Special Publication SJ2002-SP5

Quantification of Ground Water Discharge And Nutrient Loading to the Indian River Lagoon

Final Report

February 15, 2002

Submitted to: St. Johns River Water Management District P. O. Box 1429 Palatka, Florida 32178

As part of Contract #99G245

Submitted by:

Jonathan B. Martin Department of Geological Sciences University of Florida

Jaye E. Cable Department of Oceanography and Coastal Sciences Louisiana State University

> Peter W. Swarzenski U.S. Geological Survey

TABLE OF CONTENTS

TABLE OF CONTENTS	1
TABLE OF FIGURES	4
TABLE OF TABLES	9
EXECUTIVE SUMMARY	11
CHAPTER 1 – INTRODUCTION	15
1.1 Statement of Problem	15
1.2 Tasks and Motivation for Contract #99G245	17
1.3 Geology and Hydrogeology of Indian River Lagoon	19
1.4 Regional Climate	
1.5 Sampling Locations	25
1.5.1 Northern area	25
1.5.2 Central area	
1.6 Field Stations and General Description of Field Sampling	29
1.6.1 Timing and Establishing Stations	
1.6.2 Pore water samples	32
1.6.2.1 Design and Construction	
1.6.2.2 Installation and Sampling	34
CHAPTER 2 – DIRECT SEEPAGE MEASUREMENTS	39
1 1 Introduction	39
2 2 Methods	39
2.2.1 Description of Seep Meters and Deployment	
2.2.2 Control Experiments: Duplicates, Blanks, and Equilibration Time	
2.3 Results	
2.4. Discussion	54
2.4.1 Origin of variation of seepage rates	54
2.4.2 Comparison with earlier seepage measurements	57
2.4.3 Flushing rates in the northern lagoon	60
2.4.4 Comparison of Seep Rates in the Northern and Central Study Areas	61
2.5. Summary and Recommendations	62
CULARTER 2 DADIUM ISOTORS AS TRACERS ACROSS THE SEDIMENT	Г
WATED INTEDEACE	65
2 1 Introduction	03
2.2 Sampling and Analytical Methods	03 67
2.2 Sampling and Analytical Methods	
2.2.1 Hydrography	
3.3.1 Hydrography 3.3.2 Ground Water	
2.2.2 Dodium Isotonos	
3.3.3 Kadium Isotopes	/0

3.3.4 Flux measurements	83
3.3.5 Benthic Flux Chambers	85
3.3.6 Pore Water Profiles	87
3.3.7 Comparison of the Three Flux Measurements	97
3.4 Summary and Recommendations	98
CHAPTER 4 –ASSESSMENT OF GROUND WATER DISCHARGE USING ²²² Rn	
AND ²²⁶ Ra	. 100
4.1 Introduction	. 100
4.2 Sampling and Analytical Techniques	. 101
4.3 Results	. 103
4.3.1 Spatial and Temporal Distributions	. 103
4.3.1.1 Lagoon Waters.	. 103
4.3.1.2 River waters	. 105
4.3.1.3 Ground Water	. 105
4.3.2 Pore Water Distributions of Ra and Rn	. 108
4.4 Discussion	. 112
4.4.1 Linking Radon-222 and Radium-226 to Seepage	. 112
4.4.2 Sources and Sinks	. 115
4.4.2.1 Sources	. 115
4.4.2.2 Sinks	. 116
4.4.2.1 Benthic Fluxes	. 117
4.5 Summary	. 118
CHAPTER 5 – SOURCES OF GROUND WATER DISCHARGE	. 120
5.1 Introduction	. 120
5.1.1 Chemical and Isotopic Tracers of Aquifer Water	. 121
5.2 Methods	. 122
5.2.1 Field Sampling and Storage of Samples	. 122
5.2.2 Analytical Methods	. 124
5.3 Results	. 125
5.3.1 Lagoon and Seep Water	. 126
5.3.2 Pore water	. 135
5.4 Discussion	. 142
5.4.1 Origin of Seep Water	. 142
5.4.1.1 Lagoon water compositions	. 142
5.4.1.2 Sources and quantities of ground water discharge	. 144
5.4.2 Pore water profiles	. 147
5.4.2.1 Conservative solutes	. 147
5.4.2.2 Constraints on flow rates	. 149
5.5 Summary and Recommendations	. 150
CHAPTER 6 – POTENTIAL NUTRIENT FLUXES ASSOCIATED WITH GROUN	D
WATER DISCHARGE	. 154
6.1 Introduction.	. 154
6.2 Analytical Methods	. 155

6.3 Results	. 156
6.3.1 Lagoon and Seep Water	. 156
6.3.2 Pore waters	. 158
6.4 Discussion	. 167
6.4.1 Pore Water Profiles	. 167
6.4.2 Nutrient Fluxes	. 169
6.4.2.1 N Flux Calculations	. 171
6.4.2.2 Comparison with other N flux calculations	. 172
6.4.2.3 P flux calculations and comparisons with other calculations	. 174
6.4.3 Comparison with nitrogen loading from other nutrient sources	. 177
6.4.4 Comparison of P loading from diffusive and advective fluxes	. 179
6.5 Summary and Recommendations	. 180
CHAPTER 7 SUMMARY AND RECOMMENDATIONS	. 182
7.1 Summary	. 182
7.2 Additional Questions	. 184
7.3 Recommendations for Future Work	. 186
REFERENCES CITED	. 189
Appendix A. Seep meter measurements of seep rates.	. 197
Appendix B. ²²³ Ra and ²²⁴ Ra activities	. 200
Appendix C. ²²² Rn and ²²⁶ Ra activities	. 211
Appendix D. Concentrations and isotope ratios of conservative solutes and nutrients.	. 228

TABLE OF FIGURES

Figure 1-1. Location map of the northern Indian River Lagoon study area. The cross section A-A' is shown in Figure 1-2. Contour lines show the potentiometric surface of upper Floridan Aquifer for September 1998. Elevation in feet above mean sealevel. Contour interval 5 ft. The boxes	
represent the outlines of areas shown in Figures 1-5 and 1-6 Figure 1-2. Stratigraphy of Indian River Lagoon. The Miocene Hawthorn Group, the confining unit for the Floridan Aquifer system is missing in the northern study area. Modified from Scott (1988).	16
Figure 1-3: Monthly total precipitation (cm) is shown versus time for (A) 1999Titusville (dk. gray bars) and 30-yr normal Daytona Beach (lt. gray bars); and (B) 2000 Melbourne (dk. gray bars) and 30-yr normal Vero Beach (lt. gray bars).	22
 Figure 1-4: Daily precipitation (cm) for Melbourne, Florida, shows the distribution of rainfall during our 2000 sampling season. Individual sampling trips in May, August, and December are highlighted in gray Figure 1-5. Location map of northern Indian River Lagoon. Position of seep stations are shown as black points and indicated by numbers. The location of ground water samples are designated by open circles labled "GW". Location of surface water sampling stations are given as HOC for Haulover Canal and TBC for Turnbull Creek. Five transects are named around the edge of the lagoon. 	24
Figure 1-6. Location map showing the approximate locations of stations sampled during the second year of project. IRL represents Indian River Lagoon and BRL represents Banana River Lagoon.	30
Figure 1-7. Design of multisampler. The length shown is the maximum length of the multisamplers. Several multisamplers were shortened for specific stations.	35
Figure 1-8. Modification to the screened interval of the multi-samplers. The original opening was the size of the end of the flexible PVC tubing. The modified opening was a grid of channels that were routed into the PVC pipe of the multisamplers.	36
 Figure 2-1. Diagram of construction and deployment of seepage meter. Seepage rate is volume of water entering bag over time. Samples of seep water are collected in clean, dry bags. Blanks are measured by deploying meters in sediment filled plastic pools. Figure 2-2. Seepage rates for Big Flounder Transect. The round symbols connected by a solid line represent the dry season and the square symbols connected by a dashed line represent the rainy season seepage rates. The lower portion of the figure represents the water depth at each station. The symbols represent average values and the error bars represent 2 σ of the 	41
replicate measurements from each station	45

Figure 2-3. Seepage rates for the deep sites that extent east-west across the	
central portion of the field area. The round symbols connected by a solid line	
represent the dry season and the square symbols connected by a dashed line	
represent the rainy season seepage rates. The lower portion of the figure	
represents the water depth at each station. The symbols represent average	
represents the water depth at each station. The symbols represent average values and the error here represent 2π of the replicate measurements from	
values and the error bars represent 2 6 of the representements from	10
each station	40
Figure 2-4. Seepage rates for the deep sites that extent north-south through the	
central portion of the field area. The round symbols connected by a solid line	
represent the dry season and the square symbols connected by a dashed line	
represent the rainy season seepage rates. The lower portion of the figure	
represents the water depth at each station. The symbols represent average	
values and the error bars represent 2 σ of the replicate measurements from	
each station	47
Figure 2-5. Seepage rates for A. transect 1, and B. transect 2. The round symbol	
connected by the solid lines represent the seepage rates for May, the square	
symbols connected by the dashed line represent the seenage rates for August	
and the triangular symbol connected by the dotted line represent the seenage	
rates for December. The symbols represent average values and the error hars	
range and the realizate measurements from each station	10
Eisen 2 (History of compare notes Marcan I Associate 1000	48
Figure 2-6. Histogram of seepage rates May and August 1999	50
Figure 2-7. Histogram of the seepage rates for A. May, B. August, and C.	
December 2000.	52
Figure 3-1. Decay chains of the U and Th series isotopes and the half life of each $(1 + 1)^{-1}$	
isotope. The vertical arrows represent alpha decay and the diagonal arrows	
represent beta decay	66
Figure 3-2. Potentiometric surface map of the Upper Floridan Aquifer in the	
Indian River Lagoon region, May 1998. (After Bradner, 1998.)	71
Figure 3-3. Potentiometric surface map of the upper Floridan Aquifer in the	
Indian River Lagoon region, May 1999. (After Knowles and Bradner, 1999.)	72
Figure 3-4. Salinity versus ^{223,224} Ra activity plots for Indian River Lagoon and	
Banana River Lagoon during May 2000.	76
Figure 3-5 Salinity versus ^{223,224} Ra activity plots for Indian River Lagoon and	
Banana River Lagoon during August 2000	77
Figure 3-6 Salinity versus ^{223,224} Ra activity plots for Indian River Lagoon and	/ /
Panana Pivar Lagoon during December 2000	79
Eigure 2.7. Salinity versus ²²³ Pa/ ²²⁴ Pa activity ratio plats for Indian Diver Lagoon	/0
Figure 5-7. Saminy versus Ra/ Ra activity fatto piots for mutal River Lagoon	70
and Banana River Lagoon surface water samples during May 2000.	/9
Figure 3-8. Salinity versus ²²³ Ra/ ²² Ra activity ratio plots for Indian River Lagoon	
and Banana River Lagoon surface water samples during August 2000	80
Figure 3-9. Salinity versus ²²³ Ra/ ²²⁴ Ra activity ratio plots for Indian River Lagoon	
and Banana River Lagoon surface water samples during December 2000	81
Figure 3-10. Water column ($z < 1.5$ m) profile of ²²³ Ra activities (dpm/L) and	
²²³ Ra/ ²²⁰ Ra activity ratios (August, 1999). The deep-water stations have been	
excluded here to look only at sediment effects and dilution.	83

Figure 3-11. Idealized placement of a benthic flux chamber into bottom	
sediments.	85
Figure 3-12. Pore water profiles for ²²⁴ Ra, ²²³ Ra and ²²⁶ Ra at IRL4. These	
interstitial waters were collected <i>in situ</i> by mini-piezometer (multi-sampler)	91
Figure 3-13. Pore water profiles for salinity, ²²³ Ra and ²²⁴ Ra at BRL2 during	
May 2000. These interstitial waters were collected <i>in situ</i> by mini-	
piezometer (multi-sampler).	94
Figure 3-14. Pore water profiles for salinity, ²²³ Ra and ²²⁴ Ra at BRL2 during	
August 2000. These interstitial waters were collected <i>in situ</i> by mini-	
piezometer (multi-sampler).	95
Figure 3-15. Pore water profiles for salinity, ²²³ Ra and ²²⁴ Ra at BRL2 during	
December 2000. These interstitial waters were collected in situ by mini-	
piezometer (multi-sampler).	96
Figure 4-1: Seasonal 1999 activity histograms of lagoon water ²²⁶ Ra and ²²² Rn in	
the northern IRL.	. 104
Figure 4-2: Seasonal 2000 activity histograms of lagoon water ²²⁶ Ra and ²²² Rn in	
the central IRL/BRL system.	. 104
Figure 4-3: Activity histograms of all lagoon waters from the northern and	
central study sites	. 106
Figure 4-4: River water activities near the northern and central sites are shown	
for 1999 (A) ²²⁶ Ra; (B) ²²² Rn; and 2000 (C) ²²⁶ Ra; (D) ²²² Rn during May	
(black), Aug. (gray), and Dec. (white). Central site riverine inputs are shown	
north to south, with the northernmost creek being closest to the study site	. 106
Figure 4-5. Seasonal distribution of ground water 222Rn activities in the northern	
IRL in 1999 for May (black bars) and August (gray bars).	. 107
Figure 4-6: Seasonal distributions of groundwater ²²⁶ Ra (left side) and ²²² Rn	
(right side) activities are given for the central IRL/BRL system in 2000 for	
May (black bars), August (gray bars), and December (white bars)	. 108
Figure 4-7: Activity histograms of groundwater ²²² Rn (black bars) and ²²⁶ Ra	
(gray bars) for the northern and central IRL system: (A) 1999 ²²² Rn; (B)	
2000 ²²² Rn; (C) 1999 ²²⁶ Ra; and (D) 2000 ²²⁶ Ra	. 109
Figure 4-8: Pore water activity depth profiles of ²²⁶ Ra (top row) and ²²² Rn	
(bottom row) in Dec-99 (solid line) in the northern IRL for IRL-4, IRL-5, and	
IRL-22, respectively. IRL-4 and IRL-22 were sampled for ²²⁶ Ra in Dec-00	
also (dashed line)	. 110
Figure 4-9: Pore water activity depth profiles of ²²⁶ Ra (top row) and ²²² Rn	
(bottom row) in May-00 (dashed line), Aug-00 (dotted line), and Dec-00	
(solid line) in the central IRL for BRL-1 and BRL-2, respectively	. 111
Figure 4-10: Water column inventories of (A) excess ²²² Rn and (B) ²²⁶ Ra at each	
station versus the mean seepage rate at individual stations for both rainy	
(solid diamonds) and dry (open diamonds) seasons	. 113
Figure 4-11: Whole transect tracer inventories versus integrated seepage during	
the rainy (solid diamonds) and dry (open diamonds) seasons for (A) ex ²²² Rn	
and (B) ²²⁶ Ra	. 114

Figure 4-12: Mean tracer inventories and mean integrated seepage for all	
transects are plotted versus monthly cumulative precipitation to demonstrate	
the difference between rainy and dry season inputs to the lagoon.	116
Figure 4-13: General box model demonstrating the sources and sinks of	
radionuclides to the water column in the Indian River Lagoon	117
Figure 5-1. Chloride concentrations of seep water at the three transects that are	
shown in Figures 2-3, 2-4, and 2-5. The solid horizontal line and the dashed	
horizontal line represent the average value for lagoon water during the dry	
season and rainy season, respectively.	129
Figure 5-2. Average Cl concentrations at each transect versus distance from the	
northernmost transect for A. May, B. August, and C. December	130
Figure 5-3. Cl concentrations versus distance from the western shore of the Indian	
River Lagoon during A. May, B. August, and C. December for transect	
number 1. The filled circles represent seep water and the filled squares	
represent lagoon water	131
Figure 5-4. Cl concentrations versus distance from the western shore of the Indian	
River Lagoon during A. May, B. August, and C. December for transect	
number 2. The filled circles represent seep water and the filled squares	
represent lagoon water	132
Figure 5-5. Cl concentrations versus distance from the western shore of the Indian	
River Lagoon during A. May, B. August, and C. December for transect	
number 3. The filled circles represent seep water and the filled squares	
represent lagoon water	133
Figure 5-6. Cl concentrations versus distance from the western shore of the Indian	
River Lagoon during A. May, B. August, and C. December for transect	
number 4. The filled circles represent seep water and the filled squares	
represent lagoon water	134
Figure 5-7. Depth profiles of Cl and SO ₄ concentrations and of Cl/SO ₄ molar	
ratios in pore water collected from multisamplers at IRL 4. IRL 5. and IRL	
22. The heavy dark line represents the sediment water interface. The water	
column samples were collected from the shallowest port of the multisampler	137
Figure 5-8 Cl concentrations 87 Sr/ 86 Sr isotope ratios and δ^{18} O values versus	
depth for pore waters at station BRL2. The circles represent samples	
collected in May 2000, the squares represent samples collected in August	
2000, and the triangles represent samples collected in December 2000. The	
arrows represent the values in the water column for each component	138
Figure 5-9 Cl concentrations 87 Sr/ 86 Sr isotope ratios and δ^{18} O values versus	
denth for pore waters at station BRL6. The circles represent samples	
collected in May 2000 the squares represent samples collected in August	
2000 and the triangles represent samples collected in December 2000. The	
arrows represent the values in the water column for each component	139
Figure 5-10 SO ₄ and SO ₄ /Cl ratios versus denth for nore waters at station RRI 2	157
The circles represent samples collected in May 2000 the squares represent	
samples collected in August 2000, and the triangles represent samples	
collected in December 2000. The arrows represent the values in the water	
concelled in December 2000. The arrows represent the values in the water	

column for each component. The line in the SO_4/Cl versus depth plot	
represent the seawater ratio.	140
Figure 5-11. SO_4 and SO_4/Cl ratios versus depth for pore waters at station BRL6.	
The circles represent samples collected in May 2000, the squares represent	
samples collected in August 2000, and the triangles represent samples	
collected in December 2000. The line in the SO ₄ /Cl versus depth plot	
represent the seawater ratio.	141
Figure 5-12. Measured and calculated Cl concentrations for BRL2. The heavy	
dashed line represents concentrations that were calculated using assumptions	
discussed in text and equation 5-4.	151
Figure 6-1. Average TN concentrations at each transect versus distance from the	
northernmost transect for A. May, B. August, and C. December	159
Figure 6-2. Average TP concentrations at each transect versus distance from the	
northernmost transect for A. May, B. August, and C. December	160
Figure 6-3. TSP, TSN, and DO versus depth in pore water collected from	
multisamplers at IRL 4, IRL 5, and IRL 22. The heavy dark line represents	
the sediment water interface, and the water column samples were collected	
from the shallowest port of the multisampler.	163
Figure 6-4. Total nitrogen and total soluble nitrogen versus depth for pore waters	
at station BRL2. The circles represent samples collected in May 2000, the	
squares represent samples collected in August 2000, and the triangles	
represent samples collected in December 2000.	164
Figure 6-5. Total phosphorous and total soluble phosphorous versus depth for	
pore waters at station BRL2. The circles represent samples collected in May	
2000, the squares represent samples collected in August 2000, and the	
triangles represent samples collected in December 2000.	165
Figure 6-6. Total soluble nitrogen and total soluble phosphorous normalized to Cl	
versus depth at station BRL2. The circles represent samples collected in	
May 2000, the squares represent samples collected in August 2000, and the	
triangles represent samples collected in December 2000.	166
$\mathbf{U} = \mathbf{U}$	

