

# CHAPTER 2: TEMPORAL STUDY OF VARIATION

## 2.1 MATERIAL AND METHODS

### 2.1.1 Objectives

- (1) To examine temporal variation in water quality over one 24 hour period at two locations assessing the relative contributions of time, tidal phase and possibly sewage discharge to changes in water quality parameters.
- (2) To assess between day (diel) variation at the two locations on 3 consecutive days, sampling on the high tide during daylight hours.

### 2.1.2 Variables

- . Dissolved Inorganic Nutrients,  $\text{NO}_2 + \text{NO}_3$ ,  $\text{NH}_4$ ,  $\text{PO}_4$
- . Total Phosphorous and Total Nitrogen
- . Particulate Nitrogen
- . Dissolved oxygen
- . Temperature
- . Chlorophyll  $a$
- .  $\text{BOD}_5$
- . Suspended solids
- . Clarity

Section 1.4.2 details the sampling procedures, whilst Appendix 2 explains the analytical procedures used for the determination of these parameters.

### 2.1.3 Experimental Design

Temporal variation of surface waters, both between days (3), and within a 24 hour period were assessed at 2 locations (Figure 2.1) from high water on the 2nd of May 1989 at 0706 hours.

#### (i) 24 Hour study

The following factors were assessed as potential sources of variability.

**Location:** Variation between two locations. Location A was located ca. 250m to the north of the sewerage pipe. Location B was situated 250 metres to the south of the sewerage pipe.

**Habitat:** Variation between the reef flat and reef slope within each location.

**Time Period:** Variation due to tidal and temporal influences. Samples were collected around high and low water and 3 hours after each of these events.

**Replication:** Replicate samples were taken 2-3 minutes apart. This factor necessarily contained components of small scale spatial and short term temporal variability.

#### (ii) Daily Study

The following factors were assessed.

**Location:** Variation between two locations. Location A was located ca. 250m to the north of the sewerage pipe. Location B was situated 250 metres to the south of the sewerage pipe.

