

U.S. DEPARTMENT OF THE INTERIOR

U. S. GEOLOGICAL SURVEY

**Gechemical Productivity Monitoring in Florida Bay**

By

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Open File Report 00-361

2000

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## INTRODUCTION

The production and transport of biogenic carbonate sediments plays a key role in developing mud banks and altering circulation patterns in Florida Bay. Accurate measurements of sediment accumulation and production rates are required to determine how these processes have changed during the last century in response to anthropogenic influences. Estimates of sediment accumulation rates and annual production rates based on standing crop and turnover of various calcifying species are available from previous research (Stockman et al., 1967; Nelson and Ginsburg, 1986; Bosence, 1989; Frankovich and Zieman, 1994). However, a discrepancy exists between long-term accumulation rates and short-term productivity measurements. For example, Stockman et al. (1967) estimated an average carbonate sediment accumulation rate of 8.0 cm/1000 years using sediment thickness to Pleistocene bedrock and dates of the start of marine sedimentation at given localities. Bosence (1989) presents the most comprehensive calculation of short-term average carbonate sediment production rates in Florida Bay banks and lakes of  $1,023 \text{ g m}^{-2} \text{ yr}^{-1}$  from standing crop surveys, growth rates, and short-term growth measurements of a variety of carbonate sediment producing organisms. This average production rate corresponds to an accumulation rate of 88.2 cm/1000 years, 910% more sediment than has accumulated based on Stockman et al.'s (1967) estimates. Clearly there is a large discrepancy between long term sediment accumulation and short-term productivity rates that cannot be accounted for by previous work on sediment dissolution rates (Walter et al., 1993; Walter and Burton, 1990) or transport of sediment out of the Bay. This suggests that either recent productivity rates have increased perhaps due to a change in water quality, accumulation measuring techniques underestimate rates, or productivity measurement techniques over-estimate sediment production.

Independent measures of sediment accumulation and productivity using different techniques are required to determine whether this incongruity is due to measurement and calculation techniques or to an actual change in productivity of the Bay. Identifying potential changes in sediment production resulting from anthropogenic influences is essential for predicting the effects of future resource management actions on the health of Florida Bay.

We have performed short-term productivity measurements in Florida Bay, including net calcification, photosynthesis, and respiration, using geochemical techniques that have proven successful for measuring production in carbonate reef and seagrass bed ecosystems (Smith, 1973; Barnes, 1983; Barnes and Devereux, 1984; Frankignoulle and Distéche, 1984; Gattuso et al., 1993). Determining productivity geochemically provides an independent measure of sediment production that incorporates all carbonate producing species in a given area and dissolution of sediments, unlike standing crop and turnover methods which are based on select species and do not consider loss of sediment to dissolution.

Carbonate sedimentation and organic productivity (calcification, photosynthesis and respiration) are most effectively determined from precise, in situ measurements of alkalinity, pH, temperature, conductivity, and air:sea CO<sub>2</sub> and O<sub>2</sub> gas fluxes (Smith and Key, 1975; Millero, 1979; Barnes, 1983; Gattuso et al., 1993; Millero et al., 1993). Productivity was determined in basins by measuring temporal geochemical changes in a large incubation chamber called the Submersible Habitat for Analyzing Reef Quality (SHARQ) deployed on seagrass beds located in basins near Buchanon and Russell Banks. Productivity on Russell Bank was determined using an upstream/downstream sampling strategy to measure spatial geochemical changes across the bank.

## SHARQ

The SHARQ consists of a 4.8(l) x 2.4(w) x 1.2(h) m. PVC frame covered with clear vinyl sheeting. A circulation system generates a current inside of the tent and carries water to the surface through a flow-through analytical system for geochemical analyses and water sampling. (Figures 1-3). We have successfully tested the SHARQ in both deep (>40 feet) and shallow (<4 feet) water in the Gulf of Mexico, the Bahamas, Hawaii and Florida Bay. Field trials have incorporated fluorescein dye injection studies to examine leak rates and mixing rates in the SHARQ, deployment of current meters to measure current characteristics generated by the circulation system, measurement of photosynthetically active radiation (PAR) attenuation by the clear vinyl used to construct the tent, and 24 hour monitoring of geochemical changes in seagrass beds.

Fluorescein dye was injected into the tent via a sample port on the flow-through analysis system during dark hours, and concentrations monitored through the duration of the experiment using a Model 10-AU Digital Fluorometer (Turner Designs). Results indicate that approximately 1.6 to 2.3 hours are required to mix water in the tent and reach peak dye concentrations. There is a slight linear decrease in fluorescein concentrations through the night consistent with rates of dye absorption to sediments and organic material, and exponential decrease during the day consistent with rates of photochemical decay of fluorescein (Figure 4). Rates of absorption of dye to carbonate sediments (2% of total concentration) and organic material (17% of total concentration) (Smart and Laidlaw, 1977) were used to generate a theoretical concentration decay during the night. An average minimum photochemical decay coefficient of  $3.1 \times 10^{-2}$  calculated from values of Smart and Laidlaw (1977) was used to generate a theoretical concentration decay during the

day. This theoretical decay curve was then used to correct raw fluorescence data to show decreases in dye concentration associated with leakage of water into or out of the tent. Results showed no decrease in corrected dye concentrations (indicating no leakage of water during the incubation period) and a water mixing rate of approximately 1.6 hours (Figure 4).

A Sontek current meter was placed on the bottom surface in seagrass beds covered with the SHARQ. Current speed and direction was measured along x, y, and z axes. Initial results indicate that flow is not laminar, and suggest that turbulent flow may occur within the tent. Additional measurements will be required to accurately characterize flow patterns.

The effects of clear vinyl sheeting were examined by measuring PAR attenuation with water depth using a LiCor 4Π quantum sensor covered with a sleeve made from the same clear vinyl sheeting used to construct the tent and performing the same measurements with the sensor uncovered. No difference in PAR attenuation occurs between sleeved and unsleeved sensor data below a depth of 3 feet (Figure 5). Clear vinyl sheeting reduces PAR by 29% at 1 foot, 21% at 2 feet, and 4% at 3 feet water depth relative to measurements taken using an unsleeved sensor.

## **BASIN PRODUCTIVITY**

Calcification, photosynthesis, and respiration were measured during winter (March) and Summer (September) of 1999 on seagrass beds located in basins near Buchanan Bank (latitude  $24^{\circ} 55.416' N$ , longitude  $80^{\circ} 45.942' W$ ) and Russell Bank (latitude  $25^{\circ} 03.756' N$ , longitude  $80^{\circ} 36.850' W$ ) using the SHARQ. Geochemical parameters including pH, dissolved oxygen, fluorescence, and temperature were measured continuously through the SHARQ's flow-through analytical system (Figure 6 and 7) throughout the duration of incubation periods (from 20-28

hours). Water samples were removed from sample ports every 4 hours for alkalinity measurements via the Gran titration method using methods of Millero (1979). Dissolved oxygen, pH and alkalinity data were used to calculate rates of net calcification, photosynthesis, and respiration for each 4-hour interval between alkalinity measurements during incubation periods. Productivity parameters were calculated using the alkalinity anomaly technique (Smith and Key, 1975) and carbonate system equations of Millero (1979), whereby  $\Delta$  concentration of each parameter/ $\Delta T \times \text{SHARQ volume}/\text{SHARQ surface area} = \text{g C m}^{-2}\text{s}^{-1}$ . Sample interval rates were then used to calculate net daily production rates that were then used to derive average hourly rates of calcification, photosynthesis, and respiration.

Preliminary results indicate net dissolution of carbonate sediments in basins near Russell and Buchanon Banks ranging from approximately  $-6 \times 10^{-3}$  to  $-0.11 \text{ g CaCO}_3/\text{m}^2/\text{hr}$ , shown graphically as negative calcification values (Figure 8). Photosynthesis shows seasonal variation in both basins with highest rates of photosynthesis occurring during winter. It must be noted, however, that salinity and temperature were high relative to annual averages in both basins during summer measurements (salinity 42 and temperature 28.5-31°C near Russell Bank, and salinity 36.5 and temperature 28.2-29°C near Buchanon Bank). Additionally, a summer algal bloom near Russell Bank reduced photosynthetically active radiation (PAR) to 8% of surface values from water surface to bottom (4 ft. depth). These conditions are likely to have stressed the benthos resulting in net oxygen consumption and negative photosynthesis values for both sites, and higher respiration values for the basin near Russell Bank shown in Figure 8.