TABLE OF TABLES

sampling sites. 21 Table 1-2: Summary of 1999 field season wind speeds at Titusville, Florida, 21 compared to 30-year monthly means and maximums at Daytona Beach, 22 Table 1-3: Description and location of sampling stations. 26 Table 1-4. Locations and depths of wells and surface waters, northern area. 28 Table 1-5. Locations and depths of wells and surface waters, central area. 31 Table 1-6. Penetration depth of multisamplers, May 2000. 37 Table 1-7. Penetration of multisamplers, August 2000. 37 Table 2-1. Seepage rate duplicates and blanks 42 Table 2-2. Summary of mean, median and ranges of seepage rates. 52 Table 2-3. Seepage rates to various estuaries and coastal zones determined by 58 Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and 74 creek/inlet water (May, August 1999). 73 Table 3-2. Year 2000 average radium activities and water column parameters. 74 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 85 Table 3-4. Pore water radium isotope activities at Station IRL4. 85 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91	Table 1-1: Summary of measured and 30-year normal rainfall for the IRL	
Table 1-2: Summary of 1999 field season wind speeds at Titusville, Florida, 24 compared to 30-year monthly means and maximums at Daytona Beach, 24 Table 1-3. Description and location of sampling stations. 26 Table 1-4. Locations and depths of wells and surface waters, northern area. 28 Table 1-5. Locations and depths of wells and surface waters, central area. 31 Table 1-6. Penetration depth of multisamplers, May 2000. 37 Table 1-7. Penetration of multisamplers, August 2000. 37 Table 1-8. Penetration of multisamplers, December 2000. 36 Table 2-1. Seepage rate duplicates and blanks 42 Table 2-2. Summary of mean, median and ranges of seepage rates. 53 Table 2-3. Seepage rates to various estuaries and coastal zones determined by 58 direct measurements, tracers, and modeling. 72 Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and 74 creek/inlet water (May, August 1999). 72 Table 3-2. Year 2000 average radium activities in two benthic flux chambers (upper 74 Indian River Lagoon). 82 Table 3-4. Pore water radium isotope activities at Station IRL4. 85 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91	sampling sites.	21
compared to 30-year monthly means and maximums at Daytona Beach, 24 Florida. 24 Table 1-3. Description and location of sampling stations. 26 Table 1-4. Locations and depths of wells and surface waters, northern area. 28 Table 1-5. Locations and depths of wells and surface waters, central area. 31 Table 1-5. Locations and depths of wells and surface waters, central area. 31 Table 1-6. Penetration depth of multisamplers, May 2000. 37 Table 1-7. Penetration of multisamplers, August 2000. 37 Table 1-8. Penetration of multisamplers, December 2000. 36 Table 2-1. Seepage rate duplicates and blanks 43 Table 2-2. Summary of mean, median and ranges of seepage rates. 53 Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling. 58 Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and creek/inlet water (May, August 1999). 73 Table 3-2. Year 2000 average radium activities and water column parameters. 74 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 82 Table 3-4. Pore water radium isotope activities at Station IRL4. 88 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 </td <td>Table 1-2: Summary of 1999 field season wind speeds at Titusville, Florida,</td> <td></td>	Table 1-2: Summary of 1999 field season wind speeds at Titusville, Florida,	
Florida 24 Table 1-3. Description and location of sampling stations. 26 Table 1-4. Locations and depths of wells and surface waters, northern area. 26 Table 1-5. Locations and depths of wells and surface waters, central area. 31 Table 1-6. Penetration depth of multisamplers, May 2000. 37 Table 1-7. Penetration of multisamplers, August 2000. 37 Table 1-8. Penetration of multisamplers, December 2000. 36 Table 2-1. Seepage rate duplicates and blanks 42 Table 2-2. Summary of mean, median and ranges of seepage rates. 52 Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling. 58 Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and creek/inlet water (May, August 1999). 72 Table 3-2. Year 2000 average radium activities and water column parameters. 74 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 85 Table 3-4. Pore water radium isotope activities at Station IRL4. 85 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91	compared to 30-year monthly means and maximums at Daytona Beach,	
Table 1-3. Description and location of sampling stations. 26 Table 1-4. Locations and depths of wells and surface waters, northern area. 28 Table 1-5. Locations and depths of wells and surface waters, central area. 31 Table 1-6. Penetration depth of multisamplers, May 2000. 37 Table 1-7. Penetration of multisamplers, August 2000. 37 Table 1-8. Penetration of multisamplers, December 2000. 36 Table 2-1. Seepage rate duplicates and blanks 42 Table 2-2. Summary of mean, median and ranges of seepage rates. 52 Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling. 58 Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and creek/inlet water (May, August 1999). 72 Table 3-2. Year 2000 average radium activities and water column parameters. 74 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 85 Table 3-4. Pore water radium isotope activities at Station IRL4. 86 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91	Florida	24
Table 1-4. Locations and depths of wells and surface waters, northern area. 28 Table 1-5. Locations and depths of wells and surface waters, central area. 31 Table 1-5. Locations and depths of wells and surface waters, central area. 31 Table 1-5. Locations and depth of multisamplers, May 2000. 37 Table 1-6. Penetration of multisamplers, August 2000. 37 Table 1-7. Penetration of multisamplers, December 2000. 36 Table 2-1. Seepage rate duplicates and blanks 42 Table 2-2. Summary of mean, median and ranges of seepage rates. 52 Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling. 58 Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and creek/inlet water (May, August 1999). 72 Table 3-2. Year 2000 average radium activities and water column parameters. 74 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 85 Table 3-4. Pore water radium isotope activities at Station IRL4. 85 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3-5. Flux measurements using various direct (lagoon budget benthic) 91	Table 1-3. Description and location of sampling stations	26
Table 1-5. Locations and depths of wells and surface waters, central area. 31 Table 1-6. Penetration depth of multisamplers, May 2000. 37 Table 1-7. Penetration of multisamplers, August 2000. 37 Table 1-8. Penetration of multisamplers, December 2000. 37 Table 2-1. Seepage rate duplicates and blanks 42 Table 2-2. Summary of mean, median and ranges of seepage rates. 53 Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling. 58 Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and creek/inlet water (May, August 1999). 73 Table 3-2. Year 2000 average radium activities and water column parameters. 74 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 85 Table 3-4. Pore water radium isotope activities at Station IRL4. 86 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3-5. Flux measurements using various direct (lagoon budget benthic) 91	Table 1-4. Locations and depths of wells and surface waters, northern area.	28
Table 1-6. Penetration depth of multisamplers, May 2000. 37 Table 1-7. Penetration of multisamplers, August 2000. 37 Table 1-8. Penetration of multisamplers, December 2000. 38 Table 2-1. Seepage rate duplicates and blanks 42 Table 2-2. Summary of mean, median and ranges of seepage rates. 52 Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling. 58 Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and creek/inlet water (May, August 1999). 73 Table 3-2. Year 2000 average radium activities and water column parameters. 74 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 85 Table 3-4. Pore water radium isotope activities at Station IRL4. 85 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3-5. Flux measurements using various direct (lagoon budget benthic) 91	Table 1-5. Locations and depths of wells and surface waters, central area	31
Table 1-7. Penetration of multisamplers, August 2000. 37 Table 1-8. Penetration of multisamplers, December 2000. 38 Table 2-1. Seepage rate duplicates and blanks 42 Table 2-2. Summary of mean, median and ranges of seepage rates. 53 Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling. 58 Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and creek/inlet water (May, August 1999). 72 Table 3-2. Year 2000 average radium activities and water column parameters. 74 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 85 Table 3-4. Pore water radium isotope activities at Station IRL4. 85 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3-5. Flux measurements using various direct (lagoon budget, benthic) 91	Table 1-6. Penetration depth of multisamplers, May 2000.	37
Table 1-8. Penetration of multisamplers, December 2000. 38 Table 2-1. Seepage rate duplicates and blanks 43 Table 2-2. Summary of mean, median and ranges of seepage rates. 53 Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling. 58 Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and creek/inlet water (May, August 1999). 73 Table 3-2. Year 2000 average radium activities and water column parameters. 74 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 85 Table 3-4. Pore water radium isotope activities at Station IRL4. 88 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3-5. Flux measurements using various direct (lagoon budget benthic) 91	Table 1-7. Penetration of multisamplers, August 2000.	37
Table 2-1. Seepage rate duplicates and blanks 42 Table 2-2. Summary of mean, median and ranges of seepage rates. 53 Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling. 58 Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and creek/inlet water (May, August 1999). 73 Table 3-2. Year 2000 average radium activities and water column parameters. 74 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 85 Table 3-4. Pore water radium isotope activities at Station IRL4. 88 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3-5. Flux measurements using various direct (lagoon budget benthic) 91	Table 1-8. Penetration of multisamplers, December 2000.	38
 Table 2-2. Summary of mean, median and ranges of seepage rates. Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling. Table 3-1. Mean radium and ²²⁸Th activities for lagoon, ground water and creek/inlet water (May, August 1999). Table 3-2. Year 2000 average radium activities and water column parameters. Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). Table 3-4. Pore water radium isotope activities at Station IRL4. Table 3-5. Calculating diffusive fluxes with ²²³Ra. Table 3-5. Flux measurements using various direct (lagoon budget, benthic). 	Table 2-1. Seepage rate duplicates and blanks	43
 Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling. Table 3-1. Mean radium and ²²⁸Th activities for lagoon, ground water and creek/inlet water (May, August 1999). Table 3-2. Year 2000 average radium activities and water column parameters. Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). Table 3-4. Pore water radium isotope activities at Station IRL4. Table 3-5. Calculating diffusive fluxes with ²²³Ra. Table 3-5. Flux measurements using various direct (lagoon budget, benthic) 	Table 2-2. Summary of mean, median and ranges of seepage rates.	53
direct measurements, tracers, and modeling	Table 2-3. Seepage rates to various estuaries and coastal zones determined by	
Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and creek/inlet water (May, August 1999). 73 Table 3-2. Year 2000 average radium activities and water column parameters. 74 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 84 Table 3-4. Pore water radium isotope activities at Station IRL4. 88 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3-5. Flux measurements using various direct (lagoon budget, benthic 91	direct measurements, tracers, and modeling	58
 Table 3-1. Mean radium and ²²⁸Th activities for lagoon, ground water and creek/inlet water (May, August 1999)		
creek/inlet water (May, August 1999)	Table 3-1. Mean radium and ²²⁸ Th activities for lagoon, ground water and	
 Table 3-2. Year 2000 average radium activities and water column parameters	creek/inlet water (May, August 1999).	73
Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon). 85 Table 3-4. Pore water radium isotope activities at Station IRL4. 88 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3 5. Flux measurements using various direct (lagoon budget, benthic). 91	Table 3-2. Year 2000 average radium activities and water column parameters	74
Indian River Lagoon). 85 Table 3-4. Pore water radium isotope activities at Station IRL4. 88 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3 5. Flux measurements using various direct (lagoon budget, benthic). 91	Table 3-3. Time series radium activities in two benthic flux chambers (upper	
Table 3-4. Pore water radium isotope activities at Station IRL4. 88 Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3-5. Flux measurements using various direct (lagoon budget, benthic) 91	Indian River Lagoon)	85
Table 3-5. Calculating diffusive fluxes with ²²³ Ra. 91 Table 3-5. Flux measurements using various direct (lagoon budget, benthic)	Table 3-4. Pore water radium isotope activities at Station IRL4.	88
Table 3.5 Flux measurements using various direct (lagoon budget benthic	Table 3-5. Calculating diffusive fluxes with ²²³ Ra.	91
rable 3-3. This measurements using various uncet (lagoon budget, benune	Table 3-5. Flux measurements using various direct (lagoon budget, benthic	
chamber) and indirect (modeled) methods. Minimum uncertainties based on	chamber) and indirect (modeled) methods. Minimum uncertainties based on	
+/- 1σ	+/- 1σ	98
Table 4-1: Rn-222 flux compilation for diffusive and total benthic fluxes in	Table 4-1: Rn-222 flux compilation for diffusive and total benthic fluxes in	
northern IRL 1999 118	northern IRL 1999.	118
Table 5-1. Definition of various water sources 121	Table 5-1. Definition of various water sources	121
Table 5-2. Estimated precision of various solutes 125	Table 5-2. Estimated precision of various solutes	125
Table 5-3. Average, median, and standard deviation of conservative tracers for	Table 5-3. Average, median, and standard deviation of conservative tracers for	
seep water and water column water in the northern study area	seep water and water column water in the northern study area.	126
1	1	
Table 6-1. Estimated precision of various solutes 156	Table 6-1. Estimated precision of various solutes	156
Table 6-2. Average, median, and standard deviation of conservative tracers for	Table 6-2. Average, median, and standard deviation of conservative tracers for	
seep water and lagoon water	seep water and lagoon water	157
Table 6-3. Average, median and standard deviation of nutrients for seep and	Table 6-3. Average, median and standard deviation of nutrients for seep and	
lagoon water, central area	lagoon water, central area.	161
Table 6-4. Estimates of nitrogen fluxes and loading	Table 6-4. Estimates of nitrogen fluxes and loading.	173
Table 6-5. Estimates of phosphorous fluxes and loading	Table 6-5. Estimates of phosphorous fluxes and loading.	176

Table 6-6. Annual Nitrogen Loading to the Indian River and Banana River	
lagoons	178
Table 6-7. Annual Phosphorous Loading to the Indian River and Banana River	
lagoons	180

EXECUTIVE SUMMARY

The discharge of ground water may provide a significant source of nutrients to estuarine environments. In order to determine the potential magnitude of this nutrient source, the St. Johns River Water Management District contracted the University of Florida to undertake a 30-month long study of ground water discharge and associated nutrient loading to the Indian River Lagoon System along the east coast of central Florida. The study was designed to answer several questions including:

- What is the rate of ground water discharge to the lagoon? How do these rates vary seasonally, specifically between typical wet and dry seasons?
- What are the sources of ground water discharge? Can proportions that originate in the Floridan, Intermediate, and Surficial aquifers be identified, and if so, what are the proportions?
- What are the fluxes of N and P to the Indian River Lagoon, and do the fluxes vary spatially and seasonally across the lagoon?
- What are the total annual loads of N and P to the Indian River Lagoon caused by ground water discharge and how do these loads compare with other sources of nutrients such as surface water runoff and atmospheric deposition?
- What additional work needs to be accomplished in order to quantify the flux of nutrients from sediment associated with ground water discharge?

These questions were addressed through an extensive field sampling program including six trips to the field areas totaling ~40 days over a period two years, measuring seep rates *in situ*, sampling lagoon water, pore water, ground water and surface water, and measuring in the laboratory a suite of chemical components that provide tracers for ground water discharge and constraints for calculations of nutrient fluxes. The chemical and isotopic measurements include concentrations of conservative solutes, concentrations of nutrients, stable isotopes ratios, and radioisotope activities.

The project focused on two areas within the Indian River Lagoon system. The northern area was sampled in May, August, and December 1999 and covers $\sim 48 \text{ km}^2$ of the northernmost end of the Indian River Lagoon, north of Titusville, FL. The central area was sampled in May, August, and December 2000 and covers $\sim 29 \text{ km}^2$ of the middle reaches of the Indian River Lagoon and $\sim 28 \text{ km}^2$ of the southern end of the Banana River Lagoon between the towns of Cocoa and Melbourne, Florida. The northern end is underlain by the Floridan and Surficial aquifers, and in this area, the Hawthorn Group,

which acts as a confining unit for the Floridan aquifer, is thin or missing. In the central field area, the Floridan aquifer is separated from the Surficial aquifer by ~ 60 m of Hawthorn Group rocks, and is thus confined.

What is the rate of ground water discharge (p. 44)?

In both areas, the rate of ground water discharge was measured using seep meters. Average rates for the study areas were found to range from 25.6 ml/m²/min to 63.1 ml/m²/min, although individual sampling stations varied between \sim 3 and \sim 140 ml/m²/min. Average rates of discharge increased by \sim 30% from May to August for both study areas, which corresponds to the change from the end of the typical dry season to the middle to end of the typical rainy season. In the central Indian River Lagoon, there is a slight increase in average seep rate from August to December 2000. (Seep measurements were not made in the northern area for the month of December 1999). In contrast, the average seep rate decreases slightly in the Banana River Lagoon over this time interval. For all seasons, the average rate of ground water discharge is \sim 40% lower in the central area than in the northern area regardless of the season.

What are sources of ground water discharge (p. 141)?

The observed temporal and spatial differences in the rate of ground water discharge could be interpreted to reflect an increased discharge rate in August and December because of elevated hydrostatic head following the rainy season. In addition, a greater discharge in the northern than central study area could be interpreted to reflect absence of the Hawthorn confining layer in the north. Discharge from the major regional aquifers, however, appears to have little influence on the rate of ground water discharge as shown by similarity between chemical compositions of water discharging from the sediment (herein referred to as seep water) and lagoon water. The composition of conservative solutes in seep water differs only slightly from the composition of the lagoon water, and indicates that at most 1 to 5% of the seep water originates from the regional fresh water aquifers. In contrast, pore water gradients from the upper 1 to 2 m of sediment show that Cl concentrations initially decrease to around 70 cm below the seafloor, and then increase in places to concentrations greater than in the lagoon. These profiles thus suggest that none of the seep water originates in the regional fresh water aquifers (herein referred to as ground water). If a small amount of ground water does make up part of the seep water, however, as implied by the seep water chemistry, the fraction is so small that it is impossible to use chemical composition to distinguish which aquifer sources the water. Given regional geologic and hydrogeological considerations, it is unlikely that any water discharges from the Floridan aquifer in the central study area. Consequently, any ground water that may be present is likely to discharge from the Surficial aquifer. In the northern study area, the discharging aquifer water is probably water mixed from both the Floridan and Surficial aquifers.

Of the water that discharges from the sediment, 95 to 99% appears to originate from the lagoon, with the remaining 1 to 5% originating from aquifer sources. Both

sources appear to mix in the upper meter of the sediment. Mixing is observed as variations of Cl concentrations and δ^{18} O values of the pore waters between the sediment-water interface and sub-bottom depths of ~70 cm over time periods of at most a few months. Downward mixing of lagoon water might explain why modeled rates of ground water discharge are commonly several orders of magnitude lower than rates measured *in situ*. The processes driving this mixing are unknown, but could include physical pumping from wave and tidal action or biological pumping from burrowing organisms. The controls and extent of this shallow pumping will be important to nutrient fluxes because of the extensive remineralization of organic matter in the shallow sediment, which would be enhanced by mixing of oxygenated lagoon water into the sediment. Consequently, the regional stratigraphy and hydrostratigraphy appear to have little control on the rate of ground water discharge. The most important factor appears to be the physical properties and chemical compositions of the bottom sediments at burial depths of less than 1 m.

What are flux rates of N and P to the Indian River Lagoon from ground water discharge (p. 168)?

Unlike the conservative tracers, nutrient concentrations of the seep water, including NH₄, TSN, TN, PO₄, TSP, TP and SiO₂ concentrations are consistently elevated in the seep water over the lagoon water. Concentrations are similar in the seep water and the shallow pore water, apparently reflecting the discharge of nutrients generated during remineralization of organic matter at shallow depths in the pore water. Concentrations in the seep water of nitrogen species TN and NH₄ are higher in the northern than the central region, and these elevated concentrations, coupled with the higher fluxes in the north generate a greater N flux there. The ammonium-N fluxes calculated using this technique range from 21 to 164 mg/m²/day and are ~80% to 700% greater than ammonium-N fluxes that are calculated assuming only diffusive loss from the sediment (Reddy et al., 1999). The calculated fluxes for seep water generate an annual load of TN to the northern study area of ~2.3 x 10⁶ kg, or ~48 x 10³ kg/km². This load is significantly greater than the central area, where the total annual load for the Indian River Lagoon is estimated to be ~0.85 x 10⁶ kg (~15 x 10³ kg/km²).

In contrast to the nitrogen species, the flux of TSP is greatest in the central Indian River Lagoon, while the fluxes are similar in the northern Indian River Lagoon and the Banana River Lagoon. These fluxes are calculated to range from 4.0 to 47.6 mg/m²/day, which are about 4 to 45 times greater than P fluxes that are calculated assuming only diffusive loss from the sediment (Reddy et al., 1999). These fluxes generate an annual load for the northern study area of 0.18×10^6 kg (~ 3.8×10^3 kg/km²). This load is larger than the load to the Banana River Lagoon study area, which is estimated to be 0.07×10^6 kg (~ 2.5×10^3 kg/km²), but is considerably smaller than the central study area of the Indian River Lagoon which is estimated to be 0.32×10^6 kg (~ 34×10^3 kg/km²). The differences in N and P loading among the study areas may result from differences in the chemical and hydrologic properties of the bottom sediment in addition to differences in seep rates for the two areas.

What are the total annual loads of N and P to the Indian River Lagoon from ground water discharge (p. 176)?

The difference in nutrient loading in the northern and central study areas, as well as the temporal variability in nutrient fluxes, limits the ability to extrapolate nutrient loads measured over small areas to the entire areas of the Indian River and Banana River lagoons. Nonetheless, such extrapolations are necessary for comparison with other lagoon-wide estimates of nutrient loading from surface water runoff and from atmospheric deposition. The most complete data for nutrient loads are available for nitrogen. Total annual loads to the Indian River and Banana River lagoons range from 10.5 to 27.9 x 10^{6} kg N on the basis of extrapolation of nitrogen loading from ground water discharge made in the three study areas (northern and central Indian River Lagoon and Banana River Lagoon). These values for nutrient loading are ~ 2 to 10 times greater than estimates of nitrogen loading from surface water runoff. These values fall in the middle of estimates of atmospheric deposition of nitrogen, which range over 4 orders of magnitude. The total annual load of P is calculated to range from 1.9 to 8.4 x 10^6 kg for the Indian River and Banana River lagoons. These values are similar to a value previously reported for advective flux of P from the sediment (Zimmermann et al., 1985), but are one to three orders of magnitude smaller than estimates based on diffusive flux. Although there is considerable uncertainty in all of the calculations of estuary-wide nutrient loading, these results indicate that nutrient loading associated with seep water discharge is a significant source to the lagoon water in the nutrient cycling of the Indian River Lagoon system.

Summary and Recommendations (p. 181).

The importance of ground water discharge to nutrient cycling indicates that future work should focus on refining measurements of this flux. The future work needs to address several specific questions that relate to three main topics. These topics include the mechanisms and magnitudes of mixing between lagoon and pore waters, the basin wide distribution of this phenomenon, and the physical and chemical relationships between the fresh water aquifers and overlying pore waters. One approach to the study of these topics should couple measurements of ground water discharge with detailed studies of the chemical compositions and physical properties of the sediment and changes in pore water chemical compositions. For example, physical property measurements should include measurements of grain size, permeability, sedimentation rates, and bioturbation structures. Chemical properties should include the nutrient compositions of the nutrients. These additional data should provide complimentary information to the direct measurement of nutrient fluxes, and constrain models of nutrient regeneration in the sediment. Study areas need to be located throughout the lagoon, but initially should be focused within and between the two previously established areas.

CHAPTER 1 – INTRODUCTION

1.1 Statement of Problem

Water budgets represent one of the primary controls of the distribution of pollutants and nutrients in estuaries (Valiela et al., 1990; Gallagher et al., 1996; Boynton et al., 1998). Parts of water budgets, including surface water runoff, atmospheric deposition, and evapotranspiration, are routinely measured and/or calculated. One important part of the budget, the diffuse discharge of water to estuaries across the sediment-water interface (herein referred to as groundwater discharge), is poorly constrained because of difficulties associated with locating and measuring the flow (e.g. McBride and Pfannkuch, 1975; Bokuniewicz, 1980; Moore, 1996; Cable et al., 1996a,b). Ground water may occur through diffuse seepage from water table aquifers along shorelines, from deep aquifers where confining layers are breached or missing, and possibly through circulation of seawater through shallow sediments from pumping mechanisms (e.g. Emerson et al., 1984; Li et al., 1999).

Ground water discharge may be particularly important for Florida's estuaries because of the occurrence of large and productive aquifer systems underlying a long coastline and extensive precipitation across the region. A good example where ground water discharge may be important is the Indian River Lagoon system, which extends 250 km along Florida's central Atlantic coast, from north of Cape Canaveral in Brevard Count to as far south as St. Lucie Inlet in Martin County (Fig. 1-1). The Indian River Lagoon system includes the Indian River Lagoon, as well as the Mosquito Lagoon which extends 30 miles north of the northern end of the Indian River Lagoon to New Smyrna Beach, and the Banana River Lagoon which is located to the east of Indian River Lagoon and separated from the northern Indian River Lagoon it by Merritt Island.

The Indian River Lagoon contains one of the most diverse biota in North America (IRLP, 1999) and is critical to the local economy. Approximately 2200 plant and 2100



Figure 1-1. Location map of the northern Indian River Lagoon study area. The cross section A-A' is shown in Figure 1-2. Contour lines show the potentiometric surface of upper Floridan Aquifer for September 1998. Elevation in feet above mean sealevel. Contour interval 5 ft. The boxes represent the outlines of areas shown in Figures 1-5 and 1-6.

animal species live within the Indian River Lagoon ecosystem, and forty of the species are rare or endangered. Pollution, including sedimentation from surface water runoff and discharge of agricultural, urban, and industrial wastewater to the lagoon threatens species diversity in the lagoon. The economic impact of the lagoon includes commercial fisheries of 21 species of finfish and 4 species of shellfish (Woodward and Clyde, 1994; IRLNEP, 1998). Additional economic impact includes a large tourist industry, largely supported by recreational fishing and boating.

Recent urban and commercial development threatens the ecosystem of the lagoon. The population surrounding the lagoon increased by ~124% from 1970 to 1990, and is expected to increase by another 60% by the year 2010 (IRLNEP, 1995) Although much of the population in Brevard County obtains potable water from Lake Washington, other counties surrounding the Indian River Lagoon rely largely on ground water for potable water. The growth in population could thus potentially alter the natural hydrologic cycle through excessive ground water withdrawal, as well as increase contaminant input.

1.2 Tasks and Motivation for Contract #99G245

Although there have been relatively few attempts to measure ground water discharge to the Indian River Lagoon, they have included both modeling and direct measurements. Using a finite element model of head difference between the lagoon and the Surficial Aquifer, Pandit and El-Khazen (1990) estimated that annual ground water discharge is ~140 m³ per meter length of shoreline in the vicinity of Port St. Lucie. Extrapolation over 250 km length of the Indian River Lagoon suggests that ground water discharge to the Indian River Lagoon, from its northern most reach to St. Lucie Inlet, is approximately 3.4×10^7 m³ annually. Direct measurements of ground water discharge in the vicinity of Jensen Beach using seep meters (e.g. Lee, 1977) showed rates that were as high as 916 ml/m²/min, although the average rate for all measurements was only 6 ml/m²/min (Belanger and Walker, 1990). Extrapolating the average rate over the entire area of the lagoon that ground water discharge is approximately 1.6×10^{13} m³ annually,

more than 4000 times greater than the volumes calculated by Pandit and El-Khazen (1990).

As a result of the discrepancy between the measured and modeled ground water flux and its potential impact on water quality and ecosystems of the lagoon, the St Johns River Water Management District (SJRWMD) contracted with the University of Florida to study ground water discharge to the Indian River Lagoon. The project had three principle goals: to measure ground water discharge using a variety of techniques and to assess the strengths and weaknesses of these techniques, to determine the sources of water discharging to the lagoon, and to assess the nutrient loading to the lagoon caused by ground water discharge. The project was divided into two phases. The first phase of the project focused on the northernmost portion of the lagoon and the second year focused on the central reaches of the lagoon between Cocoa and Melbourne Florida, including both the Indian River and Banana River Lagoons (Fig. 1-1).

Three primary techniques were used to measure rates of ground water discharge. Rates were measured directly with seepage meters (e.g. Israelson and Reeve, 1944; Lee, 1977; Cable et al., 1997a,b). Results obtained with seepage meters are described in Chapter 2 of this report. Attempts to measure rates were also made on the basis of disequilibrium of the short lived isotopes of radium (223 Ra, $t_{1/2} = 11.4$ days, and 224 Ra, $t_{1/2}$ = 3.66 days), which were used to determine the residence times of lagoon water. A detailed description of this technique, as well as the results are described in Chapter 3 of this report. Rates of ground water discharge were also calculated on the basis of mass balances of the activities of the long lived Ra isotope (226 Ra, $t_{1/2} = 1620$ yrs) and its daughter isotope 222 Rn (t_{1/2} = 3.82 days). This technique is described and its results are presented in Chapter 4 of this report. Seep meters were used to collect samples of the discharging water, and this water was used to measure chemical concentrations and isotope compositions of the discharge water. These data were used to identify the source of water discharging to the lagoon and to estimate the loading of nutrients from ground water discharge. The sources of ground water discharge is described in Chapter 5 and the nutrient fluxes associated with ground water discharge is described in Chapter 6.

1.3 Geology and Hydrogeology of Indian River Lagoon

The hydrostratigraphy of Florida can be broadly divided into three principle units including from the deepest to shallowest, the Floridan, Intermediate, and Surficial Aquifers (Miller, 1986; Scott, 1988; 1992; Groszos et al., 1992). The Floridan Aquifer consists of Oligocene and older carbonate rocks. These rocks have been extensively dissolved in the subsurface, and consequently are characterized by heterogeneous hydraulic conductivity and extensive subsurface drainage. These characteristics make the Floridan Aquifer one of the most productive aquifers in the world and thus it provides the primary source of potable water to northern Florida. The Floridan Aquifer is locally divided into the upper and lower Floridan Aquifer depending on the presence of a middle confining unit. The Intermediate Aquifer consists of carbonate lenses contained within the Miocene Hawthorne Group, which is composed of siliciclastic clay and phosphoriterich rocks (Scott, 1988). In the central region of the Indian River Lagoon, the Intermediate Aquifer is thin and relatively non-productive (Bermes, 1958; Toth, 1988). Little is known of the Intermediate Aquifer in the northern Indian River Lagoon where the Hawthorn Group and the Intermediate Aquifer are thin or missing. In the area surrounding the Indian River lagoon system, the Surficial Aquifer has been subdivided into separate units informally named the shallow rock aquifer and the shallow clastic aquifer (Toth, 1988). These aquifers consist largely of mixtures of sands, coquina, and clay layers with the clay layers providing the confinement between the aquifers.

The Hawthorn Group acts as the primary confining layer for the Floridan Aquifer. In general, the Floridan Aquifer is considered to be confined where the Hawthorn Group reaches a thickness of more than 33 m and semi-confined where the Hawthorn Group is less than 33 m thick. The boundary between confined and semi-confined Floridan Aquifer cuts across the northern portion of the Indian River Lagoon north of Titusville where the Hawthorne Group may be missing in the northernmost reaches of Indian River and Mosquito lagoons (Scott, 1988; Toth, 1988) (Fig. 1-2).

The shallow rock aquifer unit of the Surficial Aquifer is Pliocene in age and is equivalent to the Tamiami Formation. It overlies the Hawthorn Group, thickens toward the south and is missing north of Cocoa, Florida. Four additional clastic aquifers are subdivided within the Surficial Aquifer along the borders the Indian River Lagoon, including Terrace, Atlantic Coastal Ridge, Ten-mile Ridge, and Inter-ridge. Terrace Aquifer occurs on the barrier islands separating Indian River Lagoon from the Atlantic ocean and supplies potable and irrigation water to communities on the islands. The aquifer depends on local rainfall for replenishment. The Atlantic Coast Ridge occurs on the western bank of Indian River Lagoon. In the northern reaches of the Lagoon, it is composed of the Pleistocene Anastasia formation. This aquifer provides most of the water supply for the towns of Mims and Titusville on the western edge of the northern Indian River Lagoon. Water table elevations in the Atlantic Coast Ridge aquifer in this region are on the order of 6.7 to 19.5 m above mean sealevel, which implies that there can be significant mixing between the Floridan and Surficial Aquifers. Ten Mile ridge and Inter-ridge Aquifers are restricted to the central and southern Indian River Lagoon.



Figure 1-2. Stratigraphy of Indian River Lagoon. The Miocene Hawthorn Group, the confining unit for the Floridan Aquifer system is missing in the northern study area. Modified from Scott (1988).