**Day:** Variation between 3 consecutive days. Sampling occurred on the high tide of every day.

**Habitats:** Variation between the reef flat and reef slope within each location.

**Replication:** Replicate samples were taken 2-3 minutes apart.

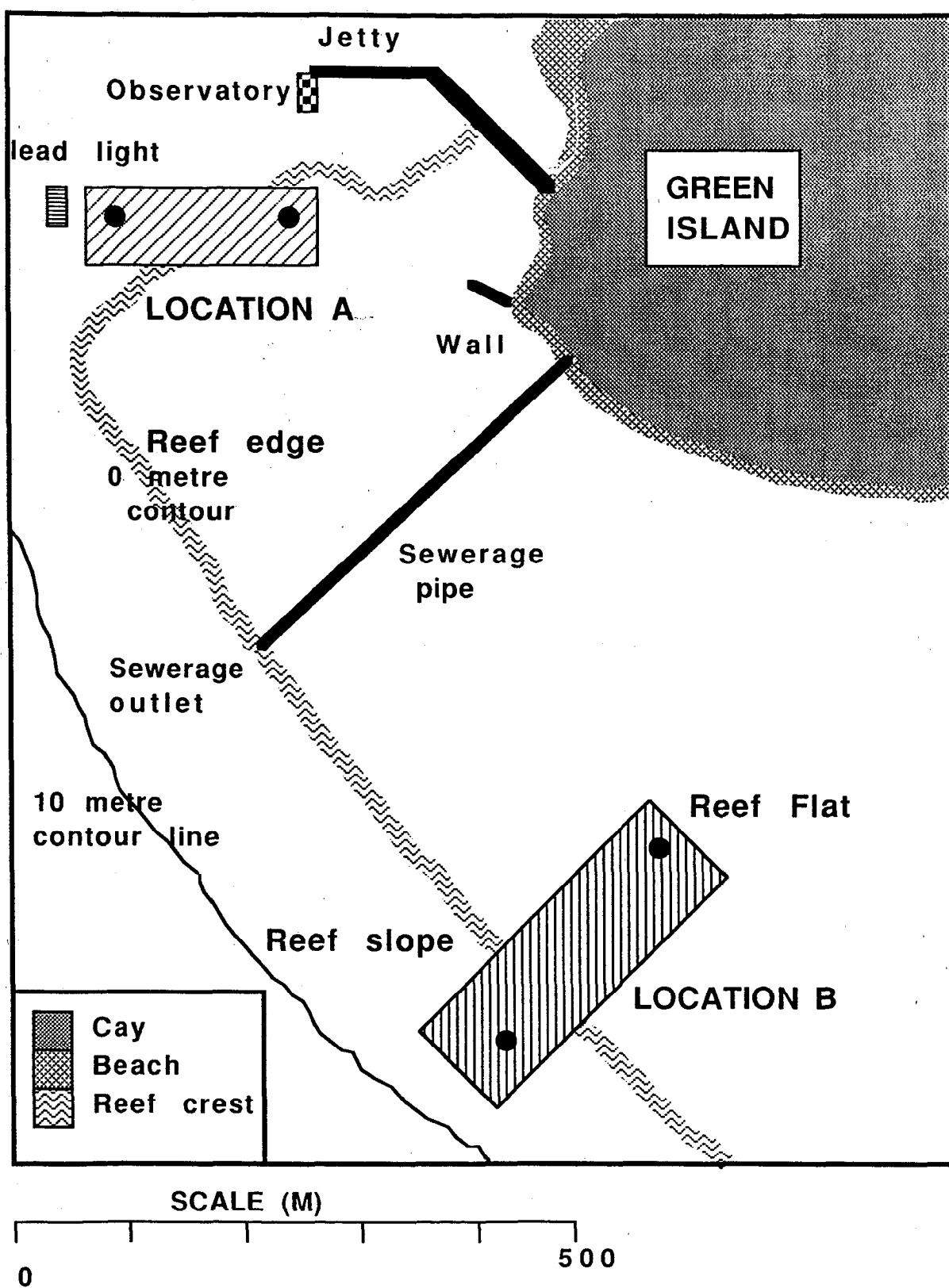
### 2.1.4 Site Selection

Two sampling locations were selected, ca. 250 metres either side of the sewerage discharge pipe (Fig. 2.1.). This placement allowed a preliminary assessment of the potential effects of sewage discharge on the ambient water by measuring upstream and downstream effects. Times of sewage discharge were noted in order to separate natural variation from potential sewage effects.

### 2.1.5 Timing

The 24 hour sampling study was undertaken from 700 hours on the 2nd of June, 1989 through until 1000 hrs on the 3rd June, 1989. Samples were collected approximately every 3 hours throughout this period. Samples for the diel study were collected on the daylight high tide from the 2nd to the 4th of June 1989.

Figure 2.1. Map of sampling locations for the Temporal pilot study.



### **2.1.6 Sampling Strategy**

Surface water measurements were collected at 3 hourly intervals at each habitat within each location. Wind and sea conditions were noted. Dissolved oxygen, temperature and secchi disk measurements were made. Water samples were collected and immediately stored in an 'esky'.

### **2.1.7 Analysis**

Temporal variability was analysed in a 3 factor design comprising Habitats (fixed) x Locations (fixed) and either time of day (fixed), or day (fixed).

## 2.2 RESULTS

### 2.2.1 24 HOUR STUDY

#### (i) Components of Variation

##### Time of Day Effects

Dissolved inorganic nitrogen was the only dissolved nutrient to vary significantly ( $F = 3.24$ ; 7,11 df;  $P = 0.040$ ) in concentration with time of day (Table 2.3.a). Significant temporal differences were found for temperature ( $F = 20.46$ ; 7,9 df;  $P < 0.0001$ ) oxygen ( $F = 6.81$ ; 7,11 df;  $P = 0.002$ ) and suspended solids ( $F = 7.80$ ; 7,12 df;  $P = 0.001$ ), consistent with changes in solar irradiation and tidal effects (Table 2.2.b.).