## **BANK PRODUCTIVITY**

Calcification, photosynthesis, and respiration were measured during winter (March) and summer (September) of 1999 on Russell Bank using an upstream/downstream sampling strategy. Spatial geochemical parameters were determined by establishing upstream and downstream sampling sites along 200-400m transects across Russell Bank (latitude  $25^{\circ} 04.052' N$ , longitude  $80^{\circ} 37.655' W$  to latitude  $25^{\circ} 03.874' N$ , longitude  $80^{\circ} 37.613' W$ ). Current directions and velocities were determined by deploying Sontek current meters on the bank (Figure 9).

Calcification, photosynthesis, and respiration were calculated from total alkalinity, pH, dissolved oxygen, air:sea  $CO_2$  and  $O_2$  gas fluxes, salinity, temperature, and wind measurements. Water samples were collected and analyzed for total alkalinity at upstream and downstream sites approximately every 4 hours throughout 24-hour time intervals. Total alkalinity was used to calculate net calcification using the alkalinity anomaly technique of Smith and Key (1975). Total carbon was calculated using carbonate system equations from Millero (1979). Air-sea  $CO_2$  fluxes were measured directly at each station inside of a floating bell (Sugiura et al., 1963; Frankignoulle and Distéche, 1984; Frankignoulle, 1988; Gattuso et al., 1993; Kayanne et al., 1995) using the procedure and calculations of Frankignoulle (1988). Air-sea  $O_2$  fluxes were determined by measuring atmospheric and water  $pO_2$  and calculating fluxes as described in Wanninkhof (1992). Differences in oxygen and carbon metabolism between upstream and downstream stations were corrected for  $O_2$  and  $CO_2$  exchange with the atmosphere as described in (Gattuso et al., 1993). Productivity and metabolic rates per unit area were calculated using the difference in concentration between upstream and downstream stations (Table 1), the volume of water transported along a transect, and the transect area such that the change in concentration of a

parameter ( $\Delta C \text{ m}^{-2}\text{s}^{-1}$ ) = ( $\Delta C \text{ m}^{-3} \times \text{m}^3\text{hr}^{-1}$ )/ $\text{m}^2$  (Barnes and Devereux, 1984). Productivity data from 4 hour sample intervals was used to calculate net daily production rates for mud banks. Net daily production rates were used to derive average hourly rates of calcification, photosynthesis and respiration. Preliminary results indicate net carbonate sediment production during winter ( $0.02 \text{ g CaCO}_3/\text{m}^2/\text{hr}$ ) and net sediment dissolution during summer ( $-4.0 \times 10^{-3} \text{ g CaCO}_3/\text{m}^2/\text{hr}$ ) (Figure 10). Negative respiration values are indicative of carbon fixation and suggest that negative photosynthesis values (based on oxygen) result perhaps from oxygen consumption through chemical oxidative processes (e.g. sulfide oxidation, etc.). Additional nutrient measurements will be made in future experiments to quantify these processes. Geochemical changes resulting from water column (as opposed to benthic) processes on Russell Bank were examined in March by incubating water from the bank top, *in situ*, but isolated from the bottom, using a bucket. Initial results show that temporal geochemical shifts in the water column resulting from planktonic components are negligible compared to those resulting from benthic processes measured using the SHARQ. Comparison of changes in calcification, photosynthesis, and respiration from the 4-hour “bucket” incubation period to the same 4-hour time period for March measurements in Russell Bank Basin using the SHARQ (shown below) indicate that carbonate sediment and photosynthetic production by the benthos is three orders of magnitude greater than for plankton:

Russell Bank and Adjacent Basin 03/99	Incubation Period	Calcification g carbon/ $\text{m}^2/\text{hour}$	Photosynthesis g carbon/ $\text{m}^2/\text{hour}$	Respiration g carbon/ $\text{m}^2/\text{hour}$
Plankton (bucket)	11:18 – 15:35	-0.0009	-0.0004	0.0002
Benthos (SHARQ)	12:00 – 16:00	0.2647	0.1391	-0.0084

Additional productivity measurements in basins and on banks are required to gain a more complete characterization of trends in carbonate sediment productivity. However, an initial comparison of these preliminary data to rates of carbonate sediment accumulation calculated from standing crop and turnover methods, sediment thickness and age, and dated cores reveals some interesting results. If, for Russell Bank, we apply the winter rate of sediment production over 6 months in a year, and the summer rate of dissolution over the other 6 months, net annual sediment production can be estimated at approximately  $85 \text{ g CaCO}_3/\text{m}^2/\text{year}$ . This corresponds to an average accumulation rate of approximately  $7.4 \text{ cm}/1000 \text{ years}$  of calcium carbonate sediment produced on the bank top. Dated cores from Russell Bank represent sediment that has been produced on the bank and remained there, and sediment that has been transported to the bank from elsewhere in the Bay. These cores indicate sediment accumulation rates of  $0.33$  to  $1.91 \text{ cm}/\text{year}$  or  $330$  to  $1,910 \text{ cm}/1000 \text{ years}$  (Holmes et al., in review). This supports findings by Halley et al. (1999) and Prager and Halley (1999) that newly formed sediment is a minor contribution to banks and much of bank sediments have been transported to their present location. Boscence (1989) estimates carbonate sediment production equivalent to approximately  $88 \text{ cm}/1000 \text{ years}$ . However, Walter and Burton (1990) suggest that much of the sediment produced is redissolved. Our results showing net dissolution of sediments in basins and periods of dissolution on banks support high carbonate sediment dissolution rates in the Bay. Lastly, it is interesting to note that bank sediment accumulation rates calculated in this study ( $7.4 \text{ cm}/1000 \text{ years}$ ) correspond well with sediment accumulation rates of Stockman et al. (1967) who estimated  $8.0 \text{ cm}/1000 \text{ years}$  based on sediment thickness and age.

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## FIGURE CAPTIONS

Figure 1. The SHARQ (Submersible Habitat for Analyzing Reef Quality) was deployed in seagrass beds in basins near Russell and Buchanon Banks. This underwater tent is 4.8(l) x 2.4(w) x 1.2-2.4(h) m in size. The clear tent is fitted over a PVC frame and contoured to the bottom by laying sand bags around the perimeter. A submersible pump circulates water in a closed system in the tent.

Figure 2. SHARQ is constructed underwater by two SCUBA divers.

Figure 3. Water is pumped from the SHARQ through a flow-through analytical system on the surface for geochemical analyses.

Figure 4. Fluorescein dye injection studies indicate no leakage of water into or out of SHARQ. Theoretical decay curve calculated from rates of dye absorption to sediments and organic material and photochemical decay constants from Smart and Laidlaw (1977).

Figure 5. Attenuation of photosynthetically active radiation (PAR) with water depth by clear vinyl sheeting used to construct SHARQ.

Figure 6. Dissolved oxygen and pH data from SHARQ deployment on seagrass bed in basin near Buchanan Bank during winter (a and b) and summer (c and d). Dissolved oxygen logged every 2 minutes, pH logged every 5 minutes during incubation periods. Red dots indicate ambient (outside of SHARQ) dissolved oxygen.