1.4 Regional Climate

The Indian River/Banana River Lagoon system rests predominantly in the humid subtropical region of the Florida peninsula north of Vero Beach. Climate for this region typically demonstrates a dry season (Jan to May), a rainy season (June to Sept), and a winter storm season (Oct to Dec). Climatic conditions during field sampling, and their comparisons with average conditions are important in order to determine how representative the data are that was collected over relatively short time periods, and thus if these data can be extrapolated to longer time scales. Examples of how climate can change the variables measured in this study include dilution of dissolved salts by rainfall and loss of gases such as Rn from high winds. Consequently, cumulative monthly precipitation data for Titusville and Melbourne are presented in Table 1-1 along with values for the 30-year average precipitation for these sites.

Month	1999 Precip. (Titusville) (cm) ^a	30-year Precip. (Daytona) (cm) ^b	2000 Precip. (Melbourne) (cm) ^c	30-year Precip. (Vero Beach) (cm) ^b
January	7.72	6.99	5.94	5.44
February	4.14	7.90	0.86	7.39
March	1.09	7.37	5.54	7.85
April	3.63	5.66	6.71	4.83
Мау	13.99	8.76	1.04	11.07
June	15.65	15.21	17.86	16.41
July	9.55	13.72	24.82	15.47
August	20.40	15.65	8.79	15.49
September	34.29	16.1	21.36	18.16
October	20.85	10.49	13.23	14.02
November	7.24	7.21	0.91	8.31
December	3.02	6.58	0.64	5.51
Annual	141.58	121 64	107 70	129 95

 Table 1-1: Summary of measured and 30-year normal rainfall for the IRL sampling sites.

^aSource: NOAA Southeastern Regional Climate Center, Columbia, South Carolina ^bSource: NOAA Monthly Station Normals, 1961-1990

^cSource: NOAA, 2001 (http://www.srh.noaa.gov/mlb/mlbclimat.html#2000)

A comparison of the 1999 and 2000 sampling seasons demonstrate distinct yearto-year climatic differences (Fig. 1-3). The 1999 field season averaged 16% higher annual precipitation than the 30-year average values recorded at Daytona Beach and represent a wetter than normal year. Monthly precipitation exceeded normals by 5.23 cm (60%) in May and by 4.75 cm (30%) in August 1999. In contrast, the 2000 field season took place during a drought year. Annual precipitation at Melbourne, Florida, was 17% below the 30-year normal at Vero Beach. Monthly precipitation was lower than 30-year normals by 10.03 cm (91%) in May, by 6.70 cm (43%) in August, and by 4.87 cm (88%) in December 2000. Overall, the annual precipitation at Titusville in 1999 was 24% higher than 2000 Melbourne precipitation. The 30-year average values recorded for Daytona and Vero Beaches were within 6% of each other.



Figure 1-3: Monthly total precipitation (cm) is shown versus time for (A) 1999 Titusville (dk. gray bars) and 30-yr normal Daytona Beach (lt. gray bars); and (B) 2000 Melbourne (dk. gray bars) and 30-yr normal Vero Beach (lt. gray bars).

A comparison to the 30-year average values for Daytona Beach precipitation shows that except for an unusually low July rainfall amount, 1999 summer precipitation was above average. After the August 1999 field trip, two hurricanes passed over the Indian River Lagoon as they moved north along the Atlantic coast of Florida. Hurricanes Floyd (Sept. 14 to 15, 1999) and Irene (Oct. 15 to 16, 1999) each contributed significant rainfall to the lagoon in the Fall. In addition, Tropical Storm Harvey (Sept. 20 to 21, 1999) moved up west central Florida, but outer rainbands reached portions of the lagoon. Winds gusted to 70 mph (31 m/sec) during the worst periods of Irene and were much less for the other storms. During September and October, 30-year peak gusts for Daytona Beach are 48 to 56 mph (22 to 25 m/sec). Mean monthly and mean/maximum daily wind speeds during our sampling trips in May and August 1999 are given in Table 1-2. Mean values ranged from 3.4 to 4.5 m/sec, which are typical for that time of year. Wind speeds commonly were strongest in the afternoon. During May 1999, wind speeds reached velocities as great as 10.3 m/sec. May 5 and 7, 1999 were particularly windy throughout the day, however. In August, 1999, the maximum daily observed wind speed was 10.3 m/sec at 13:30. Exceptional days during the sampling trip were August 14 and 17, 1999, when winds were high most of the day. August 16, 1999 was a particularly calm day with a brief gust of 5.4 m/sec at 14:00. Overall, the wind speed was normal for our sampling periods. Wind data are not available for the Melbourne site.

Precipitation during the 2000 sampling season between Cocoa and Melbourne, Florida, was about 17% below normal precipitation expected for the region (based on the Vero Beach weather station). Individual sampling trips in May and August each incorporated rain events (Fig. 1-4). Rainfall in May was low overall, but we sampled during a time when 80% of the total monthly rainfall was deposited. Our August wet season sampling trip encompassed a rain event of 2.69 cm, which was 31% of the total monthly precipitation. A small amount of rain fell in December (0.051 cm) during our transitional season sampling trip, which represented only 8% of the total monthly rainfall.

23



Figure 1-4: Daily precipitation (cm) for Melbourne, Florida, shows the distribution of rainfall during our 2000 sampling season. Individual sampling trips in May, August, and December are highlighted in gray.

Date	Daily	Maximum	Monthly	30-year Mean
	Mean (±1σ)	Daily Wind	Mean	(and Max.) Monthly
	Wind Speed	Speed	Wind Speed	Wind Speed
	(m/sec) ^a	(m/sec) ^a	(m/sec) ^a	(m/sec) ⁰
Dry Season, Ma	y, 1999			
3-May-1999	4.80 ± 1.4	6.7	4.5	4.0 (18.3)
4-May-1999	3.50 ± 2.1	6.3		
5-May-1999	4.00 ± 2.3	6.3		
6-May-1999	5.52 ± 1.3	7.6		
7-May-1999	4.51 ± 2.1	6.3		
8-May-1999	5.12 ± 2.3	10.3		
9-May-1999	2.89 ± 2.1	7.6		
Wet Season, Aug	gust, 1999			
14-Aug-1999	3.58 ± 1.7	5.4	3.4	3.2 (22.4)
15-Aug-1999	4.41 ± 1.1	6.3		
16-Aug-1999	2.55 ± 1.8	5.4		
17-Aug-1999	3.55 ± 1.6	5.4		
18-Aug-1999	3.26 ± 1.9	7.6		
19-Aug-1999	3.38 ± 2.7	10.3		

 Table 1-2: Summary of 1999 field season wind speeds at Titusville, Florida,

 compared to 30-year monthly means and maximums at Daytona Beach, Florida.

^aSource: NOAA Southeastern Regional Climate Center, Columbia, South Carolina ^bSource: NOAA Monthly Station Normals, 1961-1990

1.5 Sampling Locations

1.5.1 Northern area

The northern study area includes the northernmost reaches of the Indian River lagoon as far south as approximately 28 43' N latitude (Fig. 1-5). In this area, the missing or thin Hawthorn Group rocks suggest that the Floridan Aquifer could be a potential contributor to ground water discharge. In addition, the Floridan Aquifer across the northern Indian River Lagoon is characterized by a potentiometric surface of 1 to 2 meters above sea level (Fig. 1-1) (e.g. Bradner, 1998; Knowles and Bradner, 1999). These values apparently reflect the slight confinement provided by clay layers contained within the Surficial Aquifer.

A total of 28 stations was established in the northern area (Table 1-3 and Fig. 1-5). The locations were chosen for two specific goals: (1) to observe the overall variability of ground water discharge into the lagoon and (2) to look for specific patterns in the variation of ground water discharge with distance from shore. Consequently, 22 of the 28 stations were arranged in a total of five transects extending up to 2 km from shore. These transects were distributed evenly around the perimeter of the lagoon. Two of the transects, one at Big Flounder Creek and the other at Turnbull Creek, replicate the locations of seagrass transects that have been studied for the past several years. The remaining six stations were distributed evenly throughout the center of the study area. Two of these locations coincide with stations from previous work. One station (our station IRL-16) reoccupies the St. Johns River Water Management District water quality station IRLI01 east of Big Flounder Creek at Scottsmoor Landing. The other station (our station IRL-11) re-occupies a station set up as part of the Indian River Lagoon Hydrodynamics and Water Quality Model: Nutrient Storage and Transformations in Sediments (Reddy et al., 1999). This station is identified as SWS station #24 in Reddy et al., (1999).

In addition to the 28 lagoon stations, six wells surrounding the lagoon were sampled for the chemical and isotopic composition of the ground water (Table 1-4). One

25

Station ID	Description	Latitude N	Longitude W	Depth (m)	Samples collected* (Dry Season)	Samples collected* (Wet Season)			
Big Flounder Transect									
IRL 1	Seagrass study site south of Big Flounder	28°45.179'	80°50.570'	0.5	SR, SWC, Ra, Rn	SR, SWC, Ra			
IRL 2	Creek. Seagrass extends to IRL 5	28°45.175'	80°50.532'	0.6	SR, SWC, Rn	SR, SWC, Ra			
IRL 3	Hard sand beyond IRL 5	28°45.194'	80°50.471'	0.6	SR, SWC, Ra, Rn	SR, SWC, Ra, MS			
IRL 4		28°45.211'	80°50.414'	0.7	SR, SWC, Rn	SR, SWC, Ra			
IRL 5		28°45.207'	80°50.385'	0.8	SR, SWC, Ra, Rn	SR, SWC, MS, P			
IRL 6		28°45.213'	80°50.347'	0.9	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra, MS, P			
IRL 7		28°45.243'	80°50.208'	1.7	SR, SWC, Rn	SR, SWC, Ra, MS, P			
IRL 8		28°45.286'	80°50.039'	1.8	SR, SWC , Ra, Rn	SR, SWC, Ra			
Scottsmore Turnbull Creek Transect									
IRL 9	Seagrass study site at Turnbull Creek	28°47.101'	80°50.764'	1.1	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra			
IRL 10	Mixed seagrass and muddy bottom	28°47.116'	80°50.876'	0.6	SR, SWC, Rn	SR, SWC, Ra			
Shiloh/Palm Tree Transect									
IRL 12	NE section of northern IRL	28°46.036'	80°48.876'	0.7	SR, SWC, Rn	SR, SWC, Ra			
IRL 13	Extensive seagrass and muddy bottom	28°46.045'	80°48.087'	0.9	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra			
IRL 14		28°46.569'	80°48.683'	0.9	SR, SWC, Rn	SR, SWC, Ra			
IRL 15		28°46.577'	80°48.624'	0.6	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra			
Tower Tr	ansect								
IRL 17	SW section of northern IRL	28°42.535'	80°49.846'	0.6	SR, SWC, Ra, Rn	SR, SWC, Ra			
IRL 18	Patchy seagrass and hard sandy bottom	28°42.522'	80°49.701'	0.7	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra			
IRL 19		28°42.513'	80°49.740'	0.8	SR, SWC, Rn	SR, SWC, Ra			
IRL 20		28°42.515'	80°49.694'	0.8	SR, SWC, Ra, Rn	SR, SWC, Ra			
Duckroos	st Cove Transect								
IRL 21	SE section of northern IRL, north of the	28°43.905'	80°45.739'	1.0	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra			
IRL 22	Intracoastal Waterway	28°43.999'	80°46.054'	1.2	SR, SWC, Ra, Rn	SR, SWC, Ra, MS			
IRL 23	Patchy seagrass and hard sandy bottom	28°44.019'	80°46.244'	1.1	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra			
IRL 24		28°44.117'	80°46.546'	1.0	SR, SWC, Ra, Rn	SR, SWC, Ra			
Deep Water Sites									
IRL 11	Soil and Water Science Station #24	28°43.624'	80°49.381'	2.0	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra			
IRL 16	SJRWMD water quality station #IRLI01	28°46.272'	80°50.148'	1.7	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra			
IRL 25	Seagrass, very muddy, organic-rich bottom	28° 44.283'	80° 48.263'	1.9	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra, MS			
IRL 26	Hard, Sandy bottom	28° 43.079'	80°48.500'	2.0	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra			
IRL 27		28° 45.027'	80°48.554'	1.5	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra, MS			
IRL 28		28° 43.843'	80°47.440'	1.9	SR, SWC, WCC, Ra, Rn	SR, SWC, Ra			

Table 1-3. Description and location of sampling stations

* SR = seepage rate, SWC = Seep water chemistry, WCC = water column chemistry, Ra = Radium, Rn = Radon, WC = water chemistry, MS = Multi-sampler, P = Peeper



Figure 1-5. Location map of northern Indian River Lagoon. Position of seep stations are shown as black points and indicated by numbers. The location of ground water samples are designated by open circles labled "GW". Location of surface water sampling stations are given as HOC for Haulover Canal and TBC for Turnbull Creek. Five transects are named around the edge of the lagoon.

well (GW-3) is located to the west of the St. Johns River, and may represent a ground water basin that is separate from the Indian River Lagoon. Two wells are located on Cape Canaveral between Indian River and Mosquito Lagoon. The depths of the wells listed in Table 1-4 indicate that all but GW-6 and GW-3 penetrate the upper Floridan Aquifer. The GW-6 and GW-3 wells appear to penetrate the Surficial aquifer.

Additional samples were collected from two streams that flow into Indian River Lagoon. The stream samples include Turnbull Creek (TBC) and Haulover Canal (HOC). The sample from Turnbull Creek was collected ~20 m south of where U.S. Highway 1

Station	Description	Latitude	Longitude	Depth
ID		Ν	W	(m)
Groundw	vater water samples			
GW-1	Northgate Trailer Park 3277 1st Ave. Mims, FL 32754	28°41.481'	80° 51.505'	38.1
GW-2	Scottsmoor Post Office Brevard County, Magoon Ave	28°45.954'	80° 52.638'	36.3
GW-3	TCD Plastics Route 46	28°39.966'	80° 56.907'	4.5
GW-4	6095 Seminole St., Scottsmoor Private home (Douglas Chamberlain)	28°46.147'	80° 52.266'	39.0
GW-5	Fire Prevention Station and Staging area Cape Canaveral National Visitors Center	28°38.511'	80°43.281'	26.0
GW-6	NASA Atmospheric Sciences Field Lab	28°42.377'	80°43.611'	10.0
Surface v	water samples			
TBC	Turnbull Creek, ~20 m S of US1 bridge	28°49.216'	80°51.567	0.6
HOC	Haulover Canal at bridge	28°44.246'	80°45.262'	surface

Table 1-4. Locations and depths of wells and surface waters, northern area.

crosses the stream. The sample from Haulover Canal was collected where the Kennedy Parkway crosses the canal.

1.5.2 Central area

The central study area is located in between the towns of Melbourne and Cocoa, Florida, where the Hawthorn Group reaches a thickness of approximately 30 m, thereby effectively confining the Floridan Aquifer (Fig. 1-2). Twenty-two sampling stations were established in this area in four east-west transects that extend across the width of the Indian River Lagoon and for the northern two transects across the Banana River Lagoon (Fig. 1-7). The transects are numbered from the north to the south. Transect 1 is located at ~28 16'N and has three stations in the Indian River Lagoon and five in the Banana River Lagoon that are spaced evenly across the lagoons. Transect 2 is located at 28 14' N and has a total of six evenly spaced stations, with three each in the Indian River and Banana lagoons. Transect 3 is located at 28 10'N and transect 4 is located at 28 7'N. Both have 4 stations spaced evenly across the lagoon.

Additional stations were established around the lagoon to sample both ground and surface water (Table 1-5). Ground water was sampled from seven sites. At six of the ground water sites, water was collected from private water-supply wells and at one site water was collected from a spring. Three of the wells are deep and supply water from the Floridan Aquifer. The other three wells are shallow and supply water from the Surficial Aquifer. The spring probably flows from the Surficial Aquifer.

Surface water was sampled from five sites surrounding the field area (Table 1-5). At four of the surface water sites, water was collected from rivers flowing into the lagoon from the east. At the fifth surface water site, water was collected from Sebastian Inlet. Sebastian Inlet is located ~30 km south of the field area, but represents the northernmost natural inlet for open marine seawater to flow into the Indian River Lagoon.

1.6 Field Stations and General Description of Field Sampling

The following section represents a description of general field sampling techniques that were used to collect samples for all chemical analyses included in the report, including sampling techniques for the lagoon, surface water, and wells. Considerable detail is provided for techniques used to collect pore water samples because a new tool was developed for these samples and because this tool was used to collect samples described in chapters three through six. Additional techniques are described in subsequent chapters if they are specific for a particular component that is only discussed in that chapter.

1.6.1 Timing and Establishing Stations

During the course of the study, six trips were made to collect samples from the lagoon and surrounding areas. The northern area was sampled in 1999 between May 3 and 9, August 13 and 19, and December 12 and 13. The central area was sampled in 2000 between May 12 and 18, August 12 and 18, and December 6 and 12. The sampling



Figure 1-6. Location map showing the approximate locations of stations sampled during the second year of project. IRL represents Indian River Lagoon and BRL represents Banana River Lagoon.

Station	Description	Latitude	Longitude	Depth	Aquifer			
ID		Ν	W	(m)				
Ground water samples								
GW331	331 Coral Way West,	28°07.815'	80°35.550'	73.2	Floridan			
	Cocoa Beach							
GW921	921 South Brevard Ave.,	28°18.096'	80°36.612'	10.7	Surficial			
	Cocoa Beach							
GW1472	1472 Casa Road,	28°15.286'	80°41.487'	5.9	Surficial			
	Melbourne							
GW1473	1473 Casa Road,	28°15.286'	80°41.487'	84.7	Floridan			
	Melbourne							
GW1580	1580 West Riverside Dr,	28°09.988'	80°38.793'	18.3	Surficial			
	Melbourne							
GW1647	1647 Highland Avenue,	28°08.035'	80°37.725'	106.7	Floridan			
	Melbourne							
Blue Heaven	2455 South Tropical Trail,	28°08.035'	80°37.725'	Surface	Surficial			
Spring	Merritt Island							
Surface water samples								
SEBINL	St. Sebastian Inlet	27°51.583'	80°26.875'					
STSEBR	St. Sebastian River	27°50.693'	80°29.861'					
EAUGALL	Eau Gallie River	28°04.651'	80°36.140'					
TURKEYCR	Turkey Creek	28°50.845	80°36.066'					
CRANECR	Crane Creek	28°04.652'	80°36.138'					

 Table 1-5. Locations and depths of wells and surface waters, central area.

done during May was designed to coincide with the end of the normal dry period, and sampling done during August was designed to coincide with the end of the normal rainy period (Figure 1-3). Sampling during December 1999 was not included as a task for the first year of the project, but selected instruments were installed during the August, 1999 sampling trip that required equilibration prior to sampling. Results determined during the first year of the project indicated that it would be important to have complete sampling done during the transition from the rainy season to the dry season, and consequently, a third trip was included in the sampling protocol for the second year of the study.

During the first trip to both the northern and central area, stations were established by deploying one seepage meter at each location and surveying its location with a handheld Global Positioning System (GPS) unit. At the end of the first trip to the northern area, the seep meters were removed from the lagoon and then relocated during the second trip using a hand-held GPS. The accuracy of the GPS during the 1999 sampling trips was approximately 20 m, and thus the location of the second deployment of the meters could be up to 40 m from their initial position. With the exception of IRL13, all meters were re-installed during the first day of the August sampling trip. Station IRL13 could not be relocated and thus this station was re-established at the location given in Table 1-3. During the December 1999 trip, only pore waters were sampled with equipment that had been installed during the August trip.

In the central area, the station locations were also established by installing seep meters. In order to accurately relocate the meters, these stations were marked by buoys tethered to cinder blocks by ¹/₄" rope prior to the removal of the seep meters. Only one of the 14 buoys and six of the eight buoys remained in the Indian River Lagoon and Banana River lagoons respectively at the time of the second sampling trip. The ropes may have been cut by barnacles growing on the buoys or fishermen may have removed the buoys. Where buoys remained, the seep meters were deployed at the location of the cinder blocks. Where buoy were missing, the stations were relocated using GPS and the recorded latitude and longitude (Table 1-3). Because GPS signals were not scrambled by the military during the 2000 sampling trips, the stations can be relocated to within a few meters of their original locations. While deploying seep meters during the second and third sampling trips, several cinder blocks were found even though they no longer had buoys attached, reflecting the precision with which stations can be relocated with GPS.

Field sampling consisted of deployment of the seep meters and allowing them to equilibrate. In the northern area, the water column was sampled during this time. In the central area, both water column and pore water were sampled. After the seep meters had equilibrated, they were sampled for rates of ground water discharge. In general, the final samples that were collected included the ground and surface water sampling sites.

1.6.2 Pore water samples

Although pore waters were not included in the first year of the contract, pore water at four stations in the northern area were collected using donated equipment. This equipment consisted of multilevel piezometers and are referred to as "multisamplers". The results of the initial pore water sampling indicated the importance of the composition of the shallow pore waters to the chemistry of the lagoon water. A major component of

32

the year two sampling thus focused on gradients of dissolved solutes in the shallow pore waters. Details of the design and use of the multisamplers are given below.

1.6.2.1 Design and Construction

The multisamplers used during the 1999 sampling season consist of $\frac{3}{4}$ inch diameter PVC pipe with $\frac{1}{4}$ in. OD polyethylene tubing attached to the outside. The ends of the polyethylene tubes were covered with screening material (Nytex, 250 µm mesh) and the pipe and tubing were jetted into the sediment by pumping lagoon water down the interior of the pipe. The multisamplers were inserted into the sediment as deeply as possible, up to 2 m below the sediment-water interface. The $\frac{1}{4}$ in. tubes extended from the sediment to above the water level of the lagoon either by extending up the tube or by being attached to a float.

Seven multisamplers were installed during the August 1999 trip at stations IRL4, IRL5, IRL6, IRL7, IRL22, IRL25, and IRL28. Although each multisampler was marked with a float, all floats were lost between deployment and sampling, probably because of the high winds and waves associated with the three hurricanes that passed through the area. At the time of sampling in December 1999, only the four of the multisamplers (IRL4, IRL5, IRL6, and IRL22) could be located and sampled. These multisamplers were located in shallow water and had PVC piping sticking out of the water column. The multisampler at station IRL22 was completely encrusted with barnacles, preventing sampling from above the water level. At this station, the multisampler tubing was cut at the sediment-water interface and new tubing was attached. Pore water was withdrawn through the new tubing. The tubing at the other three multisampler locations was free of barnacles so that water could be sampled through the original tubing that extended above the water level of the lagoon.

The experience gained during the 1999 sampling trip led to major modifications of the multisampler design and installation procedure for the central area. The newly designed multisamplers consist of 2" ID schedule 80 PVC pipe with $\frac{1}{4}$ " OD (3/8" ID) PVC tubing fed through the interior of the pipe (Fig. 1-7). The PVC tubing is glued to ports in the pipe and each port is screened with 250 µM screening material (Nytex). The

ports exit the 2" pipe in a spiral fashion with each one located 90° offset from the ports above and below. This arrangement retains more strength of the PVC pipe as well as increases the volume of sediment from which pore water is extracted. The tubing is lead outside the PVC pipe through a T joint. Multisamplers are driven as far as possible into the sediment using a hammer. The distribution of ports is variable along the length of the multisamplers, with the ports more closely spaced at the top than at the bottom (Fig. 1-7). This distribution allows higher resolution sampling of the pore water near the sediment-water interface where concentration gradients are likely to change more rapidly with depth because of diagenetic reactions.

Some of the ports did not yield water when pumped. Presumably these ports were located within sedimentary layers with lower permeability than those layers next to the ports that did yield water. , The ports for the multisamplers were thus modified following the August 2000 trip in order to increase the area of the screened interval from 0.3 cm^2 to 13.3 cm^2 (Fig. 1-8). The increased area of the screened interval allowed 34 samples to be collected from multisamplers during the December 2000 trip as compared with 27 and 25 during the May and August trips respectively. The change in the design of the ports increases the length of the port to 5.7 cm. Because the ports are separated by 20 to 40 cm, the sampled interval represents ~14 to 28% of the total interval of sediment between the ports.

1.6.2.2 Installation and Sampling

Multisamplers were installed at eight of the stations in the central area. Five of the multisamplers were installed in the Banana River Lagoon at stations BRL1, BRL2, BRL5, BRL6, and BRL7. The remaining three multisamplers were installed in the Indian River Lagoon at stations IRL29, IRL31, and IRL32. These stations were chosen because they provided the deepest penetration into the sediments of the multisamplers. Several attempts were made to install multisamplers in the central two transects, but the deepest penetration possible was ~40 cm. At this depth, the multisamplers apparently hit a hard layer, possibly the Anastasia Fm, which crops out along the banks of the lagoon.



Figure 1-7. Design of multisampler. The length shown is the maximum length of the multisamplers. Several multisamplers were shortened for specific stations.


Figure 1-8. Modification to the screened interval of the multi-samplers. The original opening was the size of the end of the flexible PVC tubing. The modified opening was a grid of channels that were routed into the PVC pipe of the multisamplers.

Although the unconsolidated sediment was thicker in the northern portion of the central field area, multisamplers would penetrate to their maximum depth of 230 cm only at station BRL2. The depths of penetration at the other stations were variable, and consequently not all ports were inserted into the sediment during the May 2000 sampling trip (Table 1-6). Consequently, the multisamplers were modified for the August 2000 trip by shortening their overall lengths, allowing the penetration of additional ports after they had been inserted (Table 1-7). Even after this modification, multisamplers could not be inserted to their full, but shorter lengths at stations BRL5 and BRL7. Evidently the surface of the hard layer is uneven causing the thickness of unconsolidated sediment to be variable across the lagoon. The multisamplers for BRL5 and BRL7 were further shortened prior to the December 2000 sampling trip and during this trip all multisamplers were inserted to their new shortened lengths (Table 1-8).

