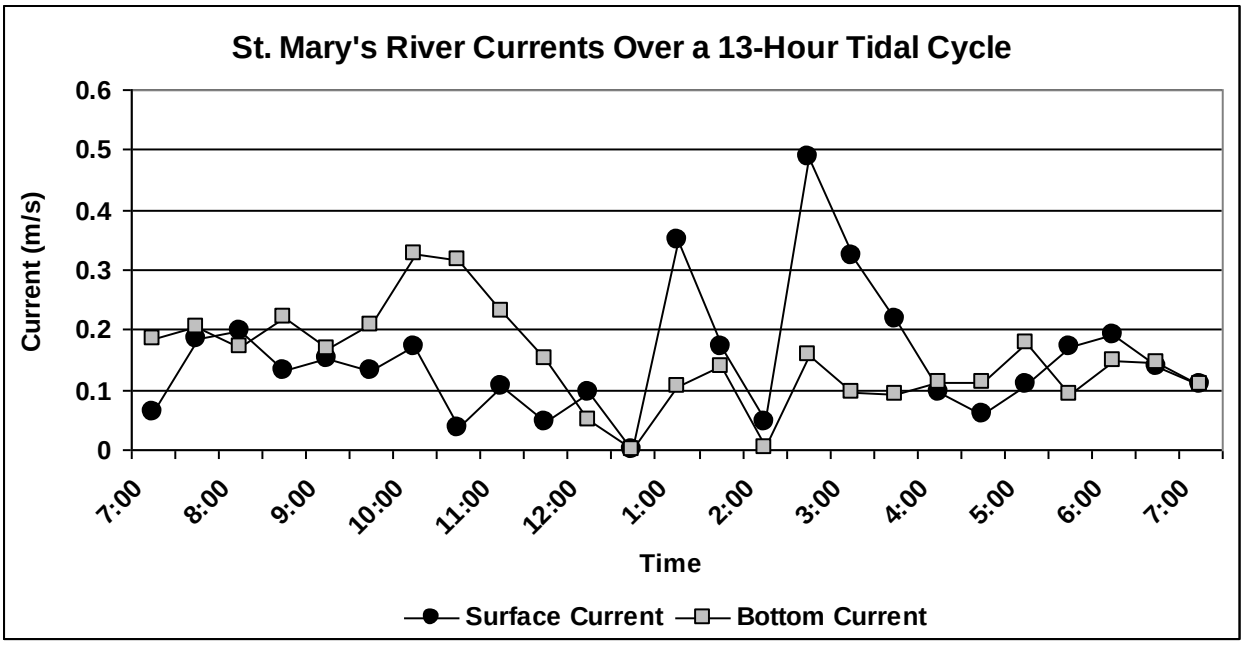

Figure 11. Surface and bottom water current measurements observed during a 13-hour tidal cycle on September 13, 2007.

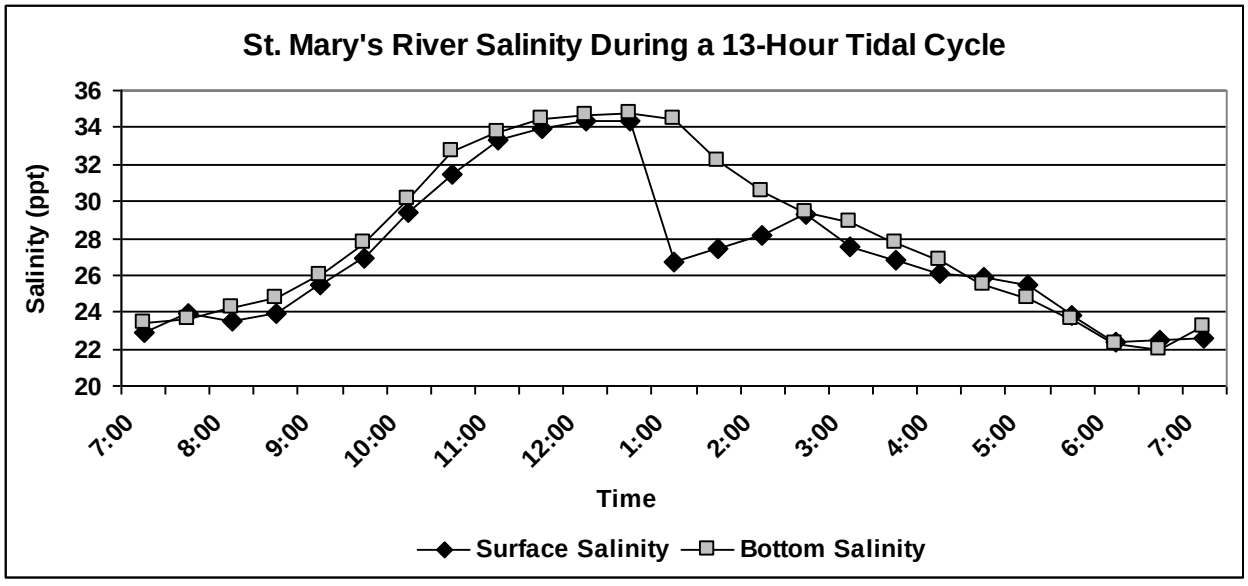

Figure 12. Salinity observations recorded during a 13-hour tidal cycle on September 13, 2007.