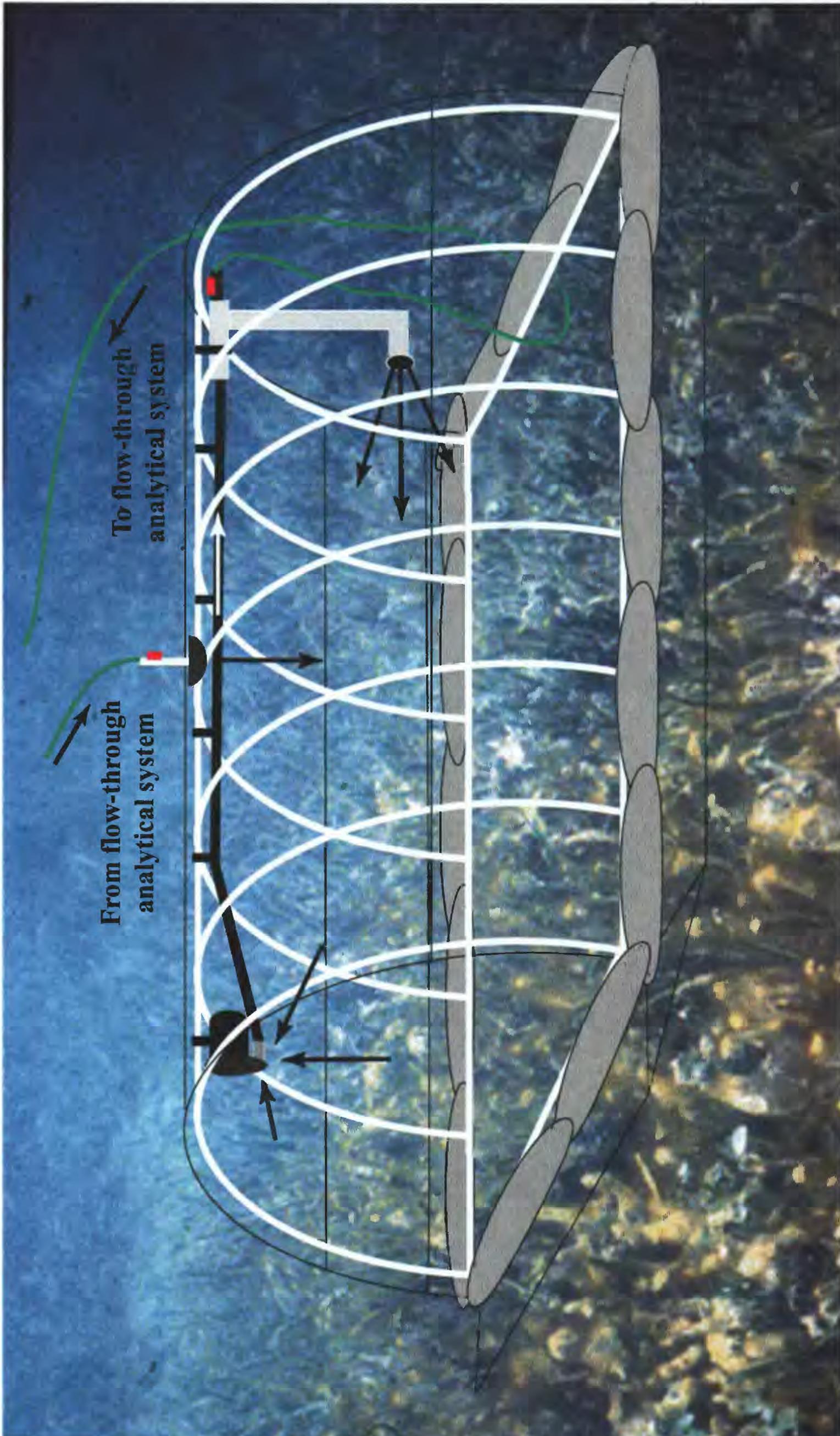
Figure 7. Dissolved oxygen and pH data from SHARQ deployment on seagrass bed in basin near Russell Bank during winter (a and b) and summer (c and d). Dissolved oxygen logged every 2 minutes, pH logged every 5 minutes during incubation periods.

Figure 8. Average rates of calcification, photosynthesis, and respiration in grams of carbon (a.) and carbonate sediment in grams of calcium carbonate (b.) for basins near Russell and Buchanan Banks measured using SHARQ during winter and summer.

Figure 9. Example of raw current data from Russell Bank (summer) used to establish upstream/downstream sample sites. Transition from positive to negative values indicates 180° change in direction.

Figure 10. Average rates of calcification, photosynthesis, and respiration in grams of carbon (a.) and carbonate sediment production in grams of calcium carbonate (b.) for Russell Bank measured using upstream/downstream sampling approach during winter and summer.

Figure 1.





**Figure 2.**

Figure 3.

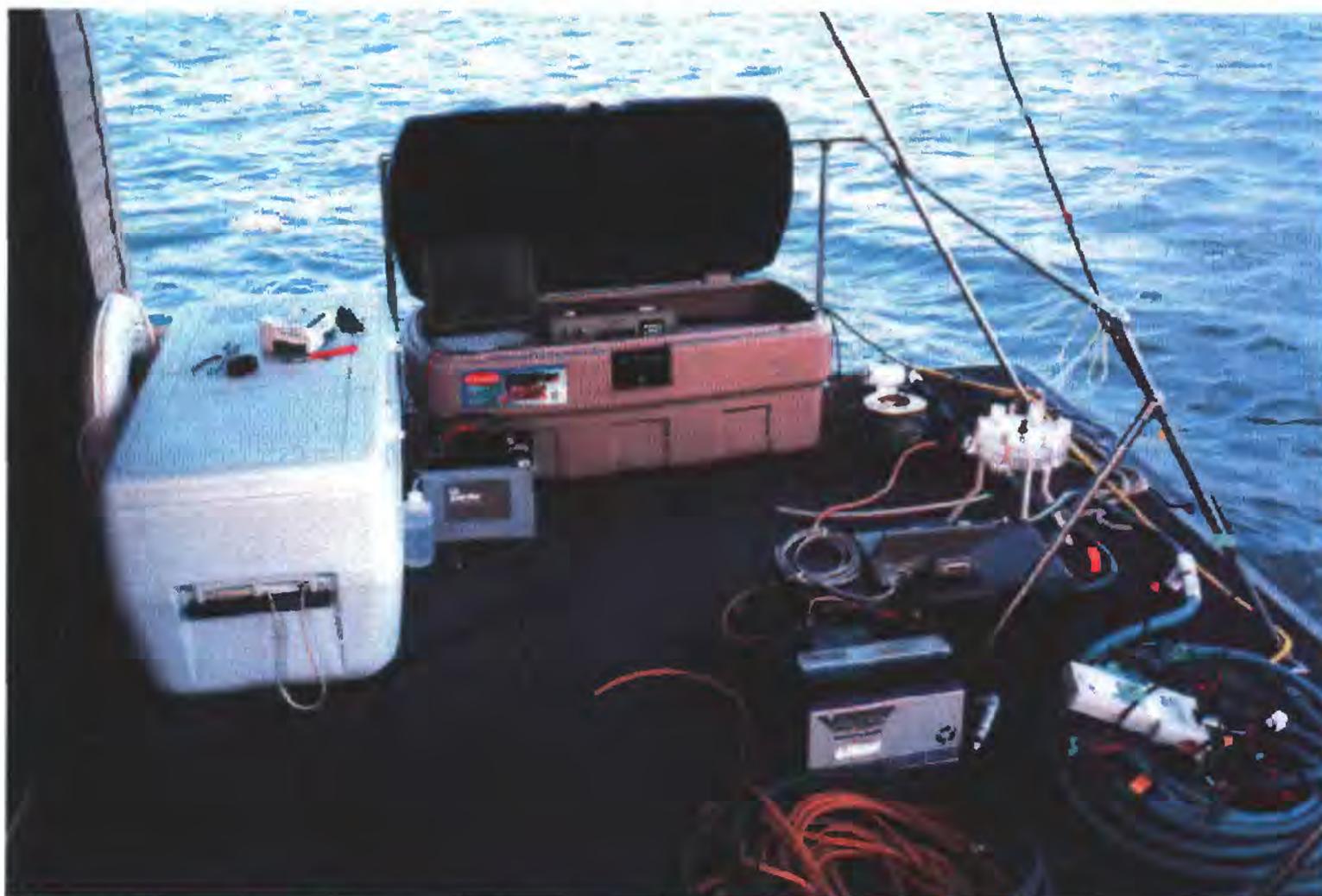


Figure 4.