Multi-sampler Station	Depth in Sediment (cm)	Numbers of buried ports	Ports sampled
IRL 29	137	5-8	none
IRL 31	197	3 – 8	7,8
IRL 32	114	6 - 8	6,7,8
BRL 1	190	3 – 8	3,5,6,7
BRL 2	230	1 – 8	1 - 8
BRL 5	130	5-8	5,8
BRL 6	168	4 - 8	4,5,6,8
BRL 7	194	3 – 8	3,4,5,6,7

Table 1-6. Penetration depth of multisamplers, May 2000.

In both the northern and central field areas, each of the tubes of the multisamplers was sampled with a peristaltic pump. The water was pumped at a rate of \sim 1 ml/second into a small plastic bucket and the oxygen concentration, conductivity, and temperature were monitored, until the values remained constant, which usually occurred after \sim 2 to 5 minutes of pumping depending on the flow rate of the water. Once the values were constant, their values as well as those of pH and salinity were recorded and water samples were collected. Water samples were collected for a variety of measurements included Ra (Chapter 3), Rn (Chapter 4), conservative chemical tracers (Chapter 5) and nutrients (Chapter 6).

Multi- sampler Station	Modified length (cm)	Distance: sediment to T (cm)	Penetration depth (cm)	Numbers of buried ports	Ports sampled
IRL 29	203	0	122	1-6	4 - 6
IRL 31	278	0	197	1 - 7	none
IRL 32	198	0	117	1 – 5	lost
BRL 1	284	0	203	1 - 7	1, 5, 6
BRL 2	309	0	228	1 – 8	1 - 8
BRL 5	236	10	145	2 - 5	2 - 5
BRL 6	244	0	163	1 - 6	1 - 4, 6
BRL 7	273	36	156	3 - 7	3

 Table 1-7. Penetration of multisamplers, August 2000.

Multi- sampler Station	Modified length (cm)	Distance: sediment to T (cm)	Penetration depth (cm)	Numbers of buried ports	Ports sampled
IRL 29	203	0	122	1 – 6	2,4,5
IRL 31	278	0	197	1 – 7	1
IRL 32	198	0	117	1 – 5	1-4
BRL 1	284	0	203	1 – 7	1,2,5,6
BRL 2	309	0	228	1 - 8	1 – 8
BRL 5	246	0	145	1 - 5	1 - 5
BRL 6	244	0	163	1 - 6	1-4, 6
BRL 7	237	0	156	1 - 6	3-6

 Table 1-8. Penetration of multisamplers, December 2000.

CHAPTER 2 – DIRECT SEEPAGE MEASUREMENTS

1.1 Introduction

Ground water discharge has long been measured using instruments called seep meters (Bouwer et al., 1963; Lee, 1977; Sonzogni et al., 1977; Cable et al., 1997; Krupa et al., 1998). Seep meters function by funneling water that flows from the sediment into an easily removed chamber, typically a plastic bag, for a known amount of time. The volume of water entering the bag, when divided by the length of time of the collection and the surface area covered by the meter yields a seepage flux in units of volume of water per surface area per time, or as a face (ie. linear) velocity. Measurement of ground water discharge made using seep meters provide a point measurement of the flux, but numerous meters need to be deployed in order to calculate an average (or integrated seepage flux) over a large region. Seepage meters were deployed at each station in both the northern and central study areas in order to measure the heterogeneity of point seepage as well as to compare with the integrated seepage measurements that are derived from chemical and isotopic tracers.

2.2 Methods

2.2.1 Description of Seep Meters and Deployment

Seep meters were constructed from the ends of 55-gallon drums (Fig. 2-1). The ends of the drums were cut from the sides so that 15 cm of the drum wall remained

attached to the ends. All rough and rusted parts of the ends of the barrels were sanded, and two coats of marine epoxy paint were applied to all surfaces. Half inch holes were drilled into the flat top in order to install connectors for the seepage bags. The holes are offset ~6 cm from the edge of the barrel. The connectors consist of the male end of common garden hose fittings. Silicon sealant was applied to the joint between the metal and the fittings in order to prevent water from leaking through the joint. The female end of the garden hose fittings contain a valve and are attached to the seepage bag. The fitting and the bag are attached using zip ties and electrical tape and thus are water tight. This construction allows the bags to be attached and removed from the seep meters without water leaking into or out of the bag during deployment. Rubber handles were screwed into the sides of the meters.

All meters are identical in size. When deployed, they cover a surface area of 0.28 m^2 . Meters were pushed into the sediment without the aid of SCUBA gear so that at least half of the vertical sides penetrate the sediment, creating a seal with the sediment (Fig. 2-1). With half of the side penetrating the sediment, the meters contain at most 0.02 m^3 (20L) of lagoon water. When deployed their tops had a slight tilt with the port located on the upper end of the meter. The tilt and offset port allowed gases, such as H₂S, to escape, preventing the meters from floating free of the sediment. The edges were visually inspected to be certain that the entire rim of the meter was inserted into the sediment, thereby preventing exchange of water around the base of the meters.

After deployment of the meters, they were allowed to equilibrate for at least 24 hours before measuring the seep rates. This equilibration time is necessary to allow flow to reestablish after water is pushed into the sediment during deployment of the meters (e.g. Cable et al., 1997). Some lagoon water may mix into the meters during the equilibration period, but the volumes should be small because net flow is out of the meters. Once the meters equilibrated, seep rates were measured by pre-filling a sample bag with exactly 1000 ml of surface lagoon water (collected at the sampling station and measured with a volumetric flask), swimming to the seep meter, attaching the bag to the meter, and opening the valve to the meter. The bags were either 1.5 or 4 mm thick polyethylene bags that measured 30 by 45 cm. When attached to the hose fittings, the thin-walled bags could hold ~4 liters of water, while the thick-walled bags could hold ~5



Figure 2-1. Diagram of construction and deployment of seepage meter. Seepage rate is volume of water entering bag over time. Samples of seep water are collected in clean, dry bags. Blanks are measured by deploying meters in sediment filled plastic pools.

liters of water. The bags were attached to the meters and left open for times ranging from one to two hours. After this time, the valves were closed, the bags were immediately removed from the meters and returned to the boat. The total volume of water in the bag was measured with a graduated cylinder and the 1000 ml of pre-filled lagoon water was subtracted from the total. Each meter was measured this way at least three times sequentially over a total period of four to six hours.

2.2.2 Control Experiments: Duplicates, Blanks, and Equilibration Time

Duplicate measurements were made at the Big Flounder transect in the northern study area during August 1999 and at BRL1 and BRL3 during May and August 2000. The Big Flounder duplicates were made in two ways. Two seepage meters, separated by ~2 m were deployed at station IRL6 and designated IRL6 and IRL6B. Ground water discharge rates were measured initially along the entire transect including IRL6B on August 14, 1999 (Table 2-1). The seep meter at IRL6B was then moved to within 1 m of the second seep meter, designated IRL6C, and allowed to equilibrate for three days. Ground water discharge rates were remeasured along the entire transect including IRL6C on August 17, 1999. With the exception of one station, all flow rates were greater on August 17th than on August 14th. The difference in flow rates on these two dates are within the error of the measurements, and thus their difference are not significant. The flow rates at IRL6 and IRL6B are significantly different, reflecting heterogeneous flow rates. The flow rates at IRL6 and IRL6C are nearly identical (Table 2-1).

In the central area, duplicates were measured at BRL1 and BRL3 in order to represent shallow and deep water sites, respectively. No duplicates were measured during the December trip because of the difficulty and hazardous conditions associated with working in the field during the winter. The duplicates meters were placed next to each other and seep rates were measured simultaneously from both meters. The flow rates are within a factor of two of each other at all stations during both sampling trips. Although there is a wide range of seepage from the duplicate meters, the values for each of the duplicate stations are within the sampling error of the individual measurements.

Blank measurements were made at IRL3 and IRL7 in the Big Flounder transect during the August sampling trip in the northern area and at BRL1 during the May and August sampling trip in the central area. At these sites, two plastic wading pools (~1.5 m diameter and 25 cm high) were placed on the bottom of the lagoon. At station IRL7 the pool was filled half way with fine grained sandbox sand and then completely filled with lagoon sediment. At station IRL3 and BRL1 the pool was filled with sediment from the bottom of the lagoon. Seepage meters were deployed into the sediment directly in the middle of the wading pools using the same technique as for all other stations. This deployment resulted in ~0.5 m of sediment between the meter and the edge of the pool

Station*	14-Aug-99	17-Aug-99		Change	
	(ml/m²/min)		(ml/m²/min)		(%)
Big Flound	der Transect				
IRL 1	43.0 ±	14.5	57.57 ±	25.71	25
IRL 2	55.3 ±	18.7	87.74 ±	42.63	37
IRL 3	43.7 ±	5.6	85.05 ±	66.30	49
IRL 4	46.4 ±	11.6	87.72 ±	21.50	47
IRL 5	35.5 ±	5.9	29.98 ±	4.78	-18
IRL 6	102.8 ±	13.9	178.87 ±	44.53	43
IRL 6B	59.6 ±	19.8			
IRL 6C			164.44 ±	36.25	
IRL 7	144.4 ±	10.8	172.33 ±	19.80	16
IRL 8	100.9 ±	9.40	174.55 ±	26.61	42
Time Serie	es Seepage Rates	*			
IRL6 - 1 (8	:25 - 10:28)		22.32		
IRL6 - 2 (1	0:30 - 12:31)		61.90		
IRL6 - 3 (12	2:31 - 13:57)		83.90		
IRL6 - 4 (1	3:59 - 15:35)		88.64		
IRL6 - 5 (15:36 - 19:14)¶			89.94		
Blanks					
IRL 3			9.57 ±	11.06	
IRL 7			12.62 ±	8.05	
BRL 1	(May 2000)	7.7 ±	5.2	
BRL 1	(Aug. 2000)	6.3 ±	7.2	

Table 2-1. Seepage rate duplicates and blanks

* The time represents the length of time the seepage bags were on the meters. The seepage rate is a minimum because the bag was full when removed.

and ~ 20 cm between the bottom edge of the meter and the base of the pool. After allowing the meters to equilibrate for 24 hours, seepage rates were measured at these meters using the same technique as for the environmental seepage meters (Table 2-1). Although there was some flow into the seep meters, the flow is 5 to 10 times lower than the flow measured from seep meters at the same locations.

The timing required to establish equilibrium was tested by placing a seep meter in the sediment at station IRL6 in August 1999 and immediately start measuring seepage rates. A total of five of these time series samples were collected over a period of nearly 11 hours. During this time, ~11 liters had flowed from the seep meter. Initially the flow rate initially increased rapidly, presumably because the back pressure created during

deployment of the meter dissipated. The rate became constant after approximately five and a half hours (Fig. 2-2). This rate was intermediate between the rates measured at Stations IRL6, IRL6B, and IRL6C, again reflecting heterogeneous flow rates. The rapid establishment of a constant flow rate within 11 hours indicates that 24 hours is sufficient time to reestablish flow following deployment of the meters. The total volume of water that flowed from the meter (~11 L) represents more than half of the water contained in the head space of the seep meter.

2.3 Results

The results of seepage rates are provided for all stations in both tabular and in figure forms. The results for the northern area are reported in Appendix A.1 for both the May and August 1999 sampling trips, and for the central area in Appendix X.2 for the three 2000 sampling trips. The seepage rates and fluxes have not been corrected for artifacts in the sampling method such as frictional resistance and head losses within the meter and sampling bags (Belanger and Montgomery, 1992) which have been shown to be as much as 77% of the actual flow rate with laboratory tank measurements. Considering the lower values from laboratory experiments, the values reported in Appendix A should thus be considered to be minimum values.

Selected results for the northern area are plotted in Figure 2-2 against distance from shore for the Big Flounder Transect (see Figure 1-6 for locations of transects), in Figure 2-3 for the stations that extend across the central portion of the field area, and for all deep water sites in Figure 2-4. All three transects show the water depth at each individual station. The seepage rates for each transect in the central study area are plotted versus distance from the shore in figure 2-5.

The rate of ground water discharge ranged widely during all five of the sampling trips (Table 2-2). In May 1999, the seepage fluxes range from $\sim 3 \text{ ml/m}^2/\text{min}$ at IRL25, to more than 100 ml/m²/min at IRL23. Only one seepage meter (IRL25) yielded a rate that was less than the blank value reflecting a positive flux of water from all locations. During August 1999, the seepage rates ranged from 22 to 144 ml/m²/min with the slowest



Figure 2-2. Seepage rates for Big Flounder Transect. The round symbols connected by a solid line represent the dry season and the square symbols connected by a dashed line represent the rainy season seepage rates. The lower portion of the figure represents the water depth at each station. The symbols represent average values and the error bars represent 2 σ of the replicate measurements from each station



Figure 2-3. Seepage rates for the deep sites that extent east-west across the central portion of the field area. The round symbols connected by a solid line represent the dry season and the square symbols connected by a dashed line represent the rainy season seepage rates. The lower portion of the figure represents the water depth at each station. The symbols represent average values and the error bars represent 2 σ of the replicate measurements from each station



Figure 2-4. Seepage rates for the deep sites that extent north-south through the central portion of the field area. The round symbols connected by a solid line represent the dry season and the square symbols connected by a dashed line represent the rainy season seepage rates. The lower portion of the figure represents the water depth at each station. The symbols represent average values and the error bars represent 2 σ of the replicate measurements from each station



Figure 2-5. Seepage rates for A. transect 1, and B. transect 2. The round symbol connected by the solid lines represent the seepage rates for May, the square symbols connected by the dashed line represent the seepage rates for August, and the triangular symbol connected by the dotted line represent the seepage rates for December. The symbols represent average values and the error bars represent 1 σ of the replicate measurements from each station.



Figure 2-5 (cont.). Seepage rates for C. transect 3 and D. transect 4.



Figure 2-6. Histogram of seepage rates May and August 1999.

seepage fluxes again at IRL25. The differences in the seepage rates between sampling trips may reflect variations in the location of the seepage meters from one trip to the next, combined with the extreme heterogeneity of seepage rates across the lagoon. Nonetheless, the area surrounding Station IRL25 represents a region of low seepage rates.

The results of the seep measurements from the northern area are plotted as histogram in Figure 2-6. There is a significant and systematic increase in average and median seepage rate from the May to August sampling trips (Table 2-2). The average and median rates are 39.9 and 37.9 ml/m²/min respectively for May, and these values increase to 63.1 and 53.1 ml/m²/min in August. The percentage increase at individual stations is variable and seven of the 28 northern stations (IRL 5, 12, 15, 18, 23, 27, and 28) show a decrease in the seep rate from dry to rainy season (Appendix A). The largest decrease is 19% (at IRL12). Most of decreases in seep rate are less than the error of the measurement (i.e. the variation of the three seepage measurements), and thus small changes from May to August could simply reflect an artifact of the measurement. In contrast with stations showing small decreases, the largest increase in seep rate is nearly 700% (at Station IRL-7), with nine other stations showing an increase in seepage rate of more than 100%. These values are substantially larger than the percentage decreases at those stations with small seepage fluxes in August compared with May.

There is also a large range in seep rates in the central study area, but overall, the average rates are lower than in the northern area. During May, the seep rates varied from a low value of 10.1 to a high of 57.7 ml/m²/min. During August, the seep rate was even more variable, ranging from a low value of 8.8 to a high of 96.0 ml/m²/min. During December, the variability was similar to August, ranging from 9.1 to 99.0 ml/m²/min. All values were greater than the blank value. The lowest values are within one standard deviation of the variation in the three sequential blank measurements, however, and consequently could represent no flow.

Similar to the northern area, the average seep rate increased in the central area from 27.7 to 39.1 ml/m²/min from May to August 2000 (Fig. 2-7). From August to December the average rate decreased only slightly to 38.9 ml/m²/min, suggesting there is no significant variation in the seepage rate from August to December. Although the increase from May to August is within the range of the standard deviations of the

51



Figure 2-7. Histogram of the seepage rates for A. May, B. August, and C. December 2000.

Location	Date	n	Average Flux	Median Flux	Rai	nge	Standard
	(mm/yy)		ml/m²/sec		High	Low	Deviation
IRL	05/99	79	39.9	37.6	103.7	2.9	21.6
IRL	09/99	86	63.1	53.1	144.4	22.0	31.0
IRL	05/00	75	25.6	22.9	57.7	10.1	13.6
IRL	09/00	69	38.0	32.5	94.3	13.0	23.1
IRL	12/00	67	41.8	35.7	98.9	9.1	25.5
BRL	05/00	75	30.7	29.9	44.5	13.1	11.7
BRL	09/00	69	40.5	41.6	96.0	8.8	25.7
BRL	12/00	67	34.3	32.1	49.6	14.3	10.7

Table 2-2. Summary of mean, median and ranges of seepage rates.

measurements, it is interesting to note that there was a similar increase from the May to August sampling periods in the northern area. This systematic difference suggests that there may be a link between the seepage rates and seasonal variables, perhaps precipitation, temperature, wind speed, or other climatic variables.

The standard deviations of the all measurements made during the 2000 sampling season at each station also reflect the large range in seepage fluxes. These standard deviations are 12.8, 23.2 and 20.8 ml/m²/min for May, August, and December 2000 respectively. The high standard deviations of seep rates made during August and December result from several stations with significantly greater seep rates than during May. The highest seep rate was 57.7 ml/m²/min in May at IRL40, but two stations had seep rates >90 ml/m²/min in Aug (BRL8 and IRL39) and one station had >90 ml/m²/min in December (IRL40). Fourteen stations showed an increase in seep rate and seven showed a decrease in seep rate between May and August. Those stations with decreases in seep rates averaged a 40% decrease. The largest decrease occurring at station BRL4 with a 57% decrease. Those stations that had an increase in seep rate averaged 45% increase, with the largest increase occurring at station IRL29 with a 71% increase.

2.4. Discussion

Within the limits of the seep meter technique, the seep rates measured for the both the northern and central study areas appear to be a robust measure of the volume of water that leaves the sediment and enters the water column. Differences in rates between stations are consistent during dry and rainy season sampling and all rates are systematically greater than those measured during blank experiments. The following discussion of seep rates thus focuses on two questions. First, what is the cause for the variations in the seepage rate across the lagoon, and second, whether these rates are similar to rates that are measured or calculated previously using comparable or complimentary techniques. Comparisons will be made in this chapter to previously published measurements of seepage into the Indian River Lagoon. In subsequent chapters, the rates will be compared with the radioisotope techniques conducted as part of this project.

2.4.1 Origin of variation of seepage rates

Rates of ground water discharge as measured by seep meters vary both spatially and temporally throughout the lagoon, but the variations are greater in the northern than in the central study area. Furthermore, there is less systematic variation in the change in seep rates through time at any one individual station in the central area than in the northern area.

There is little systematic variation in the seepage rate with distance from shore (e.g. Figs. 2-2 through 2-5) at any scale. For example, Big Flounder transect extends slightly more than 1000 m from the shore, but stations 6 and 8 exhibit the highest seepage rates, while station 7 exhibits lower seepage rates during May than the near shore stations or the stations on either side. Seepage rates are also random on longer transects, for example in the central region (fig. 5-5), where there is no consistent variation across the width of the lagoon.

At least three factors may be responsible for the large range in seepage rates across the lagoon. These explanations include heterogeneity of permeability in the source rocks, heterogeneous distribution of confining layers, and heterogeneous composition and permeability of the bottom sediments. The first two explanations assume that water from the Floridan aquifer contributes to ground water discharge.

Questions about the control that the Floridan Aquifer may exert on rates of ground water discharge can be addressed by comparing rates from the northern and central area. Because the Hawthorn Group rocks are evenly distributed and sufficiently thick to form a hydrologic separation of the Floridan Aquifer from the overlying water column in the central area, it is unlikely that the variation in seep rate there could be caused by the heterogeneous distribution of permeability in the Floridan Aquifer or by variation in the leakance of the Hawthorn Group rocks. Although there can be little to no influence on ground water discharge from the Floridan Aquifer, the seep rates are high and are variable across the area. Some factor or factors other than flow from the Floridan Aquifer thus must control ground water discharge and its variations in the central area.

The Floridan Aquifer, because of its karst nature, contains heterogeneous permeability, particularly in regions that lack a confining layer (e.g. Bush and Johnson, 1988; Upchurch, 1992). Consequently, if ground water discharge comes from the Floridan Aquifer in the northern area, it should be greater in regions with high permeability (e.g. near conduits) than in regions with low permeability. The range of seep rates suggests that the Floridan Aquifer is not the sole or even primary control of ground water discharge into Indian River Lagoon. If the range of seep rates is caused by variations in the permeability of bedrock, then the measured flow rate that is observed at individual locations should increase proportionately across the region from the dry to the rainy season. Stations with high rates during the dry season sampling should have proportionately greater flow rates following the rainy season. This change in rates is not observed. Stations with low flow during the dry season (IRL7, 25, and 26) experienced some of the greatest increases in flow rates during the rainy season, while some of the highest flow sites during the dry season (IRL18 and 23) show decreases in flow rates during the rainy season.

If the hydrostatic head from the Floridan Aquifer influences ground water discharge, the upward flow will be modified by the permeability distribution in the confining units below the lagoon. Although the distribution of both Hawthorn Group rocks and the overlying Plio-Pleistocene strata is poorly constrained by sparse well control, Hawthorn Gp rocks may be present in the northern field area as discontinuous lenses or as a thin continuous layer that is breached in places. Additional confining units occur within the Surficial Aquifer in the study area and the permeability of the Surficial Aquifer is also somewhat heterogeneous (Toth, 1988). This heterogeneous permeability distribution would contribute to variations in contributions to flow from both the Floridan and Surficial aquifers. Although the thin clay layers within the Surficial Aquifer would be difficult to observe using remote geophysical techniques, it would be possible to map the distribution of Hawthorn Group rock through geophysical techniques. This mapping would provide valuable information to compare with seepage rates in order to test the potential for seepage from the Floridan Aquifer.

The most likely cause of the wide range in seep rate may be the composition and physical properties of the bottom sediments. Visual observations of the sediments during seep meter deployment revealed a wide range of sediments types, varying from black, probably organic-rich mud, to course sand and shell hash layers. There appeared to be a crude correlation between the type of sediment and seep rate, with the slowest rates occurring in the fine grained sediment and the fastest rates occurring in the course sand. Presumably, mud would have lower permeability than the sand and would provide some control over the flow rates. Future work should be designed to compare the bottom sediment composition and physical properties with the flow rate. If a good correlation could be found between flow rate and sediment composition and properties, then the average flow rate for the entire lagoon could be better estimated by mapping the distribution of sediment type and properties over the lagoon. This technique would provide a simpler and more economic way to estimate ground water discharge to the lagoon. A systematic study of the relationship between the physical properties of the bottom sediment and seepage rates would be important to fully understand the causes and controls on groundwater seepage.

56

2.4.2 Comparison with earlier seepage measurements

Seep meters of various designs have long been used in lakes, estuaries and the deep sea to measure advection of water across the sediment water interface (e.g. Belanger and Mikutel, 1985; Belanger and Montgomery, 1992; Belanger and Kirkner, 1994; Gallagher et al., 1996; Cable et al., 1997a;b; Rutkowski et al., 1999). Other methods used to quantify groundwater fluxes into surface water bodies include numerical and analytical models and measurement of chemical tracers in the water column. Numerical models generally rely on estimations or measurements of hydrologic parameters such as potentiometric surfaces, hydraulic conductivity, as well as information of the geological framework (e.g. Pandit and El-Khazen, 1990; Li et al., 1999). These models are important for providing information on the extent of groundwater entering surface water, but like all models are limited to their assumptions and to the quality and extent of measurements of parameters. Nonetheless, models can provide critical information about the potential for groundwater discharge on the basis of the size of recharge areas and estimates of the potential recharge. Natural chemical and isotopic tracers are generally restricted to those that are highly concentrated in the groundwater, but have limited concentrations in the surface water. Recently, activities of radioisotopes of Rn and Ra and concentrations of CH₄ have been used for this purpose (e.g. Ellins et al., 1990; Cable et al., 1996a;b; Rama and Moore, 1996; Bougna et al., 1996).

Table 2-3 provides information on previous calculations and measurements of groundwater discharge to Indian River Lagoon, as well as other locations around the southeastern United States including North Inlet salt marsh in South Carolina (Rama and Moore, 1996), Chesapeake Bay (Gallagher et al., 1996), and the northeastern Gulf of Mexico (Rutkowski et al., 1999; Cable et al., 1996; 1997, Bougna et al., 1996). A variety of techniques were used to measure seep rates including chemical tracers, ground water modeling, and seep meters. The seep rates for all studies have been converted from the values reported in the studies to uniform units of volume area⁻¹ time⁻¹. Reported seep rates commonly provide only a total value for a particular region (e.g. Pandit and El-Khazen, 1990; Cable et al., 1996) and thus the conversion requires estimating the size of the study area.

Location	Technique	Flux	Reference
		(ml/m ² /min)	
Chesapeake Bay	Seep meter (max.)	50	Gallagher et al., 1996
Chesapeake Bay	Model (max)	6	Robinson and Gallagher, 1999
Salt Marsh, SC	Tracer (Ra)	0.12	Rama and Moore, 1996
S. Atlantic Bight	Tracer (Ra)	3	Moore, 1996
S. Atlantic Bight	Model	0.12	Li et al., 1999
N. Gulf of Mexico	Seep meter	10 - 100	Rutkowski et. al., 1999
N. Gulf of Mexico	Seep meter	8-55	Cable et al., 1997
N. Gulf of Mexico	Tracer (Rn & Ra)	43	Cable et al., 1996
N. Gulf of Mexico	Tracer (CH ₄)	10	Bugna et al., 1996
Indian River Lagoon, FL	Seep meter	0-920	Belanger and Walker, 1990
Indian River Lagoon, FL	Seep meter	40 - 65	Martin et al., 2000
Indian River Lagoon, FL	Tracer (Rn & Ra)	11 - 66	Martin et al., 2000
Indian River Lagoon, FL	Model	0.002	Pandit and El-Khazen, 1990

Table 2-3. Seepage rates to various estuaries and coastal zones determined by direct measurements, tracers, and modeling.