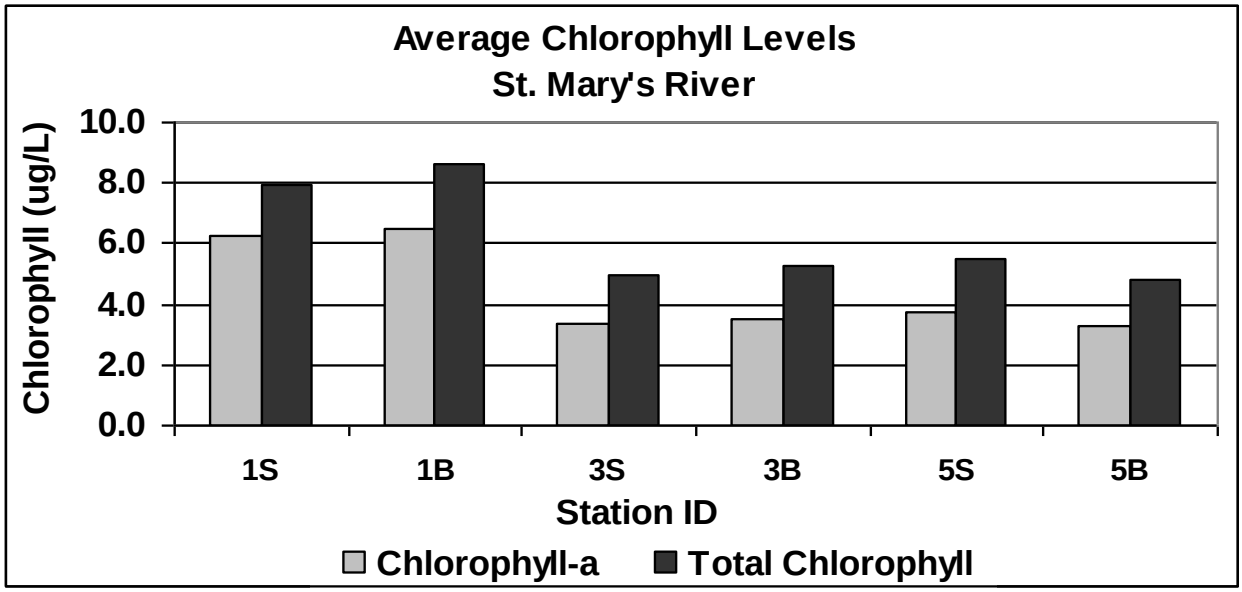

Figure 13. Average chlorophyll levels measured on the St. Marys River from November 2006 to September 2007.