### S.H.A.R.Q. Fluorescence Buchanan Bank basin

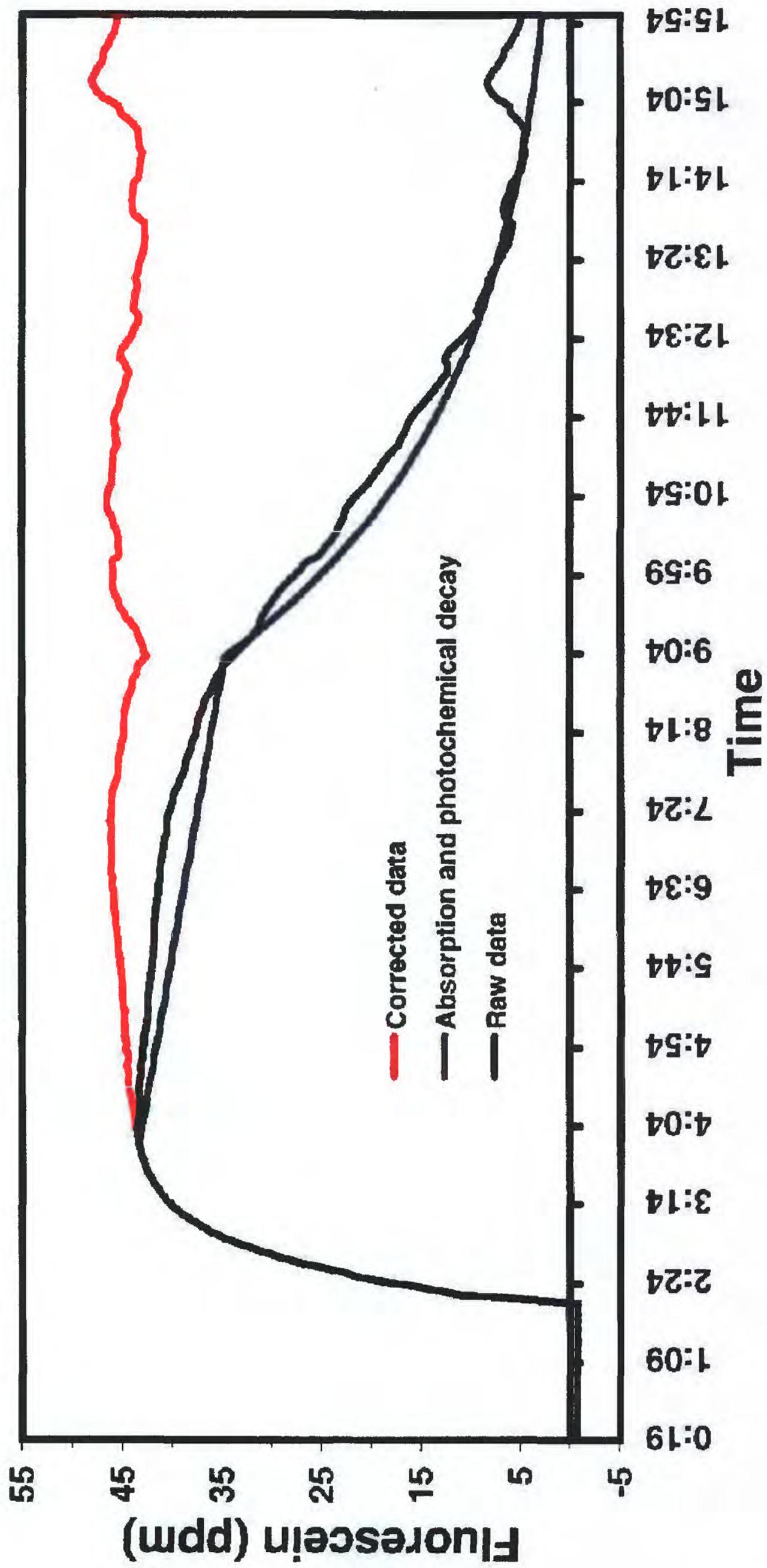


Figure 5.

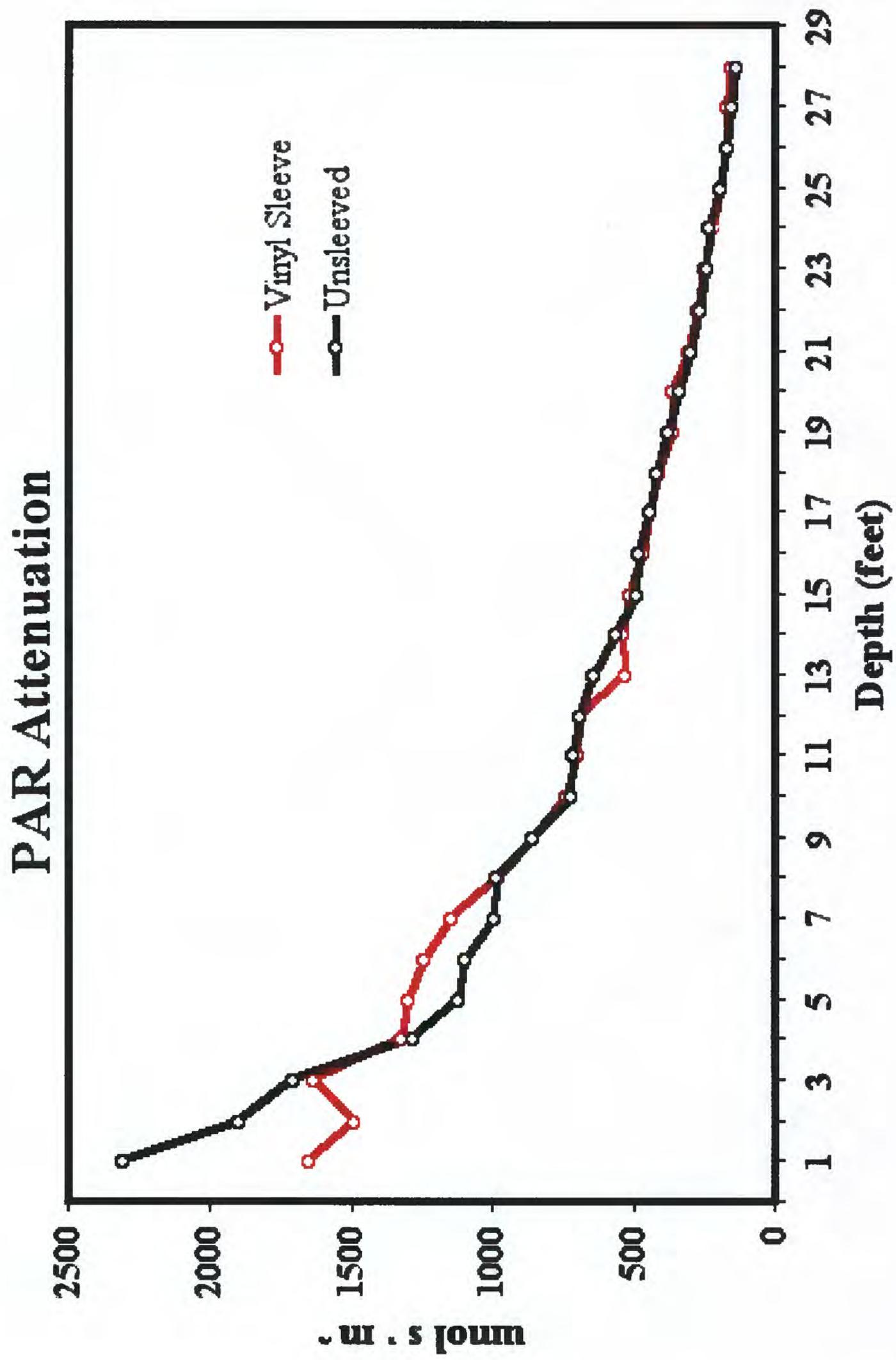


Figure 6.