##### Habitat Effects

No significant differences between reef flat and slope habitats were found for any of the nutrient parameters measured (Table 2.1.a). Mean sea temperature ( $F = 3.97$ ; 1,9 df;  $P = 0.077$ ) and oxygen ( $F = 6.44$ ; 1,11 df;  $P = 0.028$ ) were higher on the reef slope ( $25.4 \pm 0.2$  °C,  $7.8 \pm 0.2$  mg/l) than on the reef flat ( $22.5 \pm 2.5$  °C,  $7.5 \pm 0.5$  mg/l).

##### Location Effects

No significant locations effects were recorded.

##### Interaction Effects

Within each habitat, dissolved inorganic nitrogen ( $F = 4.01$ ; df 6,11;  $P = 0.023$ ) and dissolved oxygen ( $F = 4.55$ ; 5,11 df;  $P = 0.017$ ) varied significantly with respect to time of day (Tables 2.1.a., 2.1.b.)

#### (ii) Analysis of Power

The small scale temporal patterns identified in the 24 hour study are unlikely to be due to deficiencies in the sampling design. The power of the design to detect differences of small ( $< 25$  %) and moderate (50 %) changes in ambient levels of the measured parameters was  $P > 0.56$  and  $P > 0.95$  respectively.

#### (iii) Multi-variate Analysis

Clustering and ordination techniques suggested that there were consistent patterns of temporal variation on nutrient concentrations due to tidal and diurnal effects.

Sampling periods roughly divided into high water sampling and low water sampling times. DIN levels influenced mostly by increases in ammonium and were found around low water sampling times. This is consistent with tidal resuspension.

## 2.2.2 DIEL STUDY

### (i) Components of Variation

#### Diel Variation

Ammonium ( $F = 5.22$ ;  $df\ 2,8$ ;  $P = 0.035$ ) and dissolved inorganic nitrogen ( $F = 7.18$ ;  $df\ 2,8$ ;  $P = 0.02$ ) concentrations varied significantly between days. Both were both significantly lower in mean concentration on the 2/6/89 ( $0.30 \pm 0.11\ \mu\text{M}$ ,  $0.57 \pm 0.13\ \mu\text{M}$ ) than on the 3/6/89 ( $0.79 \pm 0.11\ \mu\text{M}$ ,  $1.19 \pm 0.13\ \mu\text{M}$ ) or the 4/6/89 ( $0.89 \pm 0.16\ \mu\text{M}$ ,  $1.23 \pm 0.17\ \mu\text{M}$ ). Diel variation for total phosphorous was potentially significant ( $F = 3.83$ ;  $df\ 2,8$ ;  $P < 0.075$ ). Mean sea temperature differed significantly between days ( $F = 166.4$ ;  $df\ 1,7$ ;  $P < 0.0001$ ) but problems with equipment calibration may have caused this result.

#### Habitat Effects

Dissolved inorganic nitrogen concentrations differed marginally ( $F = 9.12$ ;  $df\ 1,7$ ;  $P < 0.095$ ) between reef flat ( $0.93 \pm 0.13\ \mu\text{M}$ ) and slope ( $2.21 \pm 0.23\ \mu\text{M}$ ) environments (Table 2.4). Mean sea surface temperature differed significantly ( $F = 5.78$ ;  $df\ 1,7$ ;  $P < 0.047$ ) between habitats (Table 4.2.), but the analytical error associated with the equipment makes this result dubious.

#### Location Effects

Ammonium ( $F = 15.61$ ;  $df\ 1,8$ ;  $P < 0.019$ ) and dissolved inorganic nitrogen ( $F = 9.12$ ;  $df\ 1,8$ ;  $P < 0.019$ ) concentrations were significantly greater on all days at location B. Mean values pooled over days were  $0.89 \pm 0.16\ \mu\text{M}$  and  $1.24 \pm 0.16\ \mu\text{M}$  respectively for location B, and  $0.38 \pm 0.10\ \mu\text{M}$  and  $0.70 \pm 0.12\ \mu\text{M}$  for location A.

### (ii) Analysis of Power

The experimental design for the diel study had low power to detect small ( $< 25\%$ ) effects but reasonable power ( $P > 0.53$ ) to detect moderate ( $> 50\%$ ) changes in ambient conditions.