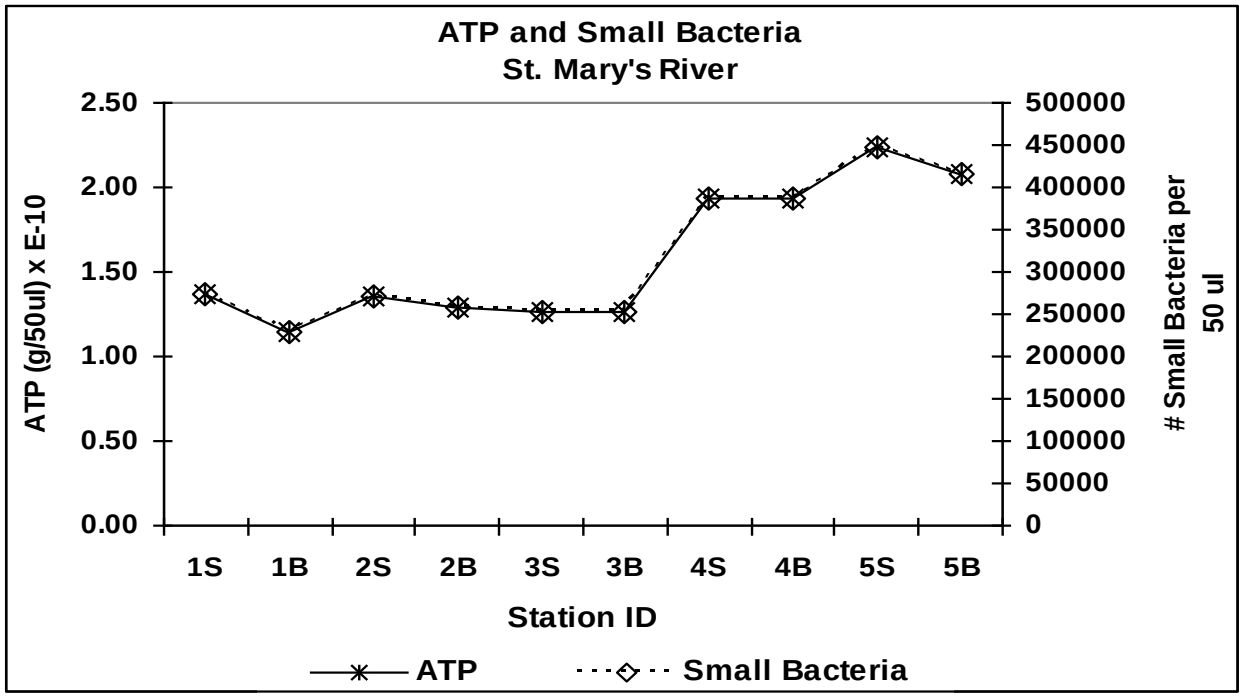

Figure 14. Average ATP measured on the St. Marys River from November 2006 to September 2007 and the associated number of small bacteria estimated from the ATP value based on 5 x 10E-16 grams of ATP per bacterium.

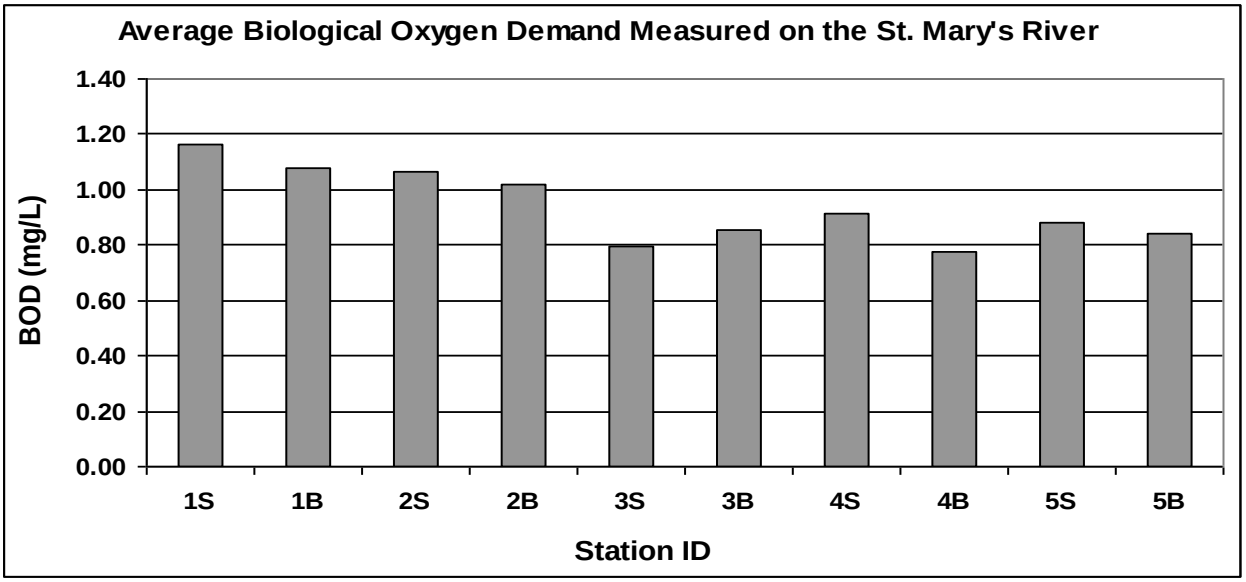

Figure 15. Average BOD levels measured on the St. Marys River from November 2006 to September 2007.