# Buchanon Bank Basin

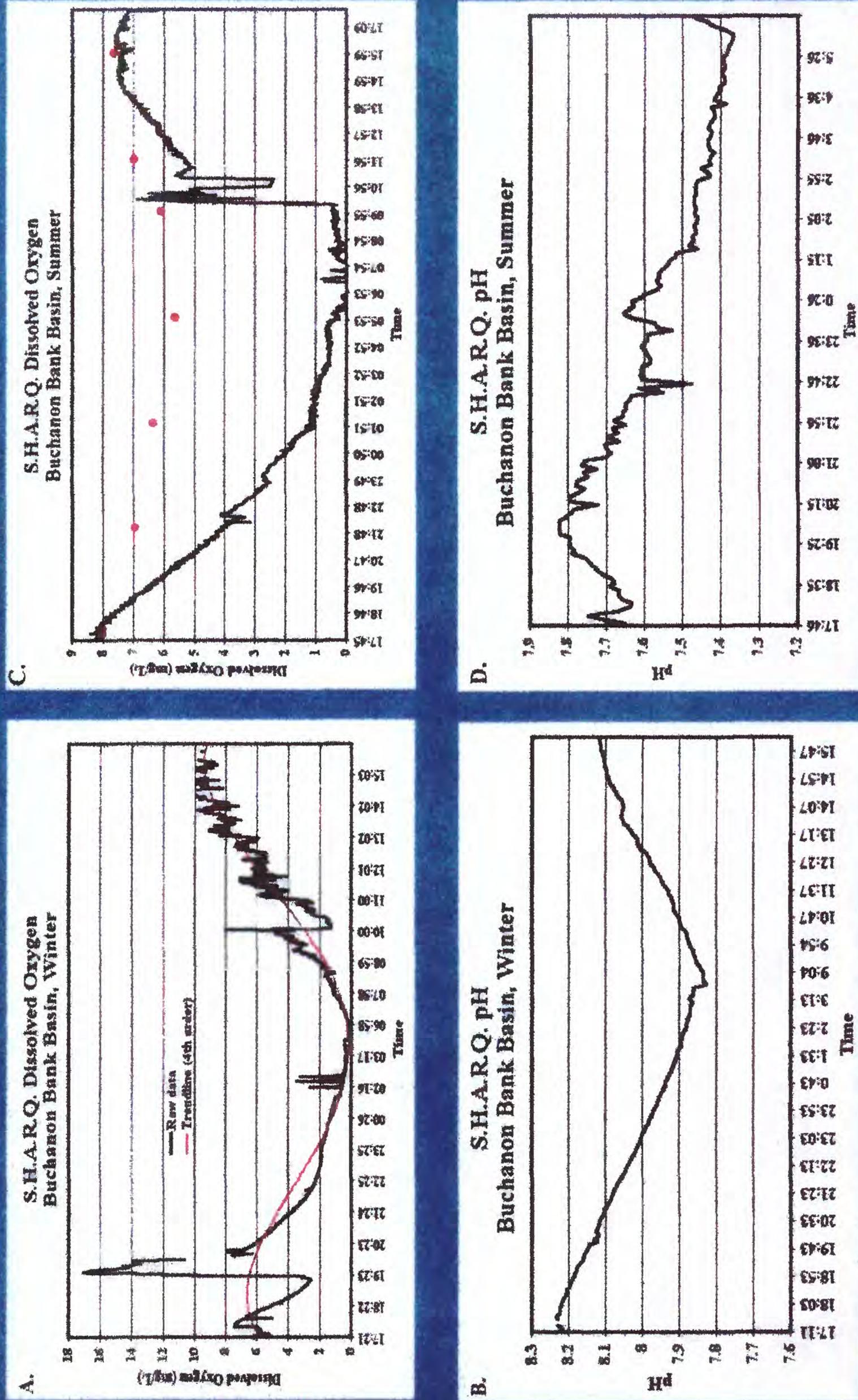
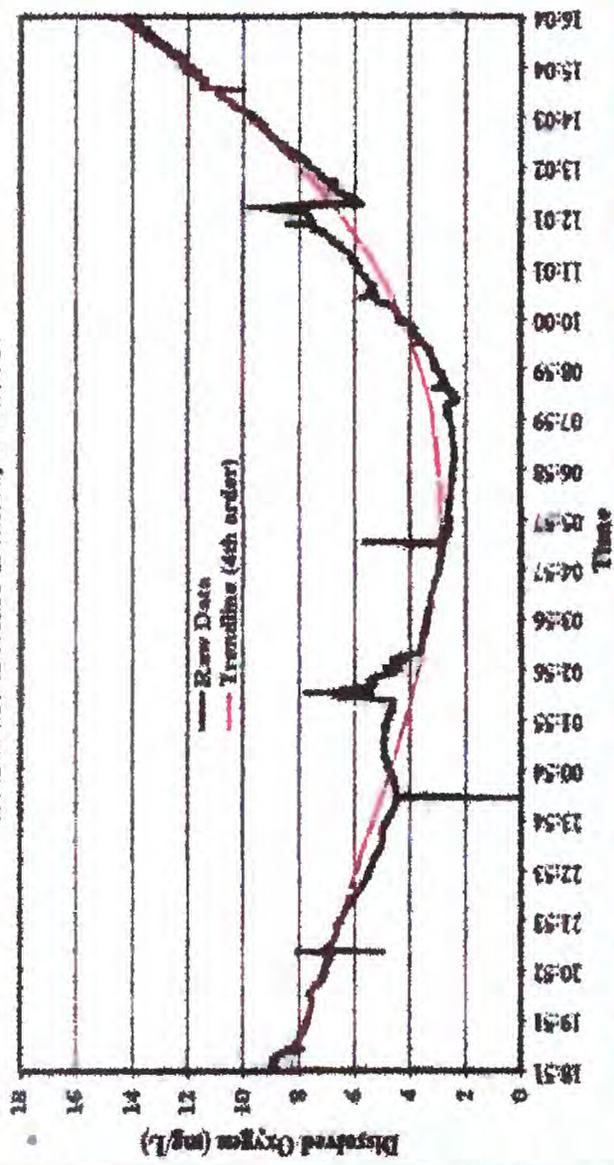


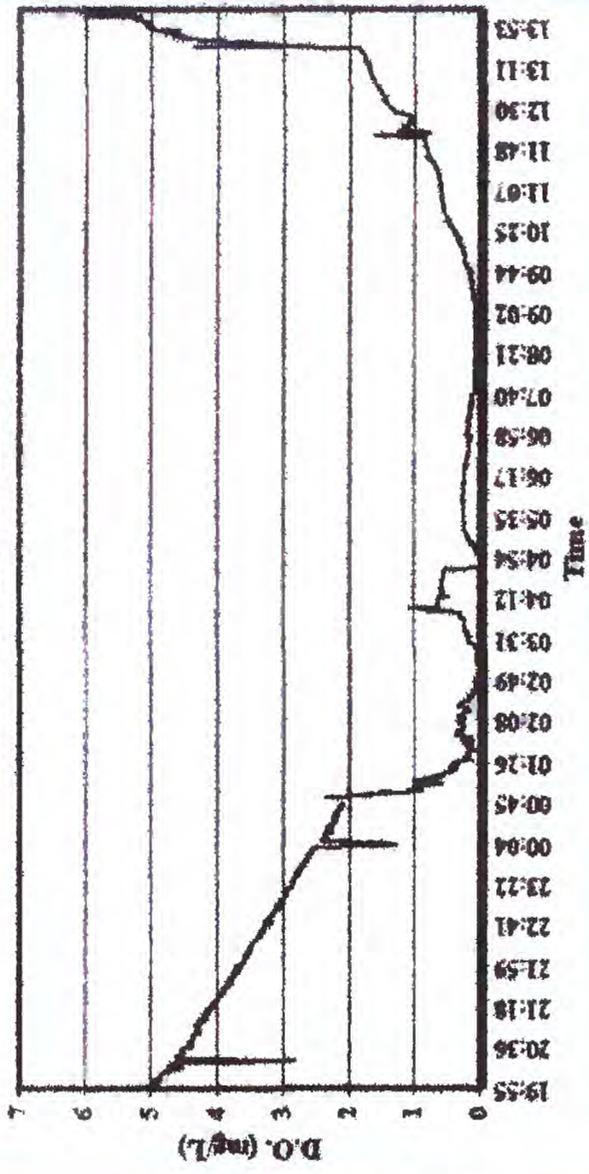
Figure 7.

# Russell Bank Basin

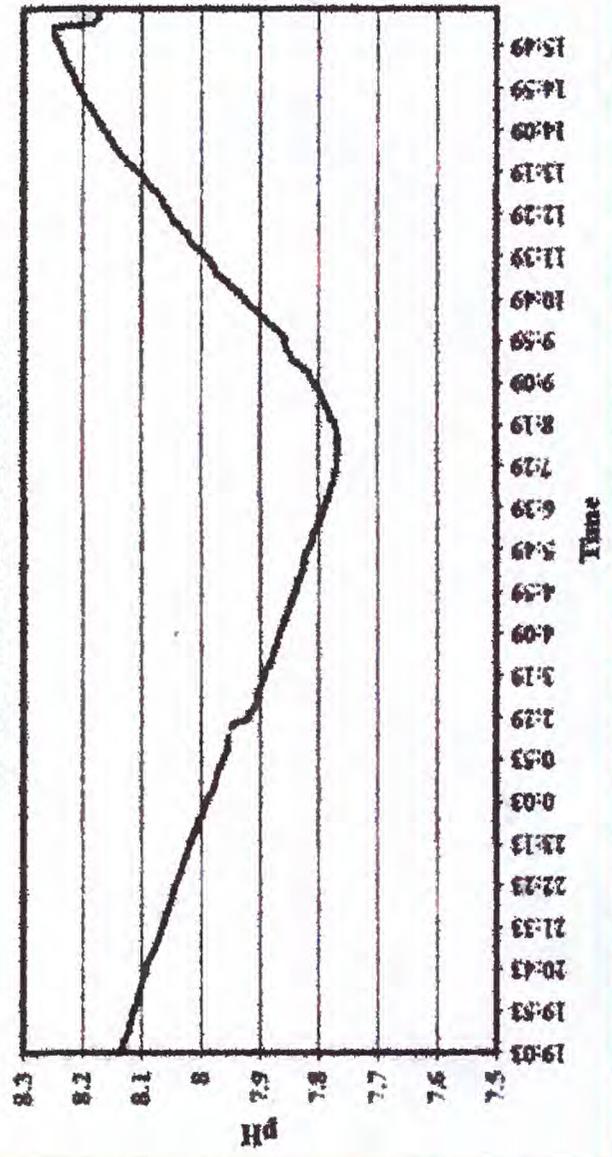
S.H.A.R.Q. Dissolved Oxygen  
Russell Bank Basin, Winter