In the northeastern Gulf of Mexico, all Miocene and younger sediments have been removed by erosion, leaving the pre-Miocene carbonate rocks of the Floridan Aquifer separated from the overlying water column only by a thin veneer of Recent sediments. This setting thus provides a similar geologic setting to the northern Indian River Lagoon. The South Carolina salt marsh and Chesapeake Bay site would be characterized by different geological settings, but are included within the table for comparative purposes.

The direct measurement techniques all show similar fluxes or ranges of fluxes for each study area, generally on the order of a few up to hundreds of ml/m²/min. These values are found regardless of the technique (either seep meter or chemical tracer) or the geological setting. The one anomalously high measurement is located in the Indian River Lagoon. Belanger and Walker (1990) suggested this high value resulted from a breach in the Hawthorn Group, which would provide a large input of groundwater. In contrast to the direct measurement techniques, the one example of modeling of ground water discharge shows input of groundwater approximately 4 to 5 orders of magnitude smaller than the directly measured ground water discharge rates (Pandit and El-Khazen, 1990). The low rates calculated by Pandit and El-Khazen (1990) could reflect difficulty determining variables required for models such as hydraulic conductivity (e.g. Belanger

and Walker, 1990). Hydraulic conductivity is particularly difficult variable to measure in heterogeneous aquifers including the Surficial Aquifer. The value from the Pandit and El-Khazen, (1990) model also represents an extrapolation to the entire 568 km² surface area of the lagoon (Smith, 1993) from a single transect across the lagoon at Jensen Beach.

An alternate explanation for the large difference between modeled and measured rates could be that the direct measurements include discharge from sources of water that are not included in the ground water models. For example, the conceptualization made by Pandit and El-Khazen (1990) for their model calculations includes only the Surficial Aquifer. In this model, the Surficial Aquifer is hydrologically separated from the Floridan Aquifer by the Hawthorn Group, i.e. the top of the Hawthorn Group is treated as a no flow boundary. The extreme heterogeneity in seepage rates found by Belanger and Walker (1990) and in this study (Appendix A) indicate that hydraulic conductivity and possibly sources of water, could vary across the study area. Although Belanger and Walker (1990) suggested that the Floridan Aquifer could provide an additional source of water, the thickness of the Hawthorn Group in the Jensen Beach area indicates that the no flow assumption in Pandit and El-Khazen's (1990) model is reasonable. An alternate source of water, however, could be from recirculated seawater (e.g. Li et al., 1999). Such a source would be sampled by direct measurement methods, but has not been included in values calculated by Pandit and El-Khazen (1990).

Recently, Li et al. (1999) derived a analytical solution to a set of equations that describe flow and chemical transport in the nearshore. Their results indicate that as much as 96% of ground water discharge comes from seawater that enters the sediment through tidal and wave pumping. The remaining 4% of ground water discharge comes from water that fell on the land surface (i.e. meteoric water) and flows through the subsurface (i.e. ground water in Pandit and El-Khazen's 1990 model). Consequently, assuming that the seep rates measured in this study and by Belanger and Walker (1990) are accurate measurements of the ground water discharge into the lagoon, but that only 4% of this seepage represents groundwater that has flowed to the lagoon following recharge of precipitation inland, the average flux rates to the lagoon of new groundwater (i.e. non-recirculated seawater) would be on the order of 1.6 to 3.3 ml/m²/min. These values are still three orders of magnitude greater than found by Pandit and El-Khazen (1990) (Table

2-3). Either there are incorrect assumptions in the model, variables are not accurately represented in the model, and/or there are additional sources of water that are measured but not included in the model. The possible sources of water flowing from seep meters is discussed in Chapter 5.

2.4.3 Flushing rates in the northern lagoon

The flux of seepage water into the northern Indian River lagoon is critical for determining the residence time or flushing rate for water in the lagoon. The residence time in turn is a critical variable for using chemical tracers (discussed in Chapters 3 and 4) because it control the expected concentrations or activities in the water column along with their chemical or radioactive decay terms. The flushing rate for Indian River Lagoon has previously been calculated using a numerical model that uses the continuity equations with measured water level data and freshwater input including precipitation, surface runoff and groundwater seepage, and water loss through evaporation (Smith, 1993). All data are well constrained with the exception of the groundwater input. For this value, Smith (1993) relied on the modeled data from Pandit and El-Khazen (1990).

Model results for the flushing rate are reported as 50% renewal time (R_{50}). This value represents the amount of time for a modeled tracer with a concentration of 1000‰ in ocean water reaches a concentration of 500‰ in the various segments of the lagoon. The model is thus arranged so that net water flow is from the ocean to the lagoon. Nonetheless, the value for R_{50} increases from the central to the northern end of the lagoon because the three inlets that connect the lagoon with the Atlantic Ocean are located in the southern half of the lagoon. The value of R_{50} ranges from 0.3 days at the inlets to 6 to 8 days in the lagoon south of Sebastian Inlet. These values of R_{50} are insensitive to the extent of precipitation or the non-tidal water level fluctuations. In the northern reaches of the lagoon where there are no inlets and little tidal exchange the value of R_{50} approaches one year and is highly sensitive to both non-tidal water levels and to precipitation.

An alternate approach to calculate the flushing rate is to estimate the volume of water entering the lagoon and to calculate the length of time required to fill the lagoon. These calculations are made below for the northern study area using the measured seep

rates and assuming that ground water discharge represents the sole input of water. The study area covers ~48 km², with an average water depth of 1.2 m. The volume of the basin is thus ~5.8 x 10^7 m³. The average groundwater seepage rate is 39.9 ml/m²/min and 63.1 ml/m²/min during May and August respectively (Table 2-2). Extrapolating these rates across the entire study area, it would take 21 and 13 days to fill the entire lagoon with rates measured in May and August respectively. If a large fraction of ground water discharge measured by seep meters actually represents recirculated seawater (e.g. Li et al., 1999), then these calculated flushing rates do not represent the amount of time for water to flow from the lagoon. Instead, they would represent the time required for lagoon water to circulate through the lagoon bottom sediments.

2.4.4 Comparison of Seep Rates in the Northern and Central Study Areas

The average seep rates are lower in the central than the northern study area. Several possibilities could cause the difference between the two areas. Although the thicker Hawthorn Gp effectively separates the Surficial and Floridan aquifers, the Floridan Aquifer probably contributes little to ground water discharge. The land surface elevation is slightly higher in the north; approximately 2 km east of the lagoon, it ranges up to ~15 m above sea level in the northern area, but only ~11.5 m above sea level in the central area. The regional subsurface geology appears to have little control over the volume of ground water discharge. Several other factors could decrease the seep rates from the north to south.

Water depth is significantly shallower in the north area than the central study area and the bottom sediment appears to be sandier in the northern than the central area. If much of the ground water discharge results from wave or tidal pumping of water through the shallow sediment, e.g. within a few 10's of centimeters to a few meters (e.g. Li et al., 1999), then the deeper water in the central study area may reduce the effect of these processes. Shallow water also may result in overall coarser grain sized sediment in the northern area because of the increased amount of winnowing of the fine grained sediment. The coarse sediment would likely be more permeable than the fine grained sediment of the central area, allowing more extensive circulation through shallow sediments by wave and tidal pumping.

An additional process that could cause circulation of water through shallow sediments is from bioturbation and biological pumping of water into the sediment (e.g. Emerson et al., 1984). The data collected as part of this project is insufficient to constrain this potential process, but future studies should be designed to distinguish and separate the different physical and biological processes that could cause pumping of lagoon water through the shallow sediments.

2.5. Summary and Recommendations

There are significant differences between the amount of ground water discharge to the Indian River Lagoon that are made on the basis of hydrologic models and that are measured directly using seepage meters. Although some of the differences could be explained by incorrect assumptions in the hydrologic models, this explanation is unlikely to cause the magnitude of the differences that have been observed. Artifacts in the measurements that are derived from the design of seep meters may also explain the differences, but extensive work has focused on determining the validity of seep meter results (e.g. Belanger and Montgomery, 1992; Cable et al., 1997). Assuming that seep meters and the hydrologic models both provide a measure of seep rates that are internally accurate within a factor of two to three, the simplest conclusion is that these two techniques measure different processes. For example, the numerical model of Pandit and El-Khazen (1990) calculates only the input of ground water to the lagoon from meteoric water that is recharged to the Surficial Aquifer. The chemical composition of the seep water is similar to that of the lagoon water (discussed in Chapter 5), and thus it is likely that the seep meter technique measured the input of lagoon water along with a small fraction (perhaps as much as 4 %, e.g. Li et al., 1999) of "new" water from either the Floridan or the Surficial aquifer. The mechanism driving the input of lagoon water to the seepage meters is unknown, but could come from wave and tidal pumping (e.g. Li et al., 1999) or from biological pumping (Emerson et al., 1984).

These results indicate that it is important to determine the cause of the differences between seep rates based on seep meters and those based on the modeling. One way to begin to understand this dilemma is through detailed spatial and temporal measurements of pore water gradients. If the flux of water to the seep meters is derived from shallow sections of the sediment, then variations in the surface water chemistry should show up as variations in the pore water chemistry as well. Work on pore water compositions was initiated during the 1999 field season and expanded during the 2000 field season. In addition to the pore water compositions, additional information about the local geology should also be collected. In particular, physical properties such as permeability and porosity of sediments near the sediment water interface in the lagoon might be able to provide information about the ability of lagoon water to circulate through the sediments. Initially this test should be done in small regions of the lagoon, for example by taking locations from both the central and northern study areas that have demonstrated high and low flows. These areas could easily be cored and the cores measured for sediment composition, porosity, and permeability. Simultaneously with the coring, the pore water gradients could be measured.

Ground Water Discharge and Nutrient Loading - Indian River Lagoon

CHAPTER 3 – RADIUM ISOTOPES AS TRACERS ACROSS THE SEDIMENT-WATER INTERFACE

3.1 Introduction

Natural isotopic disequilibria can readily occur in ground water and coastal waters between pairs of isotopes in the ²³⁸U, ²³⁵U and ²³²Th decay series. For example, disequilibria between 238 U and 234 U (i.e., 234 U/ 238 U ratios) have been observed to range from 0.5 to over 20 in varied ground waters (Osmond and Cowart, 1982; Asikainen, 1981; Dickson et al., 1983). Laboratory experiments confirm that uranium isotopes are fractionated by alpha recoil effects (Fleischer, 1982; Sun and Semkow, 1998), as well as by physico-chemical differences in oxidation states and bonding energies (Beneš et al, 1982). Similar processes also effect the fractionation of other isotopes in the U-Th decay series (Fig. 3-1), such as Th, Ra, Pb or Po (Ivanovich and Harmon, 1982). However, it is often easier to explain such disequilibria by the chemical properties and long half-lives of the intermediate radionuclides. Decay of ²³²Th to ²²⁸Th, for example, occurs via the decay of ²²⁸Ra, and in this decay sequence each parent-daughter radionuclide exhibits unique geochemical behaviors that facilitate isotopic disequilibria (Kadko, 1987). Coastal bottom sediments older than ~10 years will therefore likely have thorium activity ratio (²²⁸Th/²³²Th) much less than one (Ivanovich and Harmon, 1982), while the overlying water column activity ratios can become quite large (5-30).

In the past, often only two of the four naturally occurring isotopes of radium were considered to be useful in environmental disequilibrium studies (Cochran, 1980; Rama and Moore, 1984). As the daughter of ²³⁰Th, ²²⁶Ra ($t_{1/2}$ = 1600 yr) is usually present in excess of its parent in natural waters, and the greater solubility of Ra over Th facilitates



Figure 3-1. Decay chains of the U and Th series isotopes and the half life of each isotope. The vertical arrows represent alpha decay and the diagonal arrows represent beta decay.

the upward diffusion of radium across the sediment-water interface (Li et al., 1977; Webster et al., 1994, 1995; Hancock and Murray, 1996). Current estimates suggest that about 25% of ²²⁶Ra in seawater originates from coastal sediments via such diffusion/advection (Ivanovich and Harmon, 1982). Radium-228 ($t_{1/2} = 5.75$ yr), is the direct daughter of ²³²Th, and like ²²⁶Ra, is also found in excess of its parent in natural waters due to diffusion/advection (Hammond et al., 1990; Ghose et al., 2000). The remaining two radium isotopes, ²²³Ra and ²²⁴Ra, have much shorter half-lives of 11.4 days and 3.7 days, respectively. Only due to recent advances in detection capabilities (Moore and Arnold, 1996) can we now begin to utilize these 'new found ' isotopes as short-lived water mass or sediment-water interface tracers (Swarzenski, 1999; Hancock et al., in press). Collectively, radium isotopes can thus provide a powerful suite of naturally occurring tracers that span a time window from days to 1000's of years.

If we assume a constant rate of supply from a parent nuclide, then the activity of a particular daughter isotope in solution can be expressed by the first order decay equation:

$$A_t = A_{\infty}(1 - e^{-\lambda t})$$

where *t* is the contact time between a solid and solution, A_t is the activity at time *t*, A_{∞} is the activity at secular equilibrium, and λ is the decay constant ($\lambda = \ln 2/t_{\frac{1}{2}}$). For either ²²³Ra or ²²⁴Ra, λt is considerably larger than 1; even in relatively 'young' waters the expression ($1 - e^{-\lambda t}$) rapidly approaches 1 (equilibrium) as *t* exceeds ~ 50 days (about five half-lives). In contrast, for long-lived ²²⁶Ra, $\lambda_{226}t$ is much less than 1, and thus ($1 - e^{-\lambda t}$) remains close to the value of $\lambda_{226}t$. Therefore, where ground-water residence times are small, one will likely obtain high values of ²²³Ra/²²⁶Ra ratios relative to equilibrium (²²³Ra/²²⁶Ra = 0.046) values, i.e., (²²³Ra/²²⁶Ra)_t will approach (²²³Ra/²²⁶Ra)_∞/ $\lambda_{226}t$. One objective of this chapter is thus to evaluate the utility of short-lived radium isotopes as sediment-water interface tracers in Indian River Lagoon, where it is hydrogeologically feasible that 'recycled' or meteoric ground water can discharge into lagoon bottom waters.

3.2 Sampling and Analytical Methods

The field effort for this project was divided into two primary focus areas (north and central) that were most often sampled according to dry (May, 1999) and wet (August, 1999) precipitation seasons (see Chapters 1 and 2). An unusually large number of energetic tropical weather systems (Floyd: 09/99, Harvey: 09/99 and Irene: 10/99) directly affected our study area in 1999 by increased precipitation and associated wind-

driven storm surge (Table 1-1) that directly affected resuspension and exchange rates across the sediment-water interface.

A series of ground water samples from private and monitoring wells as well as inlet/river samples was also collected during each field effort around the perimeter of each of our field sites (Table 1-3; Figure 1-6). At these ground water sites, each well was first purged and then sampled using either a peristaltic or a rotary vane pump. To ensure adequate purge volumes, hydrologic parameters such as pH, dissolved oxygen, conductivity, salinity and temperature were simultaneously measured. The inlet/river samples were collected similarly to the lagoon surface water samples.

Twenty-liter samples of ground water were collected for radium isotopes. Water samples from the lagoon proper were collected from a series of shore-perpendicular transects, from several end-member sources (e.g., Turnbull Creek, Haulover Canal, Sebastian Inlet, and major rivers), as well as from numerous mid-lagoon sites (Table 1-1; Appendix B). For radium, large volume (40 - 150 L) lagoon samples were collected approximately 20-cm off the sediment water interface with a rotary vane/peristaltic pump. Interstitial waters were also collected for radium analyses using three unique methods; conventional-type (diameter = 60 cm) seep meters (Lee, 1977), multi-samplers consisting of an array of finely screened tubing, and 60.75-L benthic flux chambers.

Radium was quantitatively removed from all water samples onto pre-weighed MnO_2 impregnated acrylic fiber packets. A second Mn column placed in series to the first column was used to periodically monitor the efficiency of Ra adsorption onto the impregnated fiber. Uncertainties in Ra isotope activities correspond to 1σ counting errors.

Ground water and lagoon surface/interstitial water samples were analyzed for the two short-lived radium isotopes by delayed coincidence alpha scintillation counting. Mn fibers were transferred to the laboratory as soon as possible to minimize the loss of radium due to radioactive decay. The fibers were rinsed in distilled and de-ionized water to remove sea salts, partially air dried, and then placed into a He gas recirculating line linked to a 1.1-L scintillation cell directly connected to 5" photo-multiplier tubes (PMT). Scintillation signals were routed via a Ortec PMT base to a delayed coincidence computer program that time discriminated alpha decays of ²¹⁹Rn and ²²⁰Rn produced by

the radioactive decay of ²²³Ra and ²²⁴Ra (Moore and Arnold, 1996). The Mn fibers were subsequently re-analyzed after about 4 - 6 weeks to allow for the initial excess ²²⁴Ra to equilibrate with ²²⁸Th, which also quantifiably adsorbed to the fiber. Background activities in each of the two delayed coincidence systems were monitored after every sample run. Isotopic standards derived from ²²⁷Ac and ²³²Th were analyzed periodically, as well as after each batch sample run (approximately every twelfth sample). Activities of ²²⁶Ra were measured on a separate water sample either by Rn emanation or by γ -ray spectrometry (See Chapter 4).

3.3 Results and Discussion

3.3.1 Hydrography

Indian River Lagoon (IRL) is subtropical in climate, and precipitation generally follows a bimodal seasonal pattern. A typical dry season period extends from December through May. During both primary sampling trips to the northern sites in 1999, monthly precipitation values were considerably greater (~130 - 160%) than the 30-yr accumulated rainfall averages (see Chapter 1, Table 1-3). Nonetheless, during the dry season (May 1999) sampling trip, salinity in the upper study site was typically in excess of seawater (35), and averaged 38.1. Water column temperatures fluctuated daily from a low of 23 -27 °C. The \sim 9% enrichment in lagoon salinities relative to open ocean seawater values reflect heightened rates of evaporation of lagoon water relative to water mass renewal rates. The salinity of Turnbull Creek, which traverses a large wetland north of IRL, was only slightly below 35, and further suggests minimal fresh water exchange and long water residence times in the lower reaches of this distributary wetland system. Haulover Canal forms the only surface water connection between upper IRL and Mosquito Lagoon, which is another shore-parallel coastal lagoon system that does have limited exchange with the Atlantic Ocean. Small-scale baroclinic forces facilitate water exchange through Haulover Canal. The salinity of Haulover Canal (36.1) indicates an integration of water mass mixing and transport processes water within these two lagoon systems.

During August 1999 average water column salinities (36.2) and water temperatures were consistently lower than during the May cruise. In contrast, ground water samples from the same well sites reflect little change in either temperature or conductivity from wet to dry season. In 2000, there was a notable increase in average salinity values from May through December (22.3 to 28.3) in the central IRL study region, while in Banana River Lagoon (BRL) salinities were highest (salinity = 29) in August. These salinity patterns are not concomitantly observed in the average temperature ranges.

3.3.2 Ground Water

Sources for ground water on the east coast of Florida can consist of several discrete components that originate from the Surficial, Intermediate or Floridan Aquifers (see Chapter 1 for a review of the geologic setting of upper Indian River Lagoon). The Surficial Aquifer is contained within highly permeable Plio-Pleistocene strata and usually responds rapidly to local precipitation/evaporation events. There is evidence of discontinuous confining layers within the Surficial Aquifer (Toth, 1988), which could facilitate vertical ground water mixing. A deeper Eocene (~ 40 million year old) Ocala Limestone forms one of the most productive formations of the Floridan Aquifer system. Above the Ocala Formation, the clay-rich confining Hawthorn Group generally thins out in the vicinity of the northern study site (Fig. 1-2), and discontinuous, inter-bedded limestone deposits may contain ground water of various sources (Surficial to Floridan).

Regional-scale potentiometric surface maps of the Upper Floridan suggest a positive hydrostatic head differential relative to sea level in upper Indian River Lagoon (Figures 3-2 and 3-3). Based on such maps that rely on a network of variable well data, the potentiometric surface of the upper Floridan does not appear to fluctuate by more than +/-2 m seasonally.

3.3.3 Radium Isotopes

The lagoon, ground water and pore water radium isotope activities for the 1999 and 2000 field effort are compiled in Appendix B. The ensuing discussion will describe and interpret the behavior of Ra from the following sample sets: 1) overall seasonal and



Figure 3-2. Potentiometric surface map of the Upper Floridan Aquifer in the Indian River Lagoon region, May 1998. (After Bradner, 1998.)


Figure 3-3. Potentiometric surface map of the upper Floridan Aquifer in the Indian River Lagoon region, May 1999. (After Knowles and Bradner, 1999.)

Sample type	Depth	²²³ Ra	ex ²²⁴ Ra	228Th	²²⁶ Ra	223/226	224/223			
	(m)	(dpm/L)	(dpm/L)	(dpm/100L)	(dpm/L)	AR*	AR			
			May, 19	999						
Lagoon waters										
Mean	1.21	0.10	0.09	3.86	2.05	0.05	0.98			
STDEV	n/a	0.03	0.02	1.29	0.23	0.01	0.36			
Ground water	s									
Mean	29.70	1.38	6.86	23.77	3.59	0.46	9.97			
STDEV	n/a	1.54	3.49	0.41	2.06	0.41	7.41			
Creek and	l inlet wa	ters								
Mean	n/a	0.08	0.14	3.14	2.42	0.03	1.70			
STDEV	n/a	0.05	0.11	0.18	0.60	0.01	0.29			
			August, 1	1999						
Lagoon										
waters		0.4.0	0.44		• • •	0.04				
Mean	1.07	0.10	0.11	3.39	2.63	0.04	1.16			
STDEV	n/a	0.02	0.02	0.82	0.26	0.01	0.32			
Ground water	Ground waters									
Mean	29.70	0.87	5.28	23.87	n/a	n/a	6.88			
STDEV	n/a	0.31	2.70	0.38	n/a	n/a	4.54			
Creek and inlet w	vaters									
Mean	n/a	0.10	0.14	2.56	3.01	0.03	1.35			
STDEV	n/a	0.05	0.09	0.31	0.73	0.01	0.26			

Table 3-1. Mean radium and ²²⁸Th activities for lagoon, ground water and creek/inlet water (May, August 1999).

*AR =activity ratio (unitless)

yearly trends, 2) end members (ground water, inlet and river samples), 3) shoreperpendicular transects, 4) mid-lagoon stations, and 5) interstitial waters.

The two short-lived radium isotopes (^{223,224}Ra) exhibited slight spatial and temporal variability at all Indian River Lagoon sites (Table 3-1). Average radium activities were consistently higher during the rainy season (August) during both 1999 and 2000 field seasons (Table 3-2). An expected wet season imprint on decreased salinity values in the lagoon can only be observed in the inlet/river sample suite. For these samples, the salinity decreased from an average value in May/December of 25 to a value of 21.9, as observed in August of 2000. During 2000, the ^{223, 224}Ra activities of the

Site/sampling trip	Salinity	Conductivity	Oxygen	pН	Temperature	²²³ Ra	ex ²²⁴ Ra
		(mS/cm)	(mg/L)		(°C)	(dpm/100L)	(dpm/100L)
Indian River Lagoon							
May	22.3	35.3	7.3	8.3	28.1	4.57	47.07
August	28.3	43.7	6.8	8.1	28.8	6.44	50.40
December	28.4	44.7	8.0	8.5	16.8	5.41	43.36
Banana River Lagoon							
May	19.7	31.5	6.6	8.6	27.8	2.50	39.53
August	29.0	45.0	5.7	8.5	28.3	5.69	59.89
December	23.9	38.2	10.15	8.7	16.6	3.72	30.48
Ground waters							
May	1.0	1.9	0.6	7.0	26.3	26.18	86.65
August	1.1	2.1	1.3	7.5	27.7	36.18	42.37
December	1.0	1.9	1.7	7.7	27.2	75.75	80.2
Rivers/Inlets							
May	25.2	42.8	6.4	8.3	29.0	10.04	87.45
August	21.9	34.1	7.2	7.9	30.7	6.85	53.96
December	25.0	39.0	7.8	8.6	22.6	9.45	36.72

Table 3-2. Year 2000 average radium activities and water column parameters.

inlet/river samples were on average slightly higher than IRL and BRL activities. Such elevated activities may be due to heightened ground water-surface water exchange in the tidal creeks/rivers. As expected, average ground water ²²³Ra activities were almost an order of magnitude greater than ²²³Ra activities observed in lagoon waters. This observed enrichment in the ²³⁵U series radium daughter activities likely stems from the uranium-rich phosphatic deposits of the Hawthorn formation. In contrast, the ²²⁴Ra activities in the ground water samples were of similar magnitude to the river/inlet values. The two sources of surface water to upper Indian River Lagoon (Haulover Canal and Turnbull Creek) were comparable to lagoon water Ra activities. In these inlets, mean ²²³Ra activities increased slightly from May to August, while ²²⁴Ra remained constant.

Radium isotope mass balance estimates, as estimated by salinity, temperature and radium, do not suggest significant unique water exchange through either of these upper Indian River Lagoon inlets. This does not imply zero net water exchange per se (Smith, 1992), but rather indicates that surface water radium activities in the inlets and lagoon waters are insensitive to surface water mass movements.