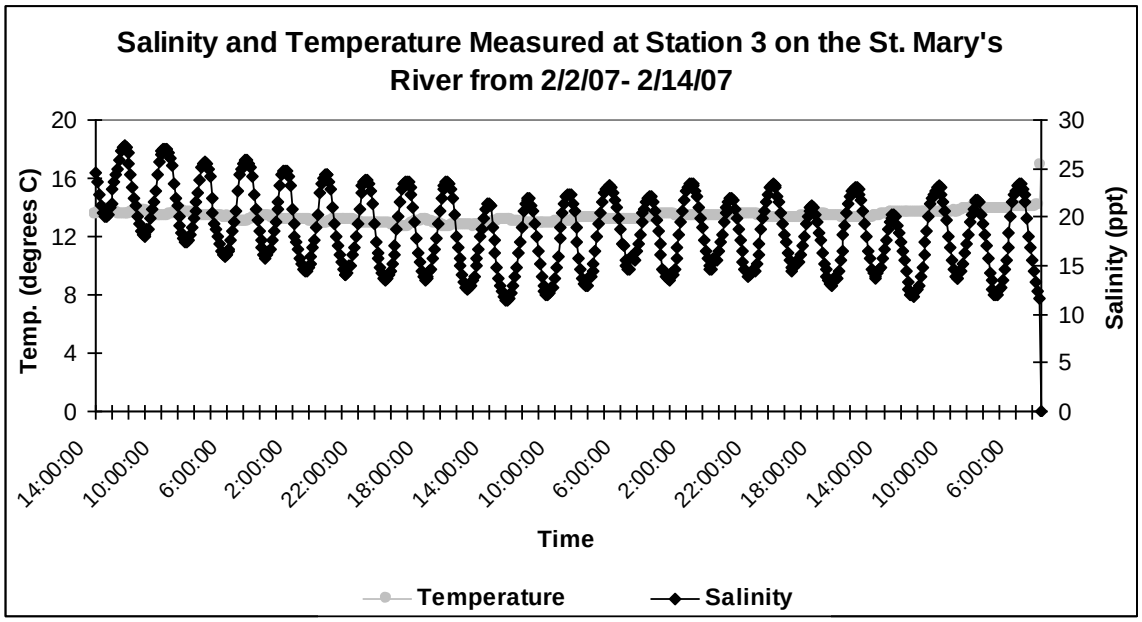

Figure 16. Salinity and temperature measured at station 3 in the St. Marys River using a continuously recording instrument (Hydrolab) from February 2 – 14th, 2007.

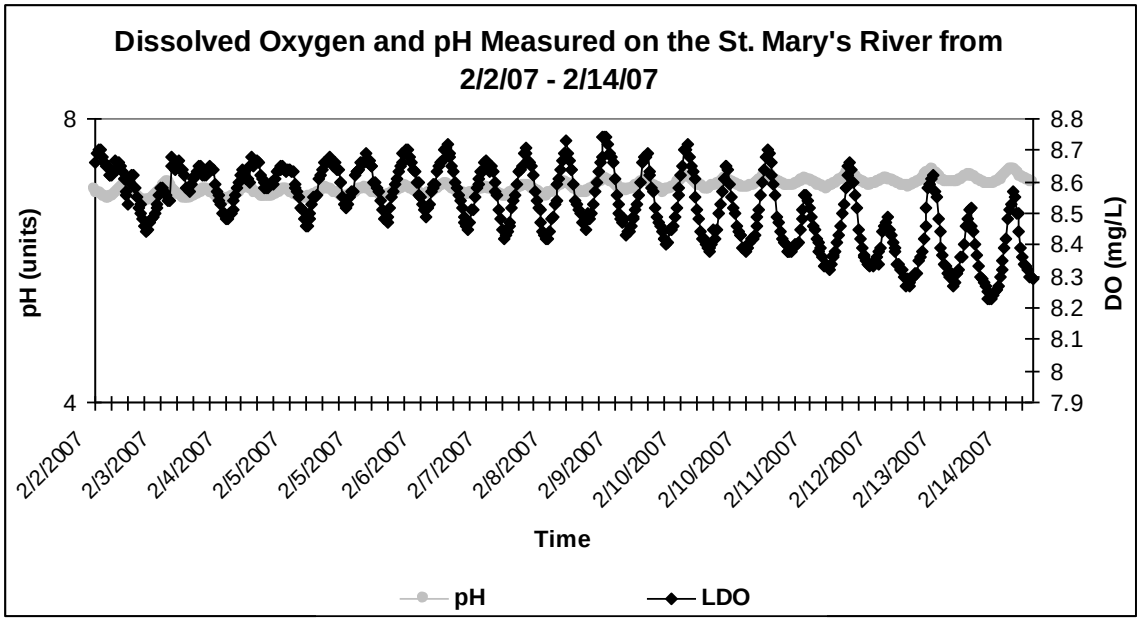

Figure 17. Dissolved oxygen and pH measured at station 3 in the St. Marys River using a continuously recording instrument (Hydrolab) from February 2 – 14th, 2007.

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