S.H.A.R.Q. Dissolved Oxygen  
Russell Bank, Summer



S.H.A.R.Q. pH  
Russell Bank Basin, Winter



S.H.A.R.Q. pH  
Russell Bank Basin, Summer

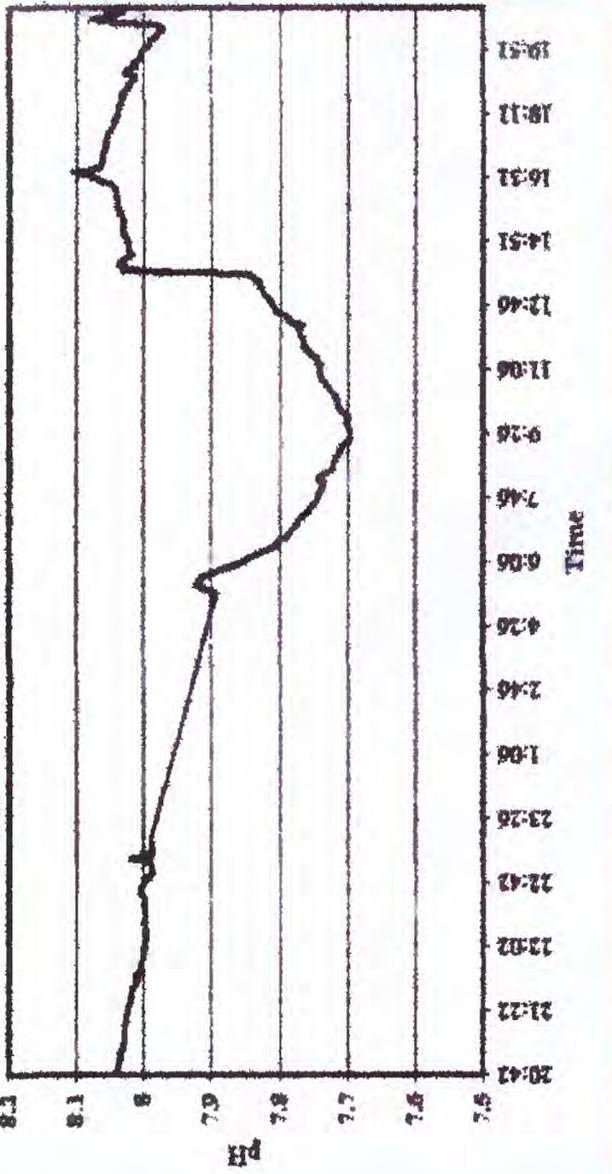
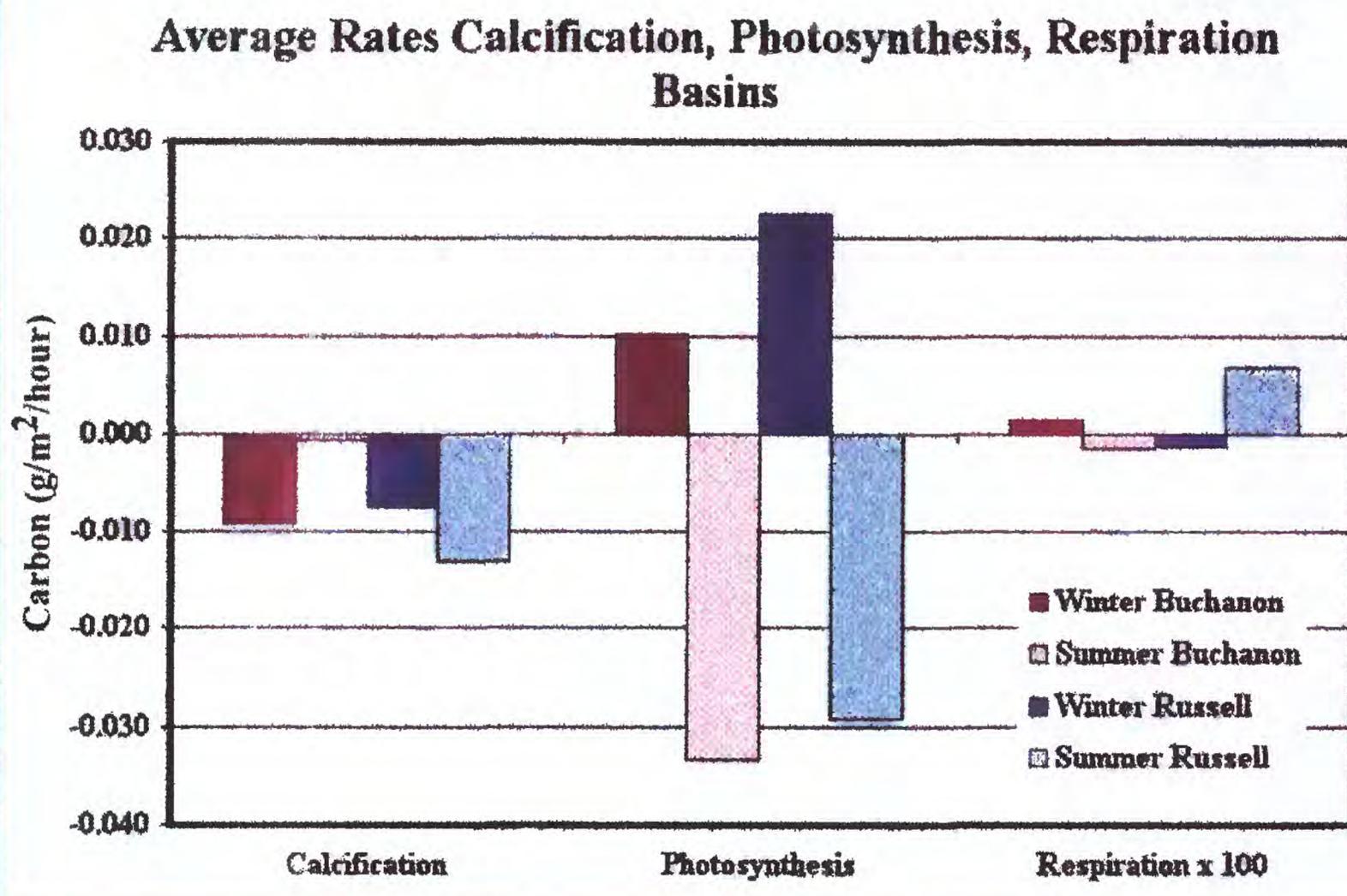


Figure 8.

# Basin Productivity

A.



B.