Ground water ^{223,224}Ra activities from wells surrounding upper Indian River Lagoon were also typically an order of magnitude greater than lagoon water activities. The highest ²²⁴Ra activities (~ 10 dpm/L) in upper IRL were observed at wells GW2,4, which are among the deepest wells (~ 37 m) in our field site and likely tap the Upper Floridan aquifer. The shallower wells (GW3,6) access the Surficial Aquifer and exhibit widely fluctuating radium activities (²²³Ra: 0.39 – 4.61 dpm/L and ²²⁴Ra: 1.34- 7.96 dpm/L). At GW4, the ²²⁴Ra/²²³Ra ratio exceeded a value of 14 during August 1999. Such elevated ratios reflect variations in U/Th isotopic compositions of the source strata (Osmond and Cowart, 1982; Rama and Moore, 1984).

There is no apparent correlation between well depth and radium activities for either field season. The variable radium activities and activity ratios suggest abundant lateral and vertical transport between the Upper Floridan and Surficial Aquifers. Well GW-3 extends only into the Surficial Aquifer (open depth = 1.5 - 4.6 m), yet it has an isotopic signature that implies a mixture of several ground water sources. The mobility of ground water can be considerably enhanced through karst conduits or through fractures. Due to rapid sorption reactions, the mobility of radium once released to solution by alpha recoil or by decay of Th is likely to be very limited. Thus the source for radium in ground water is usually close to the well structure itself (Asikainen, 1981; Dickson et al., 1983; Rama and Moore, 1984).

Shore-perpendicular transects within the lagoon generally have highest excess ²²⁴Ra and ²²³Ra activities at stations closest to shore. This is in contrast to average salinity trends that are typically either highest at mid-transect stations or show very little variation from station to station along a given transect. Plots of water column ^{223,224}Ra activities versus salinity in central IRL and BRL suggest only a weak correlation between Ra and salinity, although there is a pronounced shift in the distribution of ²²³Ra and ²²⁴Ra from May/December to August as a function of salinity (Figs. 3-4 - 3-6). IRL samples



May, 2000 water column ^{223,224}Ra activities

Figure 3-4. Salinity versus ^{223,224}Ra activity plots for Indian River Lagoon and Banana River Lagoon during May 2000.



August, 2000 water column ^{223,224}Ra activities

Figure 3-5. Salinity versus ^{223,224}Ra activity plots for Indian River Lagoon and Banana River Lagoon during August 2000.



December, 2000 water column ^{223,224}Ra actvities

Figure 3-6. Salinity versus ^{223,224}Ra activity plots for Indian River Lagoon and Banana River Lagoon during December 2000.



Figure 3-7. Salinity versus ²²³Ra/²²⁴Ra activity ratio plots for Indian River Lagoon and Banana River Lagoon surface water samples during May 2000.





Figure 3-8.Salinity versus ²²³Ra/²²⁴Ra activity ratio plots for Indian River Lagoon and Banana River Lagoon surface water samples during August 2000.



December, 2000 water column ²²³Ra/²²⁴Ra activity ratios

Figure 3-9. Salinity versus ²²³Ra/²²⁴Ra activity ratio plots for Indian River Lagoon and Banana River Lagoon surface water samples during December 2000.

collected in May 2000 exhibited the greatest range salinity (21 to 27), while the December BRL samples were clustered close to a salinity of 24. In both Indian- and Banana River Lagoons, water column ^{223,224}Ra activities were highest in August 2000.

Year 2000 water column ²²³Ra/²²⁴Ra activity ratio plots versus salinity for Banana River Lagoon and Indian River Lagoon show both spatial and temporal variability. In May 2000, the ²²³Ra/²²⁴Ra ratio increased as one moved further south in Indian River Lagoon from Transect 1 to Transect 4. This increase in ²²³Ra/²²⁴Ra activity ratios is also observed in the salinity distribution. There appears to be a direct relation between salinity and ²²³Ra/²²⁴Ra activity ratios – the greatest observed ²²³Ra/²²⁴Ra ratios were recorded in lagoon waters with the highest salinities.

In 2000, the ²²³Ra/²²⁴Ra activity ratio increased in both Indian River Lagoon and Banana River Lagoon from May to December. Because of the elevated ²²³Ra/²²⁴Ra activities ratios observed in surrounding ground water (Appendix B), it is likely that the increased water column radium ratios might reflect a heightened ground water contribution. This signal is likely to be enhanced later in the year when the aquifer becomes recharged by precipitation.

A plot of ²²³Ra from samples with water depths less than 1.5 m (removing the mid-lagoon samples) in northern IRL suggests a potential correlation with water depth (Fig. 3-10). However, such a bottom effect is clearly not evident using ²²³Ra/²²⁶Ra ratios, although most values suggest a lowered (i.e., depleted) ²²³Ra activity relative to the secular equilibrium isotopic ratio (²²³Ra/²²⁶Ra = 0.046). It is possible that this bottom effect may indicate a time-dependent dilution of water being exchanged across the sediment-water interface. Because of the short half-life of ²²³Ra and ²²⁴Ra, exchange processes at the sediment-water interface may be examined with much greater resolution than using only long-lived radium isotopes (^{228,226}Ra).

To quantify exchange across the sediment-water interface in upper Indian River Lagoon, two methods will be presented that provide an indirect measure of flux, albeit on very different spatial scales. These results will then be compared to a simple diffusion model (Berner, 1980; Santschi et al., 1990; Hammond et al., 1999) using interstitial radium profiles.

3.3.4 Flux measurements

To estimate flux across the sediment-water interface in northern Indian River Lagoon, input and removal functions for water and radium must be well constrained. The field site at upper Indian River Lagoon is assumed to be effectively isolated from adjacent surface water bodies except at Haulover Canal, which connects Mosquito River Lagoon to Indian River Lagoon. By comparing salinities, Turnbull Creek thus forms a



Figure 3-10. Water column (z < 1.5 m) profile of ²²³Ra activities (dpm/L) and ²²³Ra/²²⁶Ra activity ratios (August, 1999). The deep-water stations have been excluded here to look only at sediment effects and dilution.

northward extension of Indian River Lagoon. It is expected that only during high precipitation events that Turnbull Creek will discharge freshened waters to upper Indian River Lagoon. At the southern boundary of the study site, dredged materials from the Intracoastal Waterway form a 'quasi' sill that limits water exchange with Indian River Lagoon proper. Generalized flow in upper Indian River Lagoon can therefore be expressed simply as a function of the lagoon area, A and the time-dependent mean water depth, h(t):

$$Q = A \frac{dh}{dt}.$$
(3-2)

Water levels in this confined region of the lagoon are controlled seasonally by winds, precipitation/evaporation and tidal oscillations (Smith, 1992; 1993). Due to the small tidal amplitude of upper Indian River Lagoon, water transport through Haulover Canal is assumed to be a wind-driven process (Smith, 1992). As suggested, this is a potential source and/or sink for lagoon water radium isotopes. Although the mean inlet ²²³Ra activities are comparable to lagoon values for both field seasons (Table 3-1), ²²⁴Ra activities were consistently higher in Turnbull Creek, suggesting a possible marine source, via thorium decay.

The flux of radium in upper Indian River Lagoon is calculated first by simple mass balance ('lagoon budget method'). In doing so, the time-dependant mass of Ra in the lagoon (VRa_L) can be modeled as function of the area-integrated flux of Ra across the sediment-water interface (AJ) plus the mass of Ra being transported through Haulover Canal (QRa_{inlet}) , minus the mass of Ra lost due to radioactive decay (λVRa_L) :

$$\frac{d}{dt}(VRa_L) = AJ + QRa_{inlet} - \lambda VRa_L, \qquad (3-3)$$

where V is the volume (m³), Ra_L is the radium activity in the lagoon (dpm/L), J is the flux (dpm/m²/d) of radium from the lagoon sediment into the water column, and Ra_{inlet} is the Ra activity at Haulover Canal. The term J is estimated by adjusting its value until it matches the observed lagoon activities, Ra_L .

3.3.5 Benthic Flux Chambers

Exchange across the sediment-water interface may also be constrained on a very localized scale by the use of benthic flux chambers (Fig. 3-11). The flux of radium into such chambers can be evaluated by assessing the change in Ra activity over the deployment



Figure 3-11. Idealized placement of a benthic flux chamber into bottom sediments.

 Table 3-3. Time series radium activities in two benthic flux chambers (upper Indian River Lagoon).

Date	Time (hours)	²²³ Ra (dpm/L)	ex ²²⁴ Ra (dpm/L)	²²⁸ Th (dpm/100L)	²²⁶ Ra (dpm/L)
der Trai	nsect				
8/17/99	initial @ $t = 0$	0.12 ± 0.01	$0.11 \ \pm \ 0.01$	$3.42 \ \pm \ 0.34$	$2.34~\pm~0.43$
	t = 4				2.69 ± 0.11
	t = 8	0.14 ± 0.01	$0.13 ~\pm~ 0.01$	$3.38 \ \pm \ 0.34$	$2.93~\pm~0.17$
	Date der Tran 8/17/99	DateTime (hours)der Transect $8/17/99$ initial @ $t = 0$ $t = 4$ $t = 8$	DateTime (hours) 223 Ra (dpm/L)der Transect8/17/99initial @ $t = 0$ $t = 4$ $t = 8$ 0.14 \pm 0.01	Date Time (hours) ²²³ Ra (dpm/L) $ex^{224}Ra$ (dpm/L) der Transect (dpm/L) (dpm/L) $8/17/99$ initial @ $t = 0$ 0.12 ± 0.01 0.11 ± 0.01 $t = 4$ $t = 8$ 0.14 ± 0.01 0.13 ± 0.01	Date Time (hours) 223 Ra (dpm/L) ex^{224} Ra (dpm/L) 228 Th (dpm/100L) der Transect (dpm/2) (dpm/2) (dpm/100L) $8/17/99$ initial @ $t = 0$ 0.12 ± 0.01 0.11 ± 0.01 3.42 ± 0.34 $t = 4$ $t = 8$ 0.14 ± 0.01 0.13 ± 0.01 3.38 ± 0.34

Ground Water Discharge and Nutrient Loading - Indian River Lagoon

	initial @ $t = 0$	0.12 ± 0.01	$0.11 ~\pm~ 0.01$	$3.61 ~\pm~ 0.36$	$2.46~\pm~0.10$
Box 2	t = 4	0.11 ± 0.01	$0.10~\pm~0.01$	$3.34 \ \pm \ 0.33$	$2.50~\pm~0.14$
	t = 8	0.13 ± 0.01	$0.12 \ \pm \ 0.01$	$3.76 ~\pm~ 0.38$	$2.65 ~\pm~ 0.31$

duration. We positioned two benthic flux chambers (Boxes 1 and 2) about 3 cm into the seabed at IRL-6, in about 1 m of water. The two benthic flux chambers were placed about 2 m apart (see Chapter 4). The 45 x 45 x 30 cm boxes were periodically hand-stirred to maintain a well-mixed chamber water column. The initial (t = 0) activity of radium was measured in a water parcel adjacent to the chamber (Table 3-3).

Because an unknown amount of ambient lagoon or subsurface water may be hydraulically drawn into a benthic chamber during time-series (t = 4,8 hr) sampling, the following corrections were applied to Ra_{ch} (after Hancock et al., in press), assuming that the chambers were reasonably well-mixed for the duration of the experiment:

$$Ra_{ch} = (Ra_{18} - Ra_L)b\frac{1}{(1 - e^{-b})} + Ra_L,$$
(3-4)

where Ra_{ch} is the radium activity within the chamber, Ra_{t8} is the radium activity measured at the conclusion of the experiment (t = 8) and b is the sample-to-chamber volume ratio. Short-lived radium isotope activities increased by about 15% over the 8-hr deployment period. Similarly, ²²⁶Ra activities increased about 7 – 20% in the two chambers during the 8-hr experiment.

For a chamber of height h_c , the change in radium activity (Ra_{ch}) can be expressed as a function of the sediment-water interface flux (J):

$$\frac{dRa_{ch}}{dt} = \frac{J}{h_c} - \lambda Ra_{ch} \tag{3-5}$$

Setting the initial chamber activity equal to the corresponding lagoon activity ($Ra_{ch} = Ra_L$, t = 0) as a boundary condition and assuming a constant value for *J* (integrated over the surface area beneath the chamber) provides the following solution to Eq. 3.5:

$$\frac{J - h_c \lambda R a_{ch}}{J - h_c \lambda R a_L} = e^{-\lambda t},$$
(3-6)

which can be rearranged for *J*, as follows:

$$J = \frac{h_c \lambda (Ra_{ch} - Ra_L e^{-\lambda t})}{1 - e^{-\lambda t}}$$
(3-7)

The calculated fluxes will be compared with results from other techniques in section 3.5.7 (e.g. Table 3.5). Minimum propagated errors for *J* are based on $\pm 1 \sigma$.

3.3.6 Pore Water Profiles

Pore water profiles can provide valuable information regarding exchange rates and processes across the sediment-water interface. The exchange of radium across the sediment-water interface as well as the shape of the interstitial Ra profile depend on the rate of Ra production from sediment-bound Th isotopes, and on physico-chemical processes that can remove radium; i.e., decay and diffusion/advection (Cochran, 1979; Kadko et al., 1987; Hammond et al., 1990). Chapter 4 summarizes some of the principal processes that can affect the distribution of radium in coastal settings (excluding the atmospheric evasion term, which only affects gaseous radionuclides, such as radon).

It has been shown that horizontal transport from adjacent water bodies is not a major input function for radium to our study site. Radioactive decay is an important mass balance term for any short-lived radioisotope, and is of course quantifiable. The more difficult two terms are diffusion along reasonably static geochemical gradients (diagenetically controlled diffusion) and physically-enhanced advection/diffusion that

responds to water level fluctuations (tidal pumping, ground water upwelling) and/or water mixing. Separating these two processes is important but often a daunting task.

Pore water profiles provide an integrated summary of the subsurface biogeochemical reactions. Such profiles, when used in conjunction with other sedimentwater interface techniques (i.e., lagoon budget method and benthic chambers), can sometimes provide the necessary information to distinguish water flow across the sediment water interface from diffusive fluxes. Pore waters were collected using a minipiezometer ('multi-sampler'), which enables *in situ* interstitial water to be drawn from various sediment depths. Chloride concentrations and other hydrographic parameters of these pore waters are described in Chapter 2. Table 3-4 lists the pore water radium activities for station IRL-4.

At IRL-4, pore water radium activities for each isotope increased with depth. ²²⁴Ra exhibited the smallest down-core increase in activity (5%), while ²²⁶Ra activities increased the most (~ 40%). Because radium is continuously being generated in the bottom sediments of Indian River Lagoon, the rate of production can define pore water Ra profiles. The rate of Ra production in sediments is usually defined in terms of an exchangeable component that is available for desorption by ion-exchange processes (Webster et al., 1994, 1995; Hancock et al., in press). Exchangeable Ra is produced by the decay of particle reactive Th and Ac isotopes either at particle surface sites (or coatings), or within the mineral structure itself. Alpha recoil processes may also eject Ra atoms directly into solution (Fleisher, 1982; Sun and Semkow, 1998), where they are scavenged rapidly and then partitioned between sediment surfaces and pore water.

Table 3-4. Tore water rautum isotope activities at Station IKL	Ta	ıble 3	-4.	Pore	water	radium	isotope	activities	at Station	IRL ⁴
--	----	--------	-----	------	-------	--------	---------	------------	------------	------------------

Station	Depth (cm)	n ²²³ Ra (dpm/L)	xs ²²⁴ Ra (dpm/L)	²²⁸ Th (dpm/100L)	²²⁶ Ra (dpm/L)
Big Flounde	er Tran	sect			
Overlying w	vater*	$0.14 \ \pm \ 0.01$	$0.10 \pm \ 0.01$	4.70 ± 0.47	$2.39\ \pm\ 0.09$

	39	$2.79 \pm$	0.28	5.89	± 0.59	10.24	±	1.02	2.21	± 0.19
Pore water	64	$2.51 \pm$	0.25	4.45	± 0.45	8.38	±	0.84	2.53	± 1.16
(12/13/99)	95	$3.58 \pm$	0.36	4.69	± 0.47	11.92	±	1.19	2.82	± 0.24
	124	$3.82 \pm$	0.38	5.13	± 0.51	12.72	±	1.27	3.13	± 0.85
	156	4.21 \pm	0.42	7.47	± 0.75	13.76	±	1.38	3.20	± 0.16
	185	$4.43 \pm$	0.44	6.19	± 0.62	10.87	±	1.09	3.92	$\pm \ 0.014$

^{*} mean from IRL-5 dry and rainy season sampling (see Appendices B and C). This site was chosen as a water column end-member.

The production rate, P, of exchangeable Ra per unit volume of dry sediment can be expressed as a function of the sediment porosity (ϕ), the Ra decay constant (λ) and the activity of exchangeable Ra (Ra_{exch}) per unit volume of saturated sediment (Webster et al., 1994, 1995):

$$P = \frac{\lambda R a_{exch}}{1 - \phi}.$$

A measure of Ra_{exch} can be derived from sediment Ra/Th ratios. In upper Indian River Lagoon the mean ²²⁸Ra/²³²Th ratio for eight surface sediment samples (excluding the one potentially anomalous ²²⁸Ra measurement; 1.65 dpm/g) was 2.02 (Chapter 4), roughly two times above the secular equilibrium value of 1.0. Such enrichment in surficial sediment daughter isotopes is attributed mainly to the enhanced solubility of Ra relative to Th (upward diffusion of Ra), source rock heterogeneities, redox associated post-depositional mobility of Ra, or a ground-water influence. Such activity ratios observed in Indian River Lagoon are not excessive, especially in dynamic coastal settings (Bollinger and Moore, 1993; Webster et al., 1995; Hancock and Murray, 1998).

The pore water flux across the sediment-water interface was calculated using a derivation of Fick's first law (Berner, 1980; Aller, 1980; Santschi et al., 1990):

$$J = -\phi D_s \left(\frac{dRa_p}{dz}\right)_{z=0}$$
 3-9

where ϕ is porosity (interstitial water volume fraction), D_s is a tortuosity-corrected molecular diffusion ($D_s \theta^2$) coefficient (Li and Gregory, 1974; Boudreau, 1998; Hammond et al., 1999), Ra_p is the depth dependent pore water radium activity and z is depth below the sediment-water interface. The most difficult decision in determining calculated fluxes is the choice of concentration gradients for the dissolved pore water profiles (Fig. 3-12). We used the bottom and upper most pore water sample to determine two concentration gradients that provided a range of flux estimates. The calculated flux of dissolved radium out of the seabed could thus still over-estimate the total flux due to adsorption/precipitation across the redox boundary.

A mean (May and August) water-column Ra value from a site most proximal to IRL-4 was used as the end-member value for flux calculations. A sample calculation for the diffusive flux of ²²³Ra using Eq. 3.9 is presented in Table 3-5. The concentration gradient in pore water radium activities from a depth of 185 cm to above the sediment-water interface was smallest for ²²⁶Ra, which may be explained due to its long half-life (i.e., slow production). By contrast, both ²²⁴Ra and ²²³Ra exhibited pronounced increases in activity with depth relative to the overlying water column activities. The removal of Ra in the surface sediments is attributable to upward Ra diffusion.



Figure 3-12. Pore water profiles for ²²⁴Ra, ²²³Ra and ²²⁶Ra at IRL4. These interstitial waters were collected *in situ* by mini-piezometer (multi-sampler).

Table 3-5. Calculating diffusive fluxes with ²²³Ra.

Supporting formula and data:

$$J = -\phi D_s \left(\frac{dRa_p}{dz}\right)_{z=0}$$

 $\phi = 0.90$ (Trefry et al., 1992)

 $D_s = 6.90 \times 10^{-5} \text{ m}^2 / \text{ day}; \theta = 1.211; \text{ corrected } D_s = 5.7 \times 10^{-5} \text{ m}^2 / \text{ day}$

$$\frac{dRa_p}{dz} = \frac{4.43 - 0.14 \ dpm/L}{185 - 0 \ cm} = 2,319 \ dpm/m^4$$
$$J = 0.9(5.7x10^{-05} m^2/d)(2,319 \ dpm/m^4) = 0.119 \ dpm/m^2/d$$

Pore water ^{223,224}Ra activities have also been measured at one station in Banana River Lagoon – BRL2 during the May, August and December, 2000 field efforts. There appears to be an interesting co-variance between salinity and ^{223,224}Ra activities as a function of depth from season to season. The May profile shows a reasonably constant increasing trend in salinity and radium with depth. Such a trend would imply desorption of surface-bound radium as a function of ionic strength. In contrast, the August pore water profile indicates a separation of salinity with radium, although the two radium isotopes still increase in activity with depth. It is interesting to note that interstitial xs²²⁴Ra activities are roughly half of the May values and imply a loss possibly due to advective flushing, i.e., interstitial water movement.

The December pore water profile at BRL2 is shown in Fig. 3-15. There is a pronounced reversal in the distribution of salinity and short-lived radium isotopes at a depth of about 70 cm. Below 70 cm the observed systematic increase in radium and salinity appears to be analogous to the May pore water profile. In sediments shallower than 70 cm, however, the distribution of salinity and radium suggests either a diffusive/advective flux into the seafloor, or a renewal of radium/salinity after a submarine flushing event. While the range in observed salinities in December is comparable to May and August values, the ^{223,224}Ra activities are again substantially decreased, even relative to August values. It is interesting to note that the well behaved down core ²²³Ra and ²²⁴Ra distribution suggests a subsurface process that is either sufficiently rapid or dominant to generate such clean pore water profiles of two very reactive radionuclides. It is likely that such a process involves the mixing of two water masses in the subsurface that have varying salinities or ionic strengths. Surface exchange reactions at particle surfaces as a result of this salinity change would produce such

^{223,224}Ra pore water profiles. Submarine groundwater migration or advection of a geochemically distinct water mass would likely catalyze such surface reactions. Tidal pumping is one process that can contribute to subsurface flow and mixing in Indian River Lagoon.

To complement such diffusive flux calculations across the sediment-water interface, we also estimated the upper limit of subsurface water exchange. This in effect utilizes benthic flux measurements to derive a rate of upward water transport (cm/day). Based on the deepest pore water ²²⁶Ra activity at IRL-4 (Table 3-3; 3.93 dpm/L) and using a sediment porosity (ϕ) value of 0.90 (Trefry et al., 1992), requires an upward subsurface water flux, J_w of 6 - 17 cm/d to sustain the observed benthic flux (J_b , Table 3-3; 160 – 480 dpm/m²/d), as follows:

$$J_{w} = \frac{J_{b}}{Ra_{p}\phi}$$
 Eq. 3-10

Although the flow of subsurface water is likely much less than the values derived from Eq. 3.10, the range in J_w agrees well with similar results obtained for Indian River





Figure 3-13. Pore water profiles for salinity, ²²³Ra and ²²⁴Ra at BRL2 during May 2000. These interstitial waters were collected *in situ* by mini-piezometer (multi-sampler).



Figure 3-14. Pore water profiles for salinity, ²²³Ra and ²²⁴Ra at BRL2 during August 2000. These interstitial waters were collected *in situ* by mini-piezometer (multi-sampler).



Figure 3-15. Pore water profiles for salinity, ²²³Ra and ²²⁴Ra at BRL2 during December 2000. These interstitial waters were collected *in situ* by mini-piezometer (multi-sampler).

Lagoon during this study (Chapter 2 and 4) and others (Belanger and Montgomery, 1992).

3.3.7 Comparison of the Three Flux Measurements

Lagoon budget and benthic chamber calculations provide an integrated measurement of flux of Ra across the sediment-water interface during the sampling duration. Such results differ fundamentally from those derived via seepage meters ('direct' measurements) that produce a localized and possibly controversial flux rate. The two radium flux methods described here provide information on J over very different spatial scales. The two benthic chambers measure flux across the sediment-water interface on a small and localized scale. In contrast, the lagoon budget method provides an integrated lagoon-wide estimate of the flux across the sediment water interface. This latter method is therefore sensitive to integrated sources and sinks for Ra in the lagoon. Due to long half-life of ²²⁶Ra, the uncertainties associated with the lagoon budget method using ²²⁶Ra can be quite large. Similar flux measurements using either ^{223,224}Ra are much easier to constrain, and uncertainties are correspondingly lower (~20%, Hancock et al., in press). Table 3-5 lists direct and modeled values for J, in units of dpm/m²/day. All three techniques show reasonable agreement in calculated J. Lagoon budget methods produced a flux for the two short-lived Ra isotopes that ranged from $\sim 7 - 22$ dpm/m²/d. By contrast, the same approach using ²²⁶Ra produced a 'zero' flux rate, given the uncertainties of these methods. This difference may be explained by the vastly different half-lives of the three Ra isotopes. Their effectiveness in exchange derivations has to match the time frame of the processes being studied. Processes that affect and control the water budget in Indian River Lagoon are likely to occur over daily (e.g., storm event), weekly (e.g., precipitation) and monthly (e.g., seasonal weather changes) time scales. A combination of short-lived Ra isotopes, normalized to long-lived ²²⁶Ra may provide the best tracer suite. Benthic flux chamber results show strong agreement between ^{223,224}Ra isotopes, and these results also agree well with the lagoon budget methods using the same Ra isotopes. Benthic chamber measurements using ²²⁶Ra produced results that are

	Flux from sediment (dpm/m²/d)										
	Lagoon bu	dget method	Benthic	chamber	Pore wat	er profile					
	May August		Au	gust	mber						
Isotope	-	-	Box 1	Box 2	Minimum	Maximum					
²²³ Ra	7.4	6.5	19.0	10.4	0.1	0.4					
²²⁴ Ra	20.4	22.1	23.0	14.2	0.2	0.8					
²²⁶ Ra			480.2	160.2							

Table 3-5. Flux measurements using various direct (lagoon budget, benthic chamber) and indirect (modeled) methods. Minimum uncertainties based on +/- 1σ.

considerably greater than those generated with ^{223,224}Ra, yet these differences may be reconciled with more detailed solid phase and pore water sediment work.