### 2.2.3 SUMMARY OF TEMPORAL VARIATION

Ammonium and DIN were the only nutrient parameters to vary significantly with respect to either time of day or between days. Both were both significantly lower in mean concentration on the 2/6/89 ( $0.30 \pm 0.11 \mu\text{M}$ ,  $0.57 \pm 0.13 \mu\text{M}$ ) than on the 3/6/89 ( $0.79 \pm 0.11 \mu\text{M}$ ,  $1.19 \pm 0.13 \mu\text{M}$ ) or the 4/6/89 ( $0.89 \pm 0.16 \mu\text{M}$ ,  $1.23 \pm 0.17 \mu\text{M}$ ). Weather conditions on this day were not different in any obvious way (Table 1.1). Over 24 hours DIN levels were higher around the turn of the tide than at mid tide sampling periods (Table 2.2.a.). Dissolved inorganic nitrogen concentrations differed between reef flat ( $0.93 \pm 0.13 \mu\text{M}$ ) and slope ( $2.21 \pm 0.23 \mu\text{M}$ ) environments. Ammonium and dissolved inorganic nitrogen concentrations were significantly greater on all days at location B. Mean values pooled over days were  $0.89 \pm 0.16 \mu\text{M}$  and  $1.24 \pm 0.16 \mu\text{M}$  respectively for location B, and  $0.38 \pm 0.10 \mu\text{M}$  and  $0.70 \pm 0.12 \mu\text{M}$  for location A. This location variation was not significant over 24 hours though.

Surface values for dissolved oxygen and temperature varied significantly with respect to time of day within each habitat. Mean values were greater over sampling times 2 to 4 ( 1105 ebbing, - 1645 rising), consistent with increased light attenuation, weather conditions and tidal mixing. Suspended solids were also greater during this time consistent with tidal resuspension during low tide. Chlorophyll *a* and BOD<sub>5</sub> did not vary with respect to any of the temporal components of variation (Table 2.1.b).

**Table 2.1.a.** Summary table of analysis of variance results for nutrients in the 24 hour temporal study. All data was log transformed after residual analysis for heteroscedascity. \* = sign. at 0.1; \*\* sign. at 0.05; \*\*\* = sign. at 0.01 level.

SOURCE VARIATION	DF	NO <sub>2</sub> + NO <sub>3</sub>	NH <sub>4</sub>	PO <sub>4</sub>	DIN	TN	TP
(A) TIME PERIOD	7	NS	NS	NS	**	NS	NS
(B) LOCATION	1	NS	NS	NS	NS	NS	NS
(C) HABITAT	1	NS	NS	NS	NS	NS	NS
A*B	7	NS	NS	NS	NS	NS	NS
A*C	7	*	NS	NS	**	NS	NS
B*C	1	NS	NS	NS	NS	NS	NS
A*B*C	7	NS	NS	NS	NS	NS	NS

**Table 2.1.b.** Summary table of analysis of variance results for physical and biological parameters in the 24 hour temporal study. All data was log transformed after residual analysis for heteroscedascity. \* = sign. at 0.1; \*\* sign. at 0.05; \*\*\* = sign. at 0.01 level.

SOURCE OF VARIATION	DF	Temper- ature	O <sub>2</sub>	Suspended solids	Chl <i>a</i>	Phaeo phytin
(A) TIME PERIOD	7	***	**	***	NS	NS
(B) HABITAT	1	*	**	NS	NS	NS
A*B	6	NS	**	NS	NS	NS



**Table 2.2.a.** Summary table of analysis of variance results for nutrients in the **Diel** temporal study. All data was log transformed after residual analysis for heteroscedascity. \* = sign. at 0.1; \*\* sign. at 0.05; \*\*\* = sign. at 0.001 level.