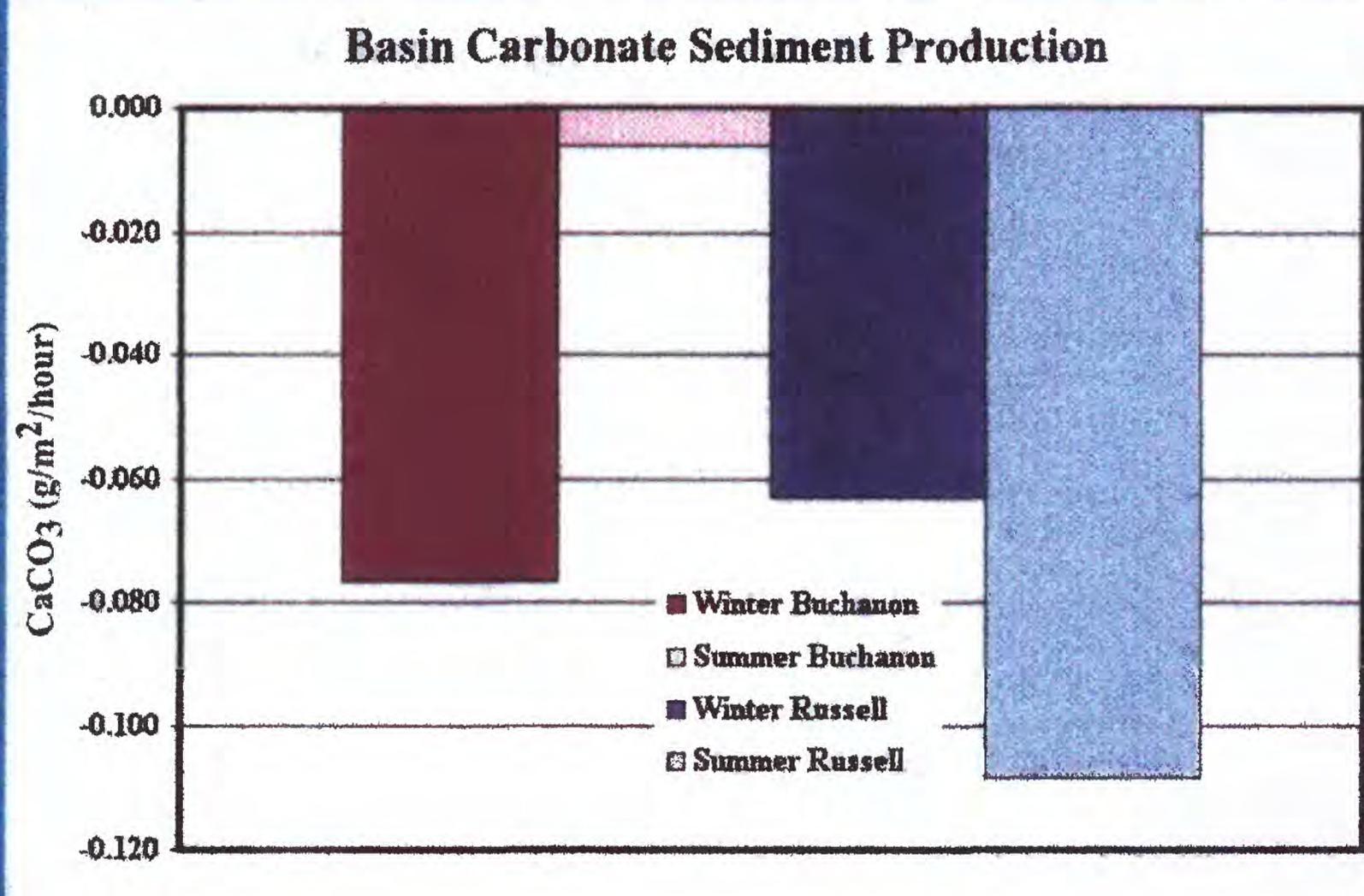


Figure 9.

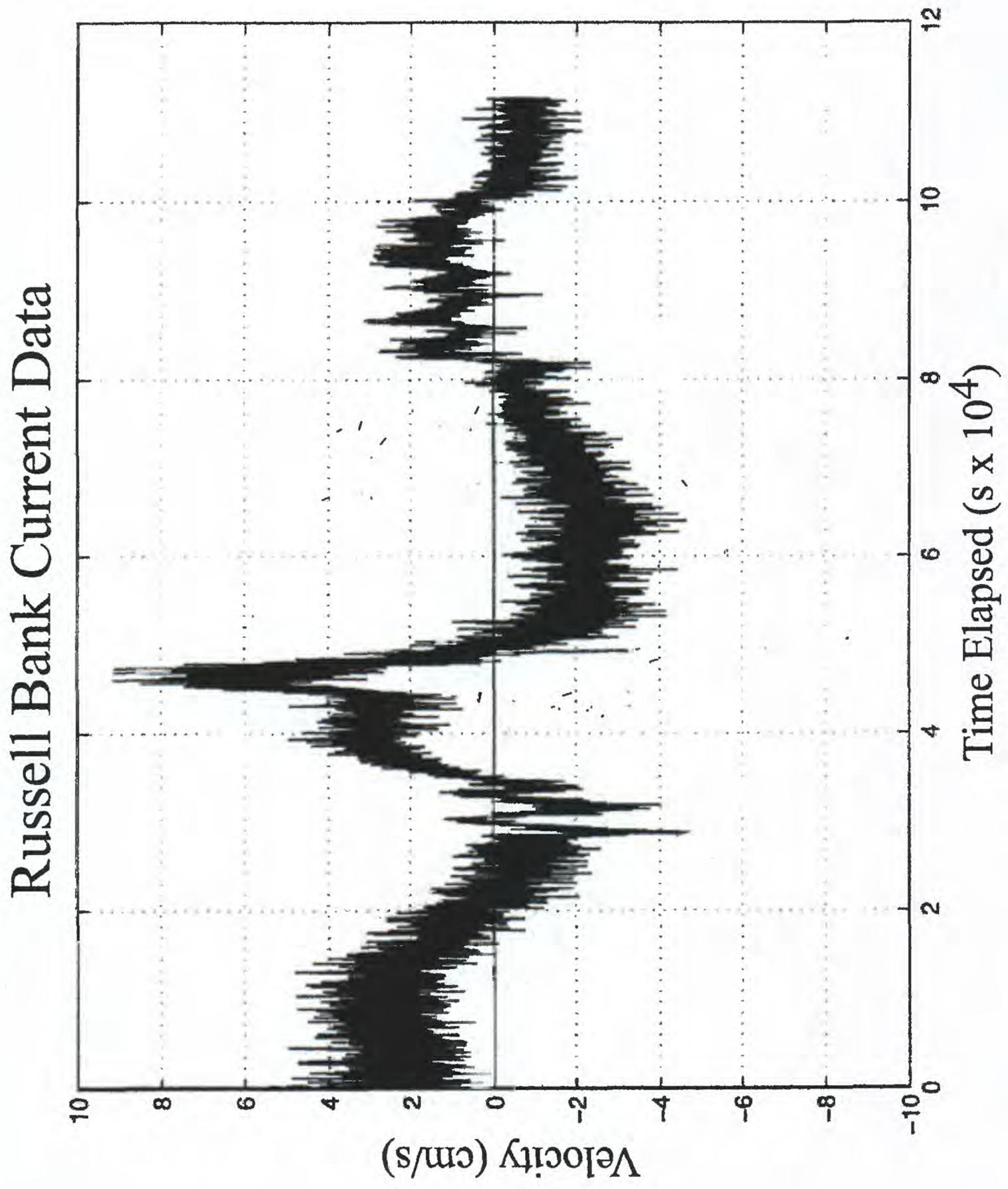
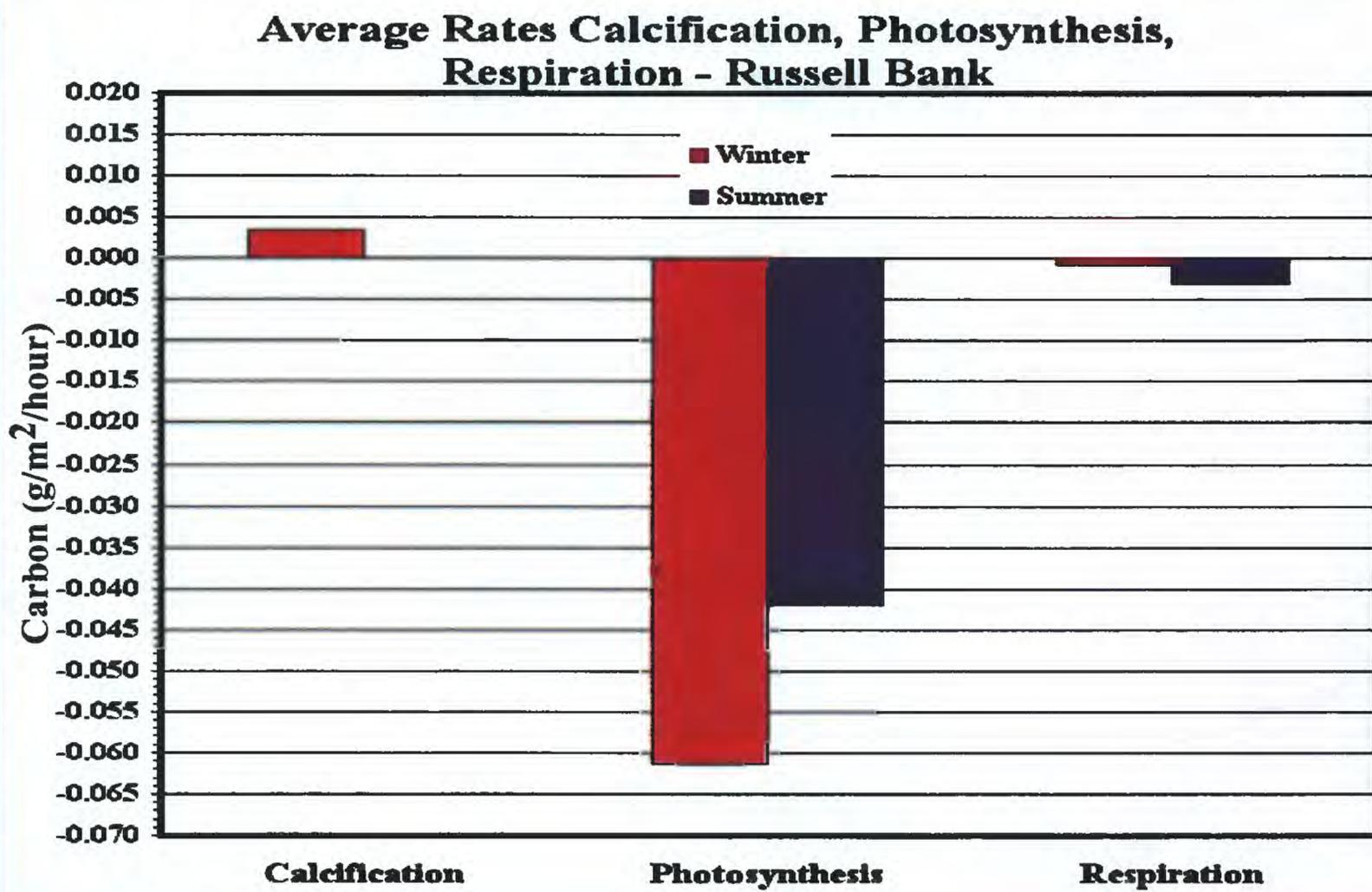