3.4 Summary and Recommendations

Sediments are often the dominant source for radium as well as nutrients in coastal waters. This chapter examined the utility of Ra as an effective sediment-water interface tracer in upper Indian River Lagoon, where the exchange of water and chemical constituents can have an important effect on water column processes. Benthic fluxes are estimated using three unique methods, lagoon budget, benthic chamber and pore water modeling. The first two yield integrated measurements of flux while the third technique generates an indirect flux estimate based on pore water profiles of radium isotopes.

Flux estimates showed a wide range that extended up to 480 dpm/m²/d. Interestingly, the lowest (lagoon budget method) and highest values (benthic flux chamber) were observed using ²²⁶Ra as a tracer. Using ²²⁶Ra, a maximum upward subsurface water flow of about 5 - 17 cm/day would be required to sustain observed benthic fluxes. These calculated values appear to corroborate our direct and calculated seepage results and also compare favorably to existing seepage values (Belanger and Montgomery 1992). This work illustrates that the determination of benthic fluxes using multiple Ra isotopes with widely variable half-lives provides a useful, complementary technique to study exchange processes across the sediment water interface over many time scales.

Future work will extend the modeling efforts to include bioturbation and advection by collecting solid-phase samples. Such efforts will also provide crucial information on Ra adsorption-desorption and ion exchange. Subsurface temperature profiling in the lagoon will provide a means to link subsurface water to tidal oscillations and seasonal variations. A valuable contribution to this work on ground water inputs to Indian River Lagoon would be to survey the lagoon sediment using a high-resolution continuous resistivity profiler. With such a survey, one can cost-effectively and rapidly identify regions (i.e., transects) where subsurface fluids are either freshened or exhibit variable porosity, and where one might thus expect enhanced exchange of ground water into lagoon bottom waters. Once such sites have been established, a low cost drilling effort would provide valuable information of the regional hydrogeologic framework and the bore holes would provide an invaluable opportunity to sample interstitial fluids for a suite of geochemical tracers.

CHAPTER 4 –ASSESSMENT OF GROUND WATER DISCHARGE USING ²²²Rn AND ²²⁶Ra

4.1 Introduction

Radioisotopes have been applied extensively in geochemistry and environmental science to understand sedimentation processes (Goldberg, 1963; and many others), track water circulation patterns (Sarmiento et al, 1983; and others), and recently, to estimate ground water discharge to coastal surface waters (Cable et al., 1996a,b; Moore, 1996). The unique half-lives and chemical behaviors of radioactive elements are used to our advantage to understand processes on many different time scales (ranging from hours to thousands of years). For instance, the short-lived isotope, ²²²Rn ($t_{1/2} = 3.83$ d), was applied in a coastal environment to trace hypoxic events related to nutrient loading (Torgersen et al., 1997). It has been shown in the Gulf of Mexico (Cable et al., 1996a,b) that radioisotope tracers have the ability to integrate seepage fluid fluxes over large areas, thus providing an advantage over the direct measurements, which can only provide an estimate of fluid flux at any one location. Heterogeneity in sediments and the uncertainty associated with estimating hydraulic conductivities sometimes make calculations of flux based on numerical models and Darcy's Law more difficult. Tracers can overcome this uncertainty by providing a regional flux.

 222 Rn is a daughter of 226 Ra (t_{1/2} = 1620 years) and occurs in the 238 U decay chain (Fig. 3-1). The advantages of using 222 Rn as a tracer are the following: it is conservative, it can be easily measured, its production and decay can be quantified, and its concentrations in ground water are typically three to four orders of magnitude greater

than in seawater. In addition, ²²⁶Ra is a member of the Group IIA alkaline earths and thus behaves chemically similar to Sr, Ba, Ca, and Mg. In a karst environment such as the Floridan Aquifer, Ra should be abundant and may be useful as a tracer as well for groundwater discharge into coastal surface waters. Thus, we have two naturally occurring tracers with which to investigate water flow across the freshwater-salt water interface. The following chapter presents results of excess ²²²Rn and ²²⁶Ra in waters associated with the upper Indian River Lagoon (IRL) near Titusville, Florida, (Year One, 1999) and the Indian River Lagoon/Banana River Lagoon system near southern Merritt Island during Year Two (2000) of our project. The objectives of this work are to assess the applicability of these tracers to the IRL system and to quantify ground water flow into the lagoon through different geologic features using these natural tracers.

4.2 Sampling and Analytical Techniques

Sample collection took place in two stratigraphically distinct field sites for three discrete sampling trips (May, August, and December): (1) 54 bottom water samples and 18 pore water samples were collected in the northern IRL in 1999; and (2) 70 bottom water samples and 90 pore water samples were collected in the central IRL/BRL system in 2000. In addition, groundwater wells, a spring, and numerous rivers and inlets were sampled to obtain a record of end-member concentrations for the tracers around the lagoon site. Bottom water samples for ²²²Rn and ²²⁶Ra analysis were collected in 4-L evacuated glass sampling bottles using either the bottle vacuum or a peristaltic pump that drew water from depth directly into the bottles. Samples were carefully collected to prevent contact with ambient air, and all bottles were sealed immediately after collection to eliminate gas loss. All samples were analyzed for ²²²Rn within 6 to 36 hours after collection using a standard cryogenic approach for ²²²Rn extraction from seawater by sparging with helium (Broecker, 1965; Key et al., 1979; Mathieu et al., 1988). This approach requires that water samples are sparged with ultra high purity helium gas for 60 minutes at 400 mL/min. As gases evade from the sample, they are filtered and trapped using liquid nitrogen (boiling point = -210° C), which allows the pre-concentration of Rn222 (freezing point = -71° C). Measurements of ²²⁶Ra were obtained by re-sparging the same sample at least 5 days after the initial ²²²Rn analysis. The unsupported or "excess" radon (total ²²²Rn at time of first analysis minus ²²⁶Ra) was decay-corrected back to the time of sampling to obtain the *in situ* excess ²²²Rn. All ²²²Rn concentrations reported in this chapter follow the convention that they are excess and corrected to the time of collection.

Pore waters were sampled using multi-port piezometers (multi-samplers), which were installed in the sediments at four stations in the study area (Chapter 2). Pore water was collected by drawing water directly out of the sediments through each tube using a peristaltic pump. The pore water was transferred quantitatively at the water surface to a 20-mL glass scintillation vial. Each vial was pre-filled with 10-mL of a mineral oil extractant for analysis of radon by alpha liquid scintillation counting. A separate sample was collected for ²²⁶Ra in 1-L plastic bottles. These samples were returned to the laboratory at Louisiana State University where the radium samples were transferred to evacuated 2.5-L glass bottles and analyzed via cryogenic extraction as described above.

²²²Rn exchange rates at the sediment-water interface were determined during the August 1999 and May 2000 sampling trips by benthic flux measurements using *in situ* chambers (Martens et al., 1980). Two clear plexiglass boxes (0.21 m²) were carefully deployed by pushing each chamber about 3 cm into the sediments. The water inside the chambers was stirred gently using manually operated paint propeller stirring rods to simulate a mixed water column. Initial, intermediate, and final (t = 0, 4, 8, and/or 24 hours) water samples were collected from the benthic chambers and analyzed for ²²²Rn and ²²⁶Ra. The ²²²Rn concentrations were corrected for decay, and the benthic flux was calculated as shown in Martens et al. (1980). Advective seepage rates may be represented as the volume flux of fluids (m³/m²/min) across the sediment-water interface or may be represented as a velocity (m/min).

Sediment slurry experiments were performed to estimate the amount of pore water ²²²Rn at equilibrium with the solid phase sediments. Each equilibration experiment consisted of mixing approximately 50-g wet sediment aliquots with 250 to 300 mL of seawater in 500-mL Erlenmeyer flasks for 30 days. After this period, radon in

the water is assumed to be equilibrated with sediment 226 Ra, and the equilibrium activity (C_{eq}) is calculated using the porosity (ϕ) and wet bulk density (ρ_{wet}) of the sediments.

4.3 Results

4.3.1 Spatial and Temporal Distributions

4.3.1.1 Lagoon Waters.

Spatial and temporal variability are observed in activities for the study sites during 1999 and 2000 (see Appendix C.1 and C.5). ²²²Rn was generally lower during the dry season and more spatially uniform than in the rainy season (Fig. 4-1). Rainy season radon activities in the bottom waters of the northern lagoon (1999) ranged from less than 1.0 dpm/L to 6.2 dpm/L (2.89 ± 1.44 dpm/L; n = 27), while in the dry season they were typically 1.0 to 4.4 dpm/L (2.23 ± 0.95 dpm/L; n = 27). ²²⁶Ra activities demonstrated similar trends in space and time. ²²⁶Ra activities averaged 2.05 ± 0.23 dpm/L in the dry season and 2.63 ± 0.26 dpm/L in the rainy season. Generally, the lagoon surface waters had higher radon and radium during the rainy season than in the dry season.

In contrast, the central IRL/BRL system of 2000 demonstrated very little excess radon present in surface waters during the dry and rainy seasons (Fig. 4-2). Rainy season excess ²²²Rn activities in the bottom waters of the lagoon ranged from 0 dpm/L to 7.17 dpm/L (2.06 ± 2.72 dpm/L; n = 13), while in the dry season they were typically 0 to 1.20 dpm/L (0.68 ± 0.33 dpm/L; n = 6). Not enough data was available to evaluate the transition season (December 2000). ²²⁶Ra activities demonstrated similar trends in space and time. ²²⁶Ra activities ranged from 2.08 to 3.33 dpm/L in the dry season (2.63 ± 0.30 dpm/L; n = 24); from 1.71 dpm/L to 4.35 dpm/L in the rainy season (2.98 ± 0.67 dpm/L; n = 21); and from 3.04 to 6.93 dpm/L in the transition season (4.99 ± 2.75 dpm/L; n = 2). Overall, the rainy season radon and radium activities were higher than the dry season activities for both the central Indian River and Banana River Lagoons.



Figure 4-1: Seasonal 1999 activity histograms of lagoon water ²²⁶Ra and ²²²Rn in the northern IRL.



Figure 4-2: Seasonal 2000 activity histograms of lagoon water ²²⁶Ra and ²²²Rn in the central IRL/BRL system.

Comparisons of all lagoon water activities revealed ²²⁶Ra in the northern site was lower and had a smaller range than the central site, while much more excess ²²²Rn was present in the northern site than the central site (Fig. 4-3). These differences in activities between sites may be caused by several physical characteristics, including (1) differences in sediment composition (i.e., radium-bearing minerals); (2) higher atmospheric evasion of ²²²Rn due to increased fetch in the central study area; (3) greater circulation and exchange in the central study area; (4) more riverine inputs in the central study area; and (5) differences in the mechanisms and quantity of groundwater delivery to the lagoon. Several of these possibilities will be explored in the forthcoming sections of this chapter.

4.3.1.2 River waters

Surface water inputs were investigated to evaluate end-member contributions of ²²⁶Ra and ²²²Rn to each lagoon site (Fig. 4-4; see also Appendix C.6, and C.7). In the northern study area, only Turnbull Creek and Haulover Canal were identified as contributors to the lagoon. Ra-226 was similar for both the rainy and dry seasons in the north. Turnbull Creek was the highest source of ²²²Rn in the dry season, but Haulover Canal was the only channel to deliver excess ²²²Rn in August. In the central site, 5 creeks or rivers and a barrier island tidal inlet were characterized for the tracers. Ra-226 demonstrated a decreasing trend in activity with increasing distance from the study site, which is likely due to the increased opportunity for exchange with oceanic waters approaching Sebastian Inlet. Excess ²²²Rn tended to decrease with increasing distance from the study site during the dry season, but during the rainy season radon was consistently high for most surface inputs. Overall, creeks and rivers in the central region were higher in tracer concentrations than the northern site.

4.3.1.3 Ground Water

Private wells were sampled around the lagoon study sites to evaluate ground water end-member radon and radium activities in underlying aquifers (Appendix C.8 and



Figure 4-3: Activity histograms of all lagoon waters from the northern and central study sites.



Figure 4-4: River water activities near the northern and central sites are shown for 1999 (A) ²²⁶Ra; (B) ²²²Rn; and 2000 (C) ²²⁶Ra; (D) ²²²Rn during May (black), Aug. (gray), and Dec. (white). Central site riverine inputs are shown north to south, with the northernmost creek being closest to the study site.



Figure 4-5. Seasonal distribution of ground water 222Rn activities in the northern IRL in 1999 for May (black bars) and August (gray bars).

C.9). Six wells were sampled surrounding the northern Indian River Lagoon site and interestingly, the dry season ²²²Rn was highest for 80% of wells sampled (Fig. 4-5). Radon in ground water ranged from 150 to 2145 dpm/L in the dry season and from 42 to 622 dpm/L in the rainy season. Ra-226 was less than 6.4 dpm/L for all wells during both seasons. Due to the discontinuous nature of the Hawthorn Formation in this region of the Indian River Lagoon, the Floridan Aquifer communicates with the surficial aquifer. Most wells sampled in this region were about 80 to 130 feet, and it is considered likely they can communicate with the surface.

Further south in the lagoon system, six wells were sampled as well as a spring found on Merritt Island (Fig. 4-6). In this region, the aquifers are defined by the presence of confining units which separate the surficial and Floridan aquifers. We sampled ground waters seasonally from 3 surficial and 3 deep Floridan aquifers to evaluate the relative differences in tracer concentrations. Generally, both ²²⁶Ra and ²²²Rn were highest in the


Figure 4-6: Seasonal distributions of groundwater ²²⁶Ra (left side) and ²²²Rn (right side) activities are given for the central IRL/BRL system in 2000 for May (black bars), August (gray bars), and December (white bars).

rainy season although one deep well showed the highest radium in December. Likewise the spring was highest in tracers in the rainy season (see Appendix C.9). Overall, tracers were higher in activity in the Floridan aquifer wells than in the surficial aquifer wells. Rn-222 in the northern aquifer region appeared in wells over a much wider range in activity (150 to 2100 dpm/L) than in the central region where activities were less than 400 dpm/L at all times (Fig. 4-7). In contrast, ²²⁶Ra was lower (2 to 6 dpm/L) in the north than the central study area where it ranged from 1 to 12 dpm/L. A more significant source of ²²⁶Ra appears to be present in the central region based on observed lagoon activities and the end-member activities of river and ground waters.

4.3.2 Pore Water Distributions of Ra and Rn

In December 1999, four pore water profiles were collected in the northern IRL site (see Appendix C.10) to evaluate the subsurface gradients for tracers underlying the lagoon. In addition, during December 2000 we collected two pore water profiles in the northern IRL at previous 1999 sampling stations for long-term temporal comparisons (Appendix D.11). Pore water profiles were also collected in the dry, rainy, and transition



Figure 4-7: Activity histograms of groundwater ²²²Rn (black bars) and ²²⁶Ra (gray bars) for the northern and central IRL system: (A) 1999 ²²²Rn; (B) 2000 ²²²Rn; (C) 1999 ²²⁶Ra; and (D) 2000 ²²⁶Ra.

seasons for the 2000 sampling effort (Appendix D.12 to D.14). Generally, we observed increasing radon activities with depth to a maxima which occurred between 80 and 150 cm. After the maxima, activities decreased for one profile at IRL-4, December 1999 (Fig. 4-8). Radon activities were greatly in excess of its parent, ²²⁶Ra, due to the emanation of radon from minerals in the aquifer substrate as the radon-rich groundwater is transported along. Due to the low volume of pore waters available for sampling, it was not always possible to obtain a complete profile for radium. However, it can generally be followed at some stations that radium activities exhibits increasing activities with depth in the sediments to some maxima which occurred between 3 and 34 dpm/L. Pore water



Figure 4-8: Pore water activity depth profiles of ²²⁶Ra (top row) and ²²²Rn (bottom row) in Dec-99 (solid line) in the northern IRL for IRL-4, IRL-5, and IRL-22, respectively. IRL-4 and IRL-22 were sampled for ²²⁶Ra in Dec-00 also (dashed line)

profiles were sampled in consecutive years in the northern IRL for ²²⁶Ra to obtain some temporal feel for the tracer behavior. Profiles at IRL-4 were similar for ²²⁶Ra in 1999 and 2000, but at IRL-22 in 2000 the ²²⁶Ra in pore water was much less than the year prior. The diffusion of radon in pore waters and the advection of radium- and radon-rich ground waters can transport the tracers through sediments, both laterally and vertically. We anticipate that some of the variability observed here can be explained by variations in advective subsurface processes (i.e., lower hydraulic head in 2000 due to reduced precipitation and recharge).

Pore water profiles collected in 2000 were primarily from the central IRL/BRL region where we evaluated the differences between two parallel lagoons and ground water delivery to the two systems. Our first important discovery was the sediment overlying hard limestone was thin and had a low permeability in the Indian River Lagoon central locations. We sampled three multi-level piezometers in this lagoon, but typically



Figure 4-9: Pore water activity depth profiles of ²²⁶Ra (top row) and ²²²Rn (bottom row) in May-00 (dashed line), Aug-00 (dotted line), and Dec-00 (solid line) in the central IRL for BRL-1 and BRL-2, respectively.

very little pore water could be extracted. In contrast, sediment in the Banana River Lagoon was more permeable and allowed deeper penetration of piezometers. We set and sampled five multi-level piezometers in this lagoon and obtained several very nice profiles of ²²⁶Ra and ²²²Rn. Typical tracer activities with depth in the sediments demonstrated that ²²⁶Ra was usually higher in this lagoon that in the northern IRL site and more uniform with depth (Fig. 4-9). Radon-222 activities in pore waters generally increased with depth, with the least changes observed in December and the greatest changes observed in August during the rainy season. The maximum concentration for ²²²Rn occurs at approximately similar sediment depths (~150 cm) for both the northern and central study sites. This may indicate a similarity in physical forcing functions that

create the profile shapes. One possibility is the effect of wind/wave mixing of the upper sediment column with lagoon waters.

4.4 Discussion

4.4.1 Linking Radon-222 and Radium-226 to Seepage

Seepage is generally dispersed and heterogeneous in nature. However, its magnitude can be volumetrically significant due to its large areal extent along coastlines. We compare here seepage rates measured with seepage meters to ²²²Rn and ²²⁶Ra measurements collected at transects perpendicular to shore during the rainy (n = 5)transects) and dry (n = 3 transects) seasons in 1999. This comparison is performed to determine the significance of variations in the tracers with physical measurements. Inventories of each tracer were calculated to investigate tracer to seepage relationships. Tracer inventories (dpm/m^2) are calculated by integrating the water column activity with water depth at each station. Individual station tracer inventories are compared to the measured seepage rate at that corresponding station (Fig. 4-10). Excess ²²²Rn inventories were significantly related to seepage rates (Fig. 4-10A) during both the dry (n = 24; $r^2 =$ +0.2; p = 0.03) and rainy seasons (n = 26; $r^2 = +0.4$; p = 0.0007). ²²⁶Ra inventories were related to seepage rates during the rainy season (n = 26; $r^2 = +0.2$; p = 0.04; Fig. 4-10B) but not during the dry season. The lack of correlation during the dry season may be due to the low seepage flux and longer half-life of 226 Ra ($t_{1/2} = 1620$ y) than 222 Rn. These relationships show that the tracers are significant at the 95 to 99% confidence levels for most of the year, thus making them useful for tracking subsurface fluid fluxes into the lagoon.

To further investigate the relationship between the tracers and seepage, total transect inventories were also calculated. Mean seepage rates (ml/m/min) at each station were integrated as a function of distance between meters to yield seepage inventories per meter of shoreline (liter/m/min) along the each entire transect for each season. Inventories of ²²²Rn (10⁴ dpm/m) and ²²⁶Ra (10⁴ dpm/m) were derived by integrating all tracer measurements with distance (m) between meters and with the corresponding water depth (m) measured at each station (i.e., they are the sum of individual inventories at each



Figure 4-10: Water column inventories of (A) excess ²²²Rn and (B) ²²⁶Ra at each station versus the mean seepage rate at individual stations for both rainy (solid diamonds) and dry (open diamonds) seasons.



Figure 4-11: Whole transect tracer inventories versus integrated seepage during the rainy (solid diamonds) and dry (open diamonds) seasons for (A) ex ²²²Rn and (B) ²²⁶Ra.

station along a transect). Linear relationships were observed (Fig. 4-11) when the whole transect ²²²Rn and ²²⁶Ra inventories were plotted against corresponding integrated seepage measurements. During the dry season neither tracers were significantly related to integrated seepage, but this can easily be explained by the fewer number of transects available to make the comparison. During the dry season, only 3 transects could be used in this relationship, so not enough data is available to adequately evaluate the relationship

via a regression analysis. However, the relationships of these tracers to integrated seepage during the dry season demonstrated that 71 to 80% of the variations in the tracers could be explained by seepage. During the rainy season, all data from each transect could be used, and significant correlations were found at the 99% confidence level. Variations in rainy season ex ²²²Rn inventories are given in Fig. 4-11A (n = 5; r² = +0.922; p = 0.009). ²²⁶Ra inventories versus integrated seepage are given in Fig. 4-11B (n=5; r² = +0.980; p = 0.001). Thus, during the rainy season, seepage fluid fluxes can explain greater than 92% of variations in the tracer activities.

As a final comparison, mean seasonal integrated seepage and tracer inventories were plotted with cumulative monthly precipitation for Titusville, Florida (Fig. 4-12). Seepage and tracer inventories were greater in the rainy season than in the dry season and varied with precipitation. Precipitation does not carry a measurable radium or radon signal. However, this source serves to recharge the surrounding aquifers and helps drive the seepage flux carrying enriched tracer activities. Thus, it is expected that changes in precipitation will be reflected in the seepage and tracer flux to the lagoon. Depending on the distance of the precipitation recharge occurrence to the lagoon, the coastal seepage and tracer flux may exhibit a lag in their response to inland recharge.

4.4.2 Sources and Sinks

4.4.2.1 Sources

To assess the relative importance of various sources and sinks for each tracer, several experiments were performed in the field and in the laboratory. Figure 4-13 depicts a generalized box model approach for assessing the sources and sinks of the tracers. Water column sources for ²²²Rn and ²²⁶Ra include diffusion from the sediments, advection from the sediments (i.e., compaction, ground water, tidal/wave pumping), creek and canal inputs, ocean inputs, and *in situ* production. Each of these sources can be individually assessed. Advective benthic fluxes were measured during the dry season in the field using benthic flux chambers and will be calculated using the pore water



Figure 4-12: Mean tracer inventories and mean integrated seepage for all transects are plotted versus monthly cumulative precipitation to demonstrate the difference between rainy and dry season inputs to the lagoon.

activities. Sediment diffusion was measured by sediment slurry experiments. River and inlet waters, ground water, and *in situ* production were all measured directly.

4.4.2.2 Sinks

In addition, each tracer has characteristic sinks associated with it. ²²⁶Ra may be lost by horizontal transport out of the study area or by in situ decay in the water column. In situ decay of ²²⁶Ra and ²²²Rn was calculated from direct activity measurements and has been accounted for in the reported activities. Because ²²²Rn is an inert gas, it experiences a sink that ²²⁶Ra does not undergo — atmospheric evasion. This loss across the air-sea



Figure 4-13: General box model demonstrating the sources and sinks of radionuclides to the water column in the Indian River Lagoon.

interface can be estimated based on knowledge of wind speeds and air and water temperature (Broecker and Peng, 1974,1982; Wanninkopf et al., 1992). The following discussion presents preliminary data on ²²²Rn and ²²⁶Ra and associated fluxes.

4.4.2.1 Benthic Fluxes

Results of duplicate benthic flux chambers deployed in the Banana River Lagoon at BRL-1 are given in Table 4-1. Benthic fluxes were calculated as the difference between initial and final collections after correcting for decay and in-growth based on an equation in Martens et al. (1980):

$$J_{ben} = \frac{V\lambda_{222} \left[C_f - (C_i e^{-\lambda_{222} t}) \right]}{A \left[1 - e^{-\lambda_{222} t} \right]}$$
(4-1)

where J_{ben} is the advective-diffusive flux across the sediment-water interface; V is the volume of the chamber above the sediments (55 L); C_f is the final ²²²Rn activity in the chamber at the end of time t; C_i is the initial activity inside the chamber; and A is the area

 Table 4-1: Rn-222 flux compilation for diffusive and total benthic fluxes in northern IRL 1999.

Method	Dry Season ex ²²² Rn Flux (dpm/m ² /day)	Rainy season ex ²²² Rn Flux (dpm/m ² /day)	Dry Season Seepage (m ³ /sec)	Rainy season Seepage (m ³ /sec)
Diffusive Flux Sediment Equilibration	253 =	± 134		
Total Benthic Flux Benthic Flux Chambers Pore water Gradient Inventory/Atm. Evasion	na 3389 ± 232 3713 ± 1416	1816 ± 1653 6420 ± 276 3003 ± 1263	$na \\ 11.7 \pm 0.5 \\ 9.0 \pm 3.4$	$\frac{10.1 \pm 1.3}{22.7 \pm 0.6}$ 7.3 \pm 3.1
Mean (±1σ)	3551 ± 824	3746 ± 2390	10.4 ± 1.9	13.4 ± 1.7

*Flux and discharge rates are reported as a mean of multiple measurements ($\pm 1\sigma$ propagated sampling and analytical error).

of the chamber (0.21 m²). The mean flux was calculated to be about 2026 dpm/m²/day at this site, which is similar in magnitude to the fluxes obtained from the pore water gradient.