SOURCE VARIATION	DF	NO <sub>2</sub> + NO <sub>3</sub>	NH <sub>4</sub>	PO <sub>4</sub>	DIN	TN	TP
(A) DAY	2	NS	**	NS	**	NS	*
(B) LOCATION	1	NS	***	NS	**	NS	NS
(C) HABITAT	1	NS	NS	NS	*	NS	NS
A*B	2	NS	NS	NS	NS	NS	NS
A*C	2	NS	NS	NS	**	NS	NS
B*C	1	NS	NS	NS	NS	NS	NS
A*B*C	3	NS	NS	NS	***	NS	NS

**Table 2.2.b.** Summary table of analysis of variance results for physical and biological parameters in the **Diel** study. All data was log transformed after residual analysis for heteroscedascity. \* = sign. at 0.1; \*\* sign. at 0.05; \*\*\* = sign. at 0.001 level.

SOURCE OF VARIATION	DF	Temperature	Suspended O <sub>2</sub>	solids	Chla	Phaeo phytin
(A) TIME PERIOD	7	***	**	***	NS	NS
(B) HABITAT	1	**	**	NS	NS	NS
A*B	6	*	**	NS	NS	NS

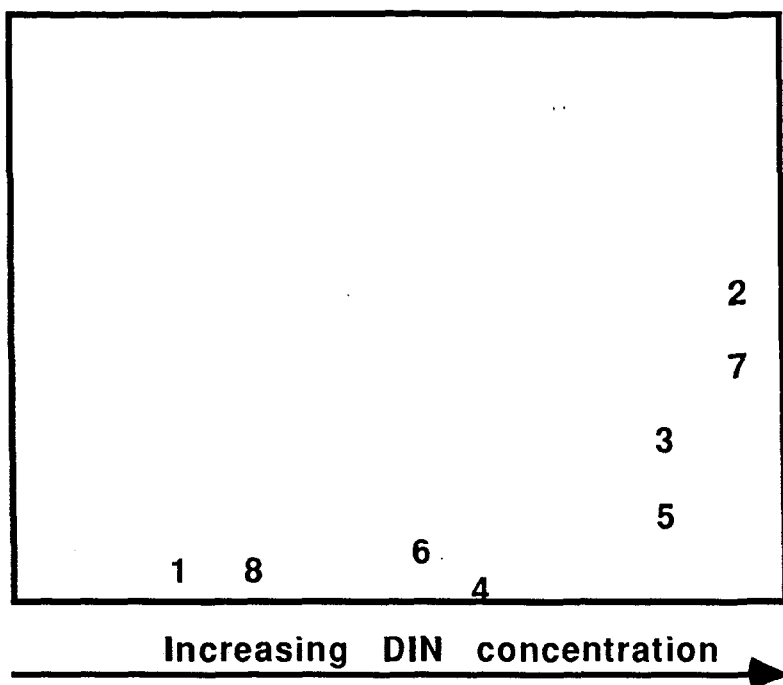
**Table 2.3. Summary Table of Nutrient Water Quality parameters by time period.**