Figure 10.

# Bank Productivity

A.



B.

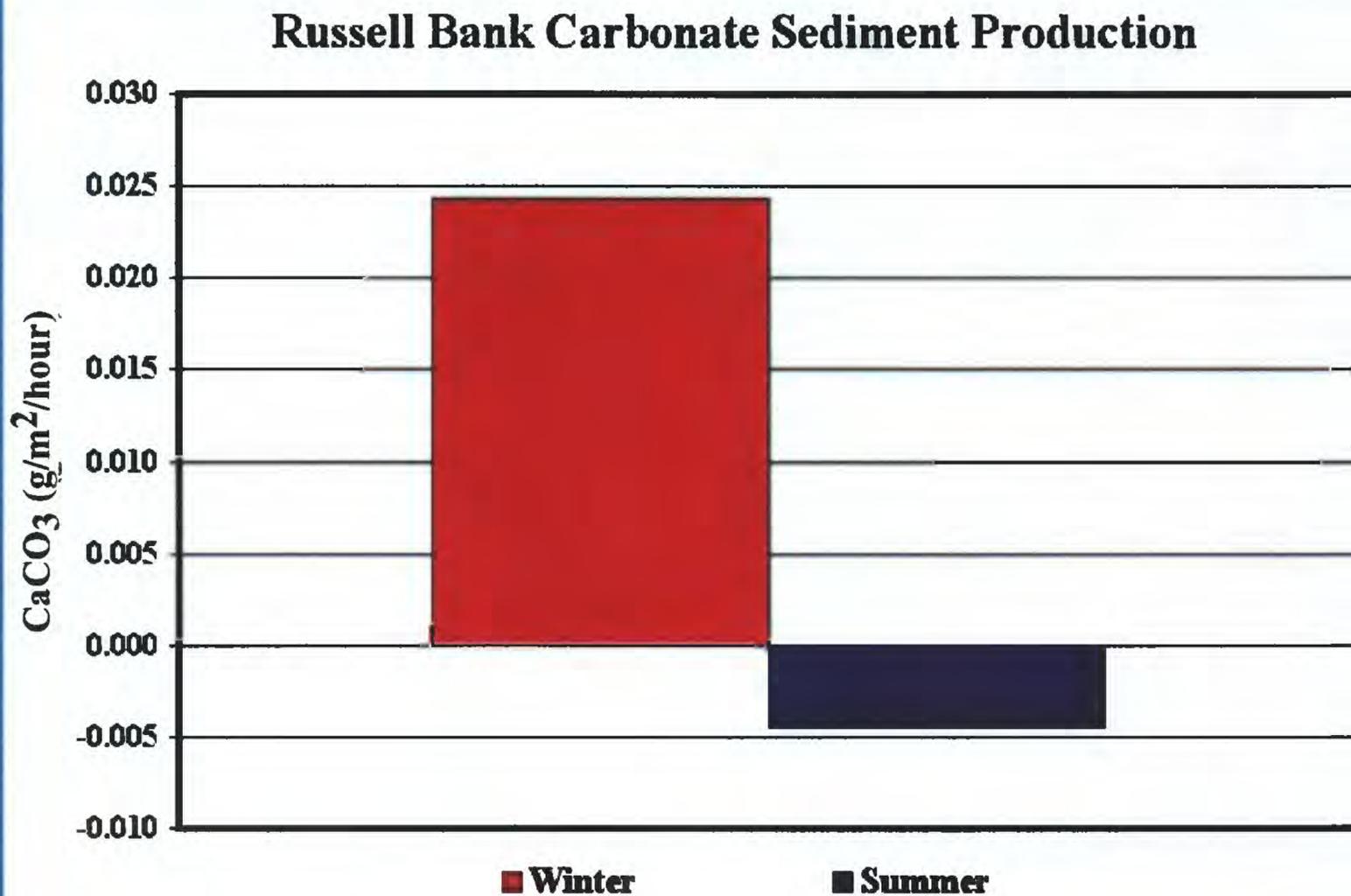


Table 1. Geochemical data from winter (A.) and summer (B.) monitoring efforts taken at upstream and downstream sample stations at 4-hour intervals over 24-hour time periods.

**A. Russell Bank Upstream/Downstream Transect Data, Winter 1999**

Transect Location	Time of day	In Situ pH	Alkalinity (meq/kg)	D.O. mg/L	CO <sub>2</sub> Flux mol <sub>s</sub> m <sup>-2</sup> s <sup>-1</sup>
Upstream	16:00	8.066	2.7908	7.13	8.69E-05
Downstream	16:32	8.085	2.7710	8.06	3.73E-05
Upstream	20:24	8.047	2.7855	6.87	6.92E-05
Downstream	21:11	8.042	2.7639	7.10	5.93E-05
Upstream	0:59	8.053	2.8371	6.93	2.90E-05
Downstream	0:12	8.031	2.7780	6.66	3.02E-05
Upstream	4:59	8.043	2.7862	6.60	2.35E-05
Downstream	4:20	8.061	2.7576	6.75	3.19E-05
Upstream	8:58	8.089	2.8047	7.53	8.65E-06
Downstream	8:20	8.064	2.7589	7.26	7.33E-06
Upstream	12:35	8.117	2.8055	8.59	2.80E-05
Downstream	12:06	8.160	2.7285	9.30	-8.43E-05
Upstream	15:47	8.102	2.7047	8.07	8.89E-06
Downstream	16:15	8.114	2.7260	8.41	-4.75E-05

**B. Russell Bank Upstream/Downstream Transect Data, Summer 1999**

Transect Location	Time of day	In Situ pH	Alkalinity (meq/kg)	D.O. mg/L	CO <sub>2</sub> Flux mol <sub>s</sub> m <sup>-2</sup> s <sup>-1</sup>
Upstream	11:45	8.184	2.4343	5.99	1.64E-04
Downstream	12:25	8.207	2.4411	6.32	1.58E-04
Upstream	16:30	8.167	2.4036	6.83	1.57E-04
Downstream	15:55	8.160	2.4176	6.68	1.75E-04
Upstream	20:00	8.168	2.4040	6.58	2.77E-05
Downstream	20:40	8.145	2.4069	6.25	3.52E-05
Upstream	0:35	8.135	2.4111	5.78	8.57E-04
Downstream	0:00	8.127	2.4171	5.69	7.99E-05
Upstream	4:35	8.116	2.4130	5.12	1.11E-04
Downstream	4:00	8.107	2.4200	4.79	1.04E-04
Upstream	8:50	8.096	2.4148	4.75	2.59E-04
Downstream	8:00	8.086	2.4027	4.33	1.79E-04
Upstream	11:55	8.134	2.4179	5.33	2.17E-04
Downstream	12:30	8.144	2.4045	5.83	1.75E-04
Upstream	16:40	8.115	2.3982	6.32	1.42E-04
Downstream	16:07	8.174	2.4151	7.10	9.25E-05