Collection Time Tide	1 710 High Water	2 1105 Low Water	3 1420 Low Water	4 1645 High Water	5 2110 High Water	6 2405 Low Water	7 2700 Low Water	8 3000
<b>Nitrite + Nitrate (<math>\mu\text{M}</math>)</b>								
Mean $\pm$ SE	0.29 $\pm$ 0.03	0.29 $\pm$ 0.03	0.34 $\pm$ 0.04	0.25 $\pm$ 0.03	0.30 $\pm$ 0.02	0.28 $\pm$ 0.02	0.32 $\pm$ 0.03	0.29 $\pm$ 0.01
Range	0.23-0.35	0.20-0.46	0.21-0.32	0.13-0.34	0.23-0.39	0.19-0.34	0.14-0.41	0.24-0.34
N	8	8	8	7	8	8	8	8
<b>Ammonium (<math>\mu\text{M}</math>)</b>								
Mean $\pm$ SE	0.30 $\pm$ 0.11	1.24 $\pm$ 0.52	0.91 $\pm$ 0.41	0.59 $\pm$ 0.15	0.80 $\pm$ 0.80	0.53 $\pm$ 0.11	1.15 $\pm$ 0.30	0.34 $\pm$ 0.17
Range	0.00-0.55	0.40-3.71	0.19-1.60	0.06-1.15	0.00-1.60	0.11-0.75	0.42-1.63	0.11-0.57
N	5	6	3	6	2	5	4	3
<b>DIN (<math>\mu\text{M}</math>)</b>								
Mean $\pm$ SE	0.57 $\pm$ 0.13	1.52 $\pm$ 0.49	1.24 $\pm$ 0.50	0.85 $\pm$ 0.15	1.13 $\pm$ 0.86	0.80 $\pm$ 0.11	1.48 $\pm$ 0.29	0.63 $\pm$ 0.17
Range	0.24-0.91	0.71-3.90	0.41-2.15	0.33-1.36	0.27-1.99	0.39-1.06	0.67-2.04	0.28-0.85
N	5	6	3	6	2	5	4	3
<b>Phosphate (<math>\mu\text{M}</math>)</b>								
Mean $\pm$ SE	0.14 $\pm$ 0.02	0.11 $\pm$ 0.02	0.19 $\pm$ 0.03	0.17 $\pm$ 0.03	0.28 $\pm$ 0.08	0.19 $\pm$ 0.04	0.21 $\pm$ 0.04	0.17 $\pm$ 0.04
Range	0.11-0.22	0.06-0.16	0.14-0.22	0.07-0.81	0.17-0.54	0.11-0.36	0.14-0.30	0.08-0.22
N	5	6	3	6	4	5	4	3
<b>Total Nitrogen (<math>\mu\text{M}</math>)</b>								
Mean $\pm$ SE	5.97 $\pm$ 0.70	7.74 $\pm$ 1.19	2.58 $\pm$ 1.56	5.37 $\pm$ 0.26	6.83 $\pm$ 0.76	6.67 $\pm$ 0.73	6.12 $\pm$ 0.39	9.63 $\pm$ 3.97
Range	4.6-10.6	4.9-15.8	3.9-14.8	4.0-6.3	3.6-10.3	5.3-10.7	5.1-8.3	4.4-37.4
N	8	8	8	7	8	7	7	8
<b>Total Phosphorous (<math>\mu\text{M}</math>)</b>								
Mean $\pm$ SE	0.2 $\pm$ 0.0	0.25 $\pm$ 0.03	0.35 $\pm$ 0.05	0.20 $\pm$ 0.00	0.33 $\pm$ 0.09	-	0.25 $\pm$ 0.05	-
Range	0.2-0.2	0.2-0.3	0.3-0.4	0.2-0.2	0.2-0.5	-	0.2-0.3	0.3-0.6
N	2	4	2	1	3	0	2	0
<b>Dissolved Oxygen (mg/l)</b>								
Mean $\pm$ SE	7.38 $\pm$ 0.20	9.53 $\pm$ 0.99	8.35 $\pm$ 0.75	8.20 $\pm$ 0.30	7.28 $\pm$ 0.22	7.20 $\pm$ 0.40	7.70 $\pm$ 0.15	6.45 $\pm$ 1.84
Range	6.8-7.7	7.6-10.9	7.6-9.1	7.9-8.5	6.8-7.8	6.4-7.7	4.8-7.9	6.1-6.9
N	4	3	2	2	4	3	3	4
<b>Temperature (<math>^{\circ}\text{C}</math>)</b>								
Mean $\pm$ SE	24.7 $\pm$ 0.0	25.2 $\pm$ 0.2	27.2 $\pm$ 0.5	25.6 $\pm$ 0.2	25.1 $\pm$ 0.0	24.9 $\pm$ 0.1	24.4 $\pm$ 0.2	24.7 $\pm$ 0.4
Range	24.6-24.8	24.8-25.4	26.7-27.6	25.4-25.8	25.1-25.2	24.7-25.0	24.0-24.7	24.3-25.1
N	4	3	2	2	4	3	3	2
<b>Suspended solids (mg/l)</b>								
Mean $\pm$ SE	2.1 $\pm$ 0.1	-	2.3 $\pm$ 0.5	2.6 $\pm$ 0.4	1.6 $\pm$ 0.1	1.9 $\pm$ 0.1	1.8 $\pm$ 0.1	1.8 $\pm$ 0.0
Range	2.0-2.2	-	2.3-2.4	2.3-3.4	1.4-1.7	1.7-2.3	1.6-2.0	1.8-1.8
N	2	0	2	4	4	4	4	4
<b>Chlorophyll a (<math>\mu\text{g/l}</math>)</b>								
Mean $\pm$ SE	-	6.41 $\pm$ 2.24	0.68 $\pm$ 0.00	2.35 $\pm$ 1.86	-	3.06 $\pm$ 1.86	-	-
Range	-	4.17-8.66	-	0.49-4.22	-	1.20-4.92	-	-
N	-	3	1	2	1	2	-	-

**Table 2.4.** Summary of **Habitat** differences of water quality parameters in Temporal Study.  
F = Flat; S = Slope.

Parameter	Habitat	24 Hour Study				Diel Study			
		N	Mean	S.E.	Range	N	Mean	S.E.	Range
Nitrite + Nitrate ( $\mu$ M)	F	31	0.31	0.05	0.13-0.55	12	0.35	0.02	0.23-0.49
	S	32	0.28	0.01	0.19-0.39	12	0.31	0.02	0.17-0.51
Ammonium ( $\mu$ M)	F	19	0.61	0.11	0.00-1.63	11	0.67	0.12	0.08-1.35
	S	15	0.89	0.23	0.00-3.71	18	0.72	0.14	0.01-1.25
DIN ( $\mu$ M)	F	19	0.93	0.13	0.27-2.15	10	1.04	0.15	0.31-1.73
	S	15	2.21	0.23	0.24-3.90	8	1.03	0.16	0.24-1.61
Phosphate ( $\mu$ M)	F	20	0.18	0.02	0.06-0.54	10	0.22	0.04	0.01-0.38
	S	16	0.17	0.01	0.08-0.26	9	0.22	0.03	0.12-0.36
Total Nitrogen ( $\mu$ M)	F	31	7.5	1.1	3.4-37.4	12	6.3	0.5	4.1-9.8
	S	30	5.9	0.5	3.6-15.8	12	7.7	0.7	4.6-12.3
Total Phosphorus ( $\mu$ M)	F	11	0.3	0.04	0.2-0.6	9	0.3	0.01	0.2-0.3
	S	5	0.2	0.02	0.2-0.3	8	0.3	0.03	0.2-0.4
Particulate N ( $\mu$ M)	F	-	-	-	-	6	1.45	0.12	1.2-1.8
	S	-	-	-	-	6	1.62	0.06	1.4-1.8
Dissolved Oxygen (mg/l)	F	9	7.01	0.56	4.8-10.9	3	7.67	0.52	6.8-8.6
	S	16	7.79	0.26	6.6-10.1	3	7.60	0.10	7.4-7.7
Temperature (°C)	F	8	24.7	0.2	24.0-25.4	5	25.1	0.4	24.5-26.8
	S	15	25.3	0.2	24.6-27.6	6	25.1	0.3	24.3-26.2
Chlorophyll <i>a</i> ( $\mu$ g/l)	F	8	3.94	1.44	0.68-8.66	2	0.43	0.04	0.40-0.53
	S	6	2.33	1.84	0.49-4.17	4	1.66	1.14	0.40-5.10
BOD <sub>5</sub> (mg/l)	F	-	-	-	-	2	0.8	0.4	0.4-1.2
	S	-	-	-	-	4	0.3	0.1	0.1-0.5
Suspended solids (mg/l)	F	10	1.9	0.2	1.6-3.4	-	-	-	-
	S	14	2.0	0.1	1.4-2.4	-	-	-	-

**Figure 2.2.a. Non-metric Multidimensional scaling (MDS) plot in 2 dimensions of pooled mean nutrient concentrations at 8 sampling times (1-8) from the temporal pilot study. Between sample similarities were calculated using the Bray-Curtis coefficient. Stress for the MDS is low at 0.03.**



**Figure 2.2.b. Dendrogram of classification of time periods in the 24 hour study by mean concentration of inorganic nutrients. Between sample similarities were calculated using the Bray-curtis coefficient, and an unweighted group mean sorting strategy was applied.**