4.5 Summary

Estimates of ground water input to coastal water bodies using multiple tracers can provide confirmation of fluid flux estimates as demonstrated in the northeastern Gulf of Mexico as demonstrated by Martin et al. (2000) for the northern IRL during 1999. We present these preliminary results for the central IRL/BRL system which indicate that the tracers, ²²²Rn and ²²⁶Ra, will be valuable to our estimates of fluid flux in this central region. In the final draft of this report we will provide fluid flux estimates for this central site and make comparisons to the previous study site in the northern region of IRL. This comparison is especially interesting due to the differing aquifer sources between the two sites and the different geomorphological and physical oceanographic characteristics of each region.

CHAPTER 5 – SOURCES OF GROUND WATER DISCHARGE

5.1 Introduction

In considering ground water discharge, there can be much confusion about terminology used to describe the different water masses located above and below the sediment water interface. For the purposes of this discussion, these waters are divided into lagoon, seep, ground, and pore water on the basis of their locations and methods of sampling (Table 5-1). Lagoon water is located within the water column. Seep water refers to all water that flows to the lagoon from sediments and rocks that underlie the lagoon. Ground water refers to water that originates in one of the three primary aquifers of the area: i.e. the Floridan, Intermediate, or Surficial aquifers. Pore water is buried at shallow depths within the interstitial spaces of the sediment and is collected by multisamplers. Seep water may thus be a combination of ground water and pore water. The chemical and isotopic compositions of seep water would thus be controlled by mixing with ground water that has been modified by fluid-solid reactions following long residence times (e.g. 10's to 1000's of years) within a particular aquifer. The chemical and isotopic composition of this water, particularly of the concentrations of reactive components such as the nutrients, could also be controlled by early diagenetic reactions in the shallowly buried sediments, including remineralization of organic matter.

The volume of seep water discharging to the lagoon is important to the hydrologic budget of the Indian River Lagoon (e.g. discussed in Chapter 2), as well as its water quality. The impact on water quality depends on the chemical composition of the seep water, which in turn depends on the sources of the water, fluid-solid reactions that may have occurred in the source regions for the water, and mixing with contaminants along its flow path. Ground water is likely to have significantly different chemical and isotopic

Water Type	Definition
Lagoon water	Water in the water column of the lagoon
Seep water	Water that is discharged from the lagoon sediment and captured in
	seep meters. May include both pore and ground water
Ground water	Water that originates in major regional aquifers, e.g. Floridan,
	Intermediate or Surficial
Pore water	Water trapped in pore spaces of the sediment underlying the lagoon

Table 5-1. Definition of various water sources

compositions from lagoon water or pore water. Because of variations in the thickness of the Hawthorn Group (Fig. 1-2), it is unlikely that the Floridan or Intermediate aquifers contribute significantly to ground water discharge in the central area and no water should originate from the Intermediate aquifer in the northern area where the Floridan aquifer is unconfined and where Floridan water mixes with Surficial aquifer water prior to discharge. The results presented in this chapter are used to estimate the relative volume of ground water and pore water contained in seep water.

5.1.1 Chemical and Isotopic Tracers of Aquifer Water

Several conservative chemical and isotopic tracers, including Cl concentrations, $\delta^{18}O_{H2O}$ values and Sr isotope ratios of the dissolved Sr, have distinct values in the lagoon water, pore water, and ground water, thus making them potential tracers to distinguish various components of seep water. Chloride concentrations and $\delta^{18}O_{H2O}$ values for lagoon water will be similar to seawater values, which are ~15.8 mg/L and ~0‰, respectively, although these values will be modified by evaporation and precipitation. The values of ⁸⁷Sr/⁸⁶Sr ratios for the lagoon water will not be significantly altered by direct precipitation or precipitation because of the low Sr concentrations in rainwater and because there is no fractionation of the isotopes during this process. The Sr isotopic composition could be altered by surface runoff because dissolution of carbonates may provide a large source of non-radiogenic Sr.

The best constrained tracer for ground water is Cl concentration because it has long been used to map the extent of seawater intrusion into coastal water supplies (e.g. Toth, 1988). A sharp gradient of increasing Cl concentrations exists in the upper Floridan aquifer across the northern study area. The concentrations increase from 50 mg/L on the western side of the lagoon to nearly 5000 mg/L on the eastern side. The low Cl concentrations on the western side of the lagoon result from hydrologic connection with the overlying Surficial aquifer along the Titusville-Mims Ridge, which represent the lowest Cl concentration in Brevard or Indian River counties (Toth, 1988). Other than this region of recharge to the Floridan aquifer, shallow clastic aquifers of the Surficial aquifer contain elevated Cl concentrations in places where it has mixed with water from the Floridan aquifer.

The distribution of 87 Sr/ 86 Sr and $\delta^{18}O_{H2O}$ values is more poorly known than Cl concentrations in the Floridan and Surficial aquifers across the study area. Nonetheless, the stable isotopic composition of the aquifer water would presumably have values similar to average precipitation and thus should have $\delta^{18}O_{H2O}$ values of -3 to -4% relative to Standard Mean Ocean Water (SMOW) and δD_{H2O} values of -14 to -22% (SMOW). (All stable isotope values in this report are compared to the SMOW standard and are reported in standard per mil notation (e.g. Faure, 1986)). In contrast to the stable isotopes, the 87 Sr/ 86 Sr ratio of ground water is controlled by the dissolution of the aquifer minerals. In north-central Florida, the Floridan aquifer has Sr isotope ratios of around 0.7079 reflecting the isotopic composition of the enclosing pre-Miocene carbonate minerals (Gordon, 1998). The Surficial aquifer should have higher values than the Floridan aquifer because of the younger age of the aquifer. If Sr is contributed from dissolution of silicate minerals, the Sr isotope ratio may be greater than modern seawater.

5.2 Methods

5.2.1 Field Sampling and Storage of Samples

The method of collecting seep water was similar to that used to measure seepage rate (see Chapter 2) except that the seep bags were clean and dry prior to attaching them to the seep meters. For most measurements, clean bags were left on the meter until at least 1 L of water had flowed into the bags. In locations with high flow rates, more than 1 L was commonly collected. At one station in the northern area (IRL25 during May 1999), the flow rate was too slow to collect sufficient water for measurements. In the central area, seep water was not collected from IRL30, IRL35, IRL37, IRL40, during May 2000, from IRL34, IRL40, BRL2, during August 2000, and from IRL31 during December 2000 for a variety of reasons including the flow was too low, the meters were turned over and lost equilibration prior to sample, or the meters malfunctioned.

After sufficient water was available for chemical analyses, the bag was removed from the seepage meter and brought on board the boat. Water was drawn from the bags into a 60 ml syringe and filtered through a 0.45 μ m filter into two 125 ml HDPE Nalgene bottles that were pre-labeled with the station and date. During all sampling trips except May 1999, a third 125 ml HDPE Nalgene bottle was filled with water that had not been filtered. One bottle with filtered water was acidified with 50 μ l of 16 N optima grade HC1. All samples were stored in an ice-filled cooler until the end of the day at which time they were transferred to a refrigerator. All nutrient samples were kept refrigerated until analyzed.

Samples for the water column were preserved in the same way as seep water. In the northern area, water was collected from the water column from at least one station for each transect, as well as from each of the deep water sites. The water was collected by submerging a 2 L plastic bucket ~0.25 m below the water surface. The field measurements of oxygen, conductivity, temperature, and salinity were made *in situ* by lowering the probes into the water column. The pH of the water column was measured by inserting the probe into the bucket of water. In the central area, the water column sampling followed a slightly different procedure. These samples were collected simultaneously with the Ra water samples. Water was pumped from approximately 50 cm above the sediment into a small plastic bucket on board the boat using a small battery powered pump. The oxygen content, conductivity, salinity, pH, and temperature were monitored until stable, at which time the water was collected and preserved in the same way as the seep water samples.

Pore water that was collected from the multisamplers was preserved in the same way as the seep and water column samples. The water was pumped using a peristaltic

123

pump into a small bucket on the boat while monitoring the temperature, conductivity and oxygen concentration. Although all parameters were monitored until they stabilized, the oxygen concentration was particularly important because when it reached a minimum value it was assumed that the water being withdrawn was pristine pore water. All samples were collected once the field parameters had stabilized.

5.2.2 Analytical Methods

One conservative chemical tracers used in this project is Cl. Sulfate concentrations were also measured as a way of determining the extent of organic matter oxidation but appear to exhibit little microbial reduction and thus is essentially another conservative tracer. Chloride concentrations were measured by titrating with AgNO₃ (Clesceri et al., 1989). The titrations were standardized using two laboratory standards with Cl concentrations of 559 and 556.5 mM. The SO₄ concentrations were measured by ion chromatography using conductivity detections (Clesceri et al., 1989). These analyses were standardized by measuring five external standards and constructing a linear standard curve. Precision of the Cl and SO₄ analyses was checked by analyzing a check standard every fourth sample and calculating the coefficient of variation of the measurements.

Other conservative isotopic tracers include δ^{18} O and δ D values of the water and ⁸⁷Sr/⁸⁶Sr isotope ratios of dissolved Sr in the water. These isotope tracers were measured on selected samples. Results of the initial year of the project indicated that the stable isotope ratios were not a robust tracer of the origin of the seep water because of the small difference in values between the lagoon and seep water. These measurements were thus not include as part of the second year of the study. Observations of the variable Cl concentrations of the pore water during the second year of the study, however, indicated that the stable isotope ratios of water might provide information about the origin of these low-Cl anomalies, and therefore, δ^{18} O values were measured on the pore water and selected lagoon water samples. The δD_{H2O} values were measured for selected samples from year one in a commercial laboratory (Mountain Mass Spectrometry in Evergreen, Colorado). The $\delta^{18}O_{H2O}$ values were measured in the Department of Geological Sciences at the University of Florida using an automated VG Prism II mass spectrometer. Each

124

Solute	Precision (%)*		
SO_4	0.8		
Cl	0.4		

Table 5-2. Estimated precision of various solutes

* Precision is the coefficient of variation, $COV = 1 \sigma/mean$.

sample was measured either in duplicate or triplicate and the reported values represent the average of the measurements. Occasionally, one of the replicate measurements differed significantly (by more than 0.2‰) from the other two, in which case the reported value represents either an average of only two of three values or if the sample was originally measured in duplicate it was remeasured. All values are reported in standard per mil notation relative to the V-SMOW standard.

The Sr isotope measurements were made on variable amounts of water depending on the concentration of Sr. For samples with seawater chlorinity, ~150 µl of water was pipetted into Teflon containers, weighed and spiked with ⁸⁴Sr spike. The spiked samples were completely dried and the salts were dissolved in 50 µl of 3.5 N distilled HNO₃. Strontium was separated from this solution with Sr selective crown ether resin following a technique modified from Pin and Bassin (1992). The Sr blank for the technique is ~100 pg. The separated Sr was loaded onto tungsten filaments and analyzed in the Department of Geological Sciences at the University of Florida using a VG Micromass 354 thermal ionization mass spectrometer. Instrumental mass fractionation was corrected to an ⁸⁶Sr/⁸⁸Sr ratio of 0.1194. Numerous replicate measurements over the past several years of the NIST-987 standard yield a ⁸⁷Sr/⁸⁶Sr value of 0.710235 with an external precision of ±0.000023 (2 σ). This external precision represents the minimum uncertainty assigned to any individual sample.

5.3 Results

Solute concentrations and isotope ratios are reported in Appendix D at the end of the report. The data are sorted initially by the sampling trip and are arranged in chronological order (i.e. the initial appendix is data from May 1999), and secondarily by

	n*	SO ₄	CI.	Sr	d18O	⁸⁷ Sr/ ⁸⁶ Sr			
		(mg/L)	(g/L)	(mg/L)	(‰)				
May 1999									
Seep water									
Average	28	2992	20.8	11.8	3.73	0.709131			
Median	28	3014	20.8	11.8	3.73	0.709118			
1σ	28	86	0.57	0.25	0.38	0.000047			
Water column									
Average	12	3023	21.09	11.82	3.60	0.709139			
Median	12	3036	21.19	11.84	3.60	0.709142			
1σ	12	87	0.41	0.31	0.24	0.000109			
August 1999									
Seep water									
Average	28	2809	20.0	10.59	3.56	0.709072			
Median	28	2815	20.1	10.16	3.52	0.709067			
1σ	28	135	0.83	1.01	0.21	0.000027			
Water column									
Average	11	2796	19.6	10.14	3.35	0.709080			
Median	11	2791	19.5	10.22	3.35	0.709054			
1σ	11	90	0.47	0.23	0.11	0.000061			

Table 5-3. Average, median, and standard deviation of conservative tracers for seep water and water column water in the northern study area.

* Number of stations where samples where collected.

the type of data. The type of data are arranged generally starting with composition of the seep water, followed by composition of the lagoon water, ground water, surface water, and pore water.

5.3.1 Lagoon and Seep Water

Conservative solutes vary slightly between stations during the May and August 1999 sampling trips in the northern study regions, and the average of the values also vary between the sampling trips (Fig. 5-1). For ease in comparison between seep and lagoon water, the average, median, and standard deviation are reported in Table 5-3 for the concentrations and isotope ratios for conservative solutes in water collected during the May and August 1999 sampling trips. On average, the May 1999 lagoon water samples have higher Cl concentrations than the seep water, but this trend reverses for the August 1999 samples. The average Cl concentration for the seep water is 1.4% lower than the Cl

concentration in the water column during May 1999. In contrast the average Cl concentration is 2% higher in the seep water than the lagoon water during August 1999. Although these differences are small, they are larger than the error of the measurement, indicating that the differences are significant. The SO₄ and Sr concentrations and the δ^{18} O values show similar decreases in value.

The spatial and temporal variations in the concentrations of the conservative solutes are considerably greater in the central area than in the northern area. For example, the Cl concentrations of the lagoon water vary longitudinally along the length of the lagoon (Fig. 5-2). These variations in water chemistry limit regional comparisons between lagoon and seep water such as are made for the northern area. Instead the comparisons must be made for individual transects. During May 2000, the Cl concentration increased from an average of 9.4 g/L from the Indian River Lagoon portion of transect 1 and 2 in the north to 10.2 and 11.5 g/L in transects 3 and 4 in the south (Fig. 5-2). The Cl concentrations were 9.0 and 9.4 g/L for transects 1 and 2 respectively in the Banana River Lagoon, values that are similar, but slightly lower than the lagoon water in the northern study area. By August 2000, the average Cl concentrations had increased substantially throughout the lagoon. This trend of increasing Cl concentration following the rainy season is opposite of what would be expected and was observed in the northern study area. The average Cl concentrations pass through a maximum of 13.8 g/L at transect 2 and decrease to an average value of 12.1 g/L at transect 4. The highest average Cl concentrations of 12.6 g/L also occur in transect 2 in the Banana River Lagoon, but the average concentrations in the Banana River Lagoon are overall lower by ~1.1 g/L than in the Indian River Lagoon portions of transects 1 and 2. The concentration gradient from the north to the south is most extreme in December 2000, decreasing from an average concentration of 14.3 g/L in transect 1 to an average concentration of 12.0 g/L in transect 4 (Fig. 5-1). The Cl concentrations in the Banana River Lagoon show no gradient during December and decrease to average values of ~ 11.5 g/L from their highest concentration values in August.

The average Cl concentrations of the seep water in all transects in the central area at all times are close to the value of the Cl concentration of the lagoon water column. Nonetheless, similar to the northern area, the Cl concentration of seep water is

127





Figure 5-1. Chloride concentrations of seep water at the three transects that are shown in Figures 2-3, 2-4, and 2-5. The solid horizontal line and the dashed horizontal line represent the average value for lagoon water during the dry season and rainy season, respectively.



Figure 5-2. Average Cl concentrations at each transect versus distance from the northernmost transect for A. May, B. August, and C. December.



Figure 5-3. Cl concentrations versus distance from the western shore of the Indian River Lagoon during A. May, B. August, and C. December for transect number 1. The filled circles represent seep water and the filled squares represent lagoon water.



Figure 5-4. Cl concentrations versus distance from the western shore of the Indian River Lagoon during A. May, B. August, and C. December for transect number 2. The filled circles represent seep water and the filled squares represent lagoon water.



Figure 5-5. Cl concentrations versus distance from the western shore of the Indian River Lagoon during A. May, B. August, and C. December for transect number 3. The filled circles represent seep water and the filled squares represent lagoon water.



Figure 5-6. Cl concentrations versus distance from the western shore of the Indian River Lagoon during A. May, B. August, and C. December for transect number 4. The filled circles represent seep water and the filled squares represent lagoon water.

consistently lower than the Cl concentration of the water column in all transects and all times except in transect 1 of the Indian River Lagoon during May 2000 (Fig. 5-3). At this time, the water column in Transect 1 in the Indian River Lagoon had the lowest Cl concentration of all the measurements. The higher Cl concentrations in seep water than in the water column at this transect is similar to the relationship between seep and lagoon water in northern area during the August sampling trip, also a period of relatively low Cl concentrations in the lagoon water.

Individual stations in the southern transects show similar patterns of the Cl concentration as the average values for the transects (Figs. 5-3, 5-4, 5-5, and 5-6). The Cl concentrations in the Indian River Lagoon are systematically greater than the Cl concentrations in the Banana River Lagoon, and the values change approximately at the same rate through time. The water in both the Indian River and Banana River lagoons increase in Cl concentration by \sim 30% from May to August 2000. Although the Cl concentrations in Transects 3 and 4 also increase through time, the increase is less than in the northern two transects. Transect 3 increases by only \sim 25% while transect 4 increases by only \sim 12%.

5.3.2 Pore water

The Cl and SO₄ concentrations are lower in the lagoon water and the shallow pore waters during December than during May or August 1999 (Appendix D and Fig. 5-7). Between August and December 1999, three hurricanes crossed the area, possibly causing the observed low concentrations. The large changes in composition of pore waters with depth, but the relatively limited data on pore water composition in the northern area, led to the inclusion of detailed pore water sampling during the second year of the project.

Similar to the northern area, pore water in the central area show large changes in the concentrations of various conservative solutes with depth (Figure 5-8, 5-9 and 5-10). As examples of the changes, concentrations of these solutes are plotted versus depth for the two most complete profiles from stations BRL2 and BRL6 (Fig. 5-8 and 5-9). These plots show a subdued minimum in Cl concentration in the pore water profiles from May 2000 and strong minima from August and December 2000. At all three sampling times,

the minima occur at a depth of about 50 to 70 cm below the seafloor (cmbsf), which is similar to the depth of the poorly-constrained minimum observed in the northern area. The uppermost sample has a Cl concentration similar to the overlying water column. At BRL2, where there are sufficient samples below the minima to constrain the gradient, Cl concentrations increase at identical rates for all three sampling time. For August and December, the difference between the Cl concentration in the overlying water column from the Cl concentration at the minimum creates a steep concentration profile in the upper 70 cm of these profiles.

At station BRL2, concentrations of SO₄ exhibit a pattern that is similar to the depth profiles of the Cl concentrations; they are similar to the lagoon water at the shallowest sampling depth, exhibiting a minimum at a depth of around 50 to 70 cmbsf (Fig. 5-10), and increasing in concentration below the minimum. When SO₄/Cl ratios are plotted versus depth, the ratio stays approximately constant to a depth of the Cl and SO₄ concentration minima (50 to 70 cmbsf) and then increase smoothly with depth. The SO4 concentrations and SO4/Cl ratios are similar at BRL6 to these profiles from BRL2 although they are more poorly constrained (Fig. 5-11). Although the profiles from the northern area are not as smooth as in the central study area, they also exhibit an increase with depth. Both the central and northern areas, the SO₄/Cl ratios are greater than the ratios in the water column below the depth of the Cl minimum.

The Sr isotope ratios and the $\delta^{18}O_{water}$ values at BRL2 show patterns that are similar to the Cl concentration, although their profiles are not as smooth as the Cl concentration (Fig. 5-8). In the shallowest samples, the $\delta^{18}O_{water}$ values are identical within error to the overlying water column. During all three sampling times, the $\delta^{18}O_{water}$ values decrease with depth in the sediment to values significantly lower than the overlying water column. At depths below ~150 cmbsf, the $\delta^{18}O_{water}$ values reach a more or less constant value of around 2 ‰. The Sr isotope ratios also show the highest value at the sediment water interface and decrease with depth, but the pattern is not as consistent as with the other solutes. The profiles versus depth of Sr isotope ratios and the $\delta^{18}O_{water}$ values are remarkably similar to the profiles of Cl concentration versus depth at station BRL6 (Fig. 5-9).



Figure 5-7. Depth profiles of Cl and SO₄ concentrations and of Cl/SO₄ molar ratios in pore water collected from multisamplers at IRL 4, IRL 5, and IRL 22. The heavy dark line represents the sediment water interface. The water column samples were collected from the shallowest port of the multisampler.



Figure 5-8. Cl concentrations, 87 Sr/ 86 Sr isotope ratios, and δ^{18} O values versus depth for pore waters at station BRL2. The circles represent samples collected in May 2000, the squares represent samples collected in August 2000, and the triangles represent samples collected in December 2000. The arrows represent the values in the water column for each component.



Figure 5-9. Cl concentrations, 87 Sr/ 86 Sr isotope ratios, and ${\delta}^{18}$ O values versus depth for pore waters at station BRL6. The circles represent samples collected in May 2000, the squares represent samples collected in August 2000, and the triangles represent samples collected in December 2000. The arrows represent the values in the water column for each component.



Figure 5-10. SO₄ and SO₄/Cl ratios versus depth for pore waters at station BRL2. The circles represent samples collected in May 2000, the squares represent samples collected in August 2000, and the triangles represent samples collected in December 2000. The arrows represent the values in the water column for each component. The line in the SO₄/Cl versus depth plot represent the seawater ratio.



Figure 5-11. SO₄ and SO₄/Cl ratios versus depth for pore waters at station BRL6. The circles represent samples collected in May 2000, the squares represent samples collected in August 2000, and the triangles represent samples collected in December 2000. The line in the SO₄/Cl versus depth plot represent the seawater ratio.

5.4 Discussion

The source of ground water seeping into the lagoon determines the concentrations of chemical components in the water and thus their fluxes. In the following discussion, sources of the components making up seep water are estimated on the basis of differences in composition of the seep water, lagoon water and pore waters. In addition, concentration gradients in pore water profiles are used to estimate sources of water to the pore spaces as well as to constrain modeled calculations of flow rates.

5.4.1 Origin of Seep Water

5.4.1.1 Lagoon water compositions

The changes in the Cl concentrations of lagoon water through time across both the northern and central study areas reflect the important role of evaporation and precipitation in the solute concentrations of the lagoons. In the northern area, the decrease in average Cl concentration of the lagoon water from May to August (e.g. Table 5-2) is expected for conservative solutes following dilution during the summer rainy period of the year. In the central study area, the change in Cl concentrations between May and August 2000 differs from this expected trend (Fig. 5-2), and may reflect a relative increase in evaporation over precipitation during this time regardless of the rain that fell during late June and July 2000 (Fig. 1-3).

The control of evaporation on the Cl concentration is reflected in the similar rate of change between the Indian and Banana River lagoons between May and August 2000. Between August to December 2000, however, average Cl concentration increased in Transects 1 and 2 of the Indian River Lagoon while the average Cl concentration decreased in the Banana River Lagoon (Fig. 5-2). These differences suggest that some processes other than regional precipitation and evaporation control the concentrations in the two lagoons. For example, local storms could form over small areas causing precipitation (and subsequent dilution) in one but not the other lagoon. Changes in the volumes of surface water runoff into the two lagoons could also affect their solute concentrations, although increased volumes of runoff would be expected to decrease the Cl concentrations in the Indian River Lagoon more than the Banana River Lagoon because of its larger catchment area.

Regardless of the changes in concentrations through time or the details of the changes in concentration across the lagoon, the spatial variation in the Cl concentrations of the lagoon water column suggests that there is significant mixing of the Indian River and Banana River lagoon water. During August and December 2000, the Cl concentrations in transects 3 and 4, which are located near Dragon Point where the Banana River and Indian River lagoons connect, approach the average value for concentrations in transects 3 and 4 are highest of all the Indian River Lagoon transects and average Cl concentrations in the Banana River Lagoon water are less than any of the Indian River Lagoon water (Fig. 5-2). The difference in the distribution of Cl concentration between May and December suggests that there is not unidirectional flow of water between the Banana River and Indian River and Indian River and Indian River and Indian River suggests that there is not unidirectional flow of water between the Banana River and Indian River lagoons.

There is little systematic variation in the Cl concentration of the lagoon or seep water with distance across the lagoon (Fig. 5-3 through 5-6). The Cl concentrations thus appear to be controlled by processes that are more local in extent than the distribution of sampling done for the study. Nonetheless, data from most of the individual stations show lower Cl concentration in the seep water than the overlying lagoon water. The largest difference occurs in the transects 3 and 4 of the Indian River Lagoon. If discharge of low-Cl concentration ground water is an important control of the Cl concentrations of the seep water, these data imply ground water discharge may be most important in transects 3 and 4.

The central two transects have layers at depths of about 50 cm below the sediment water interface that were sufficiently hard to prevent installations of multisamplers. If these hard layers are connected to the shallowly buried coquina that forms the banks of the lagoon in this region, they may provide a conduit for ground water to enter the lagoon, thereby affecting seep water chemistry if they are sufficiently close to the sediment water interface. The surface of the hard layers is highly irregular as observed by the various depths that the multisamplers could be installed. At some stations, moving
the multisampler a few meters laterally would allow additional penetration of several decimeters. If these hard layers act as conduits for fresh water, they would have more influence on the Cl concentration in the seep water where they are located close to the sediment-water interface.

5.4.1.2 Sources and quantities of ground water discharge

By comparing the compositions of conservative solutes in seep water with their compositions in the lagoon water, ground water, and pore water, it should be possible to calculate the fractions of lagoon and ground water that comprise the seep water using simple mass balance relationships. Assuming that little water is injected into the sediments during deployment of the seep meters, water discharged from the seep meters would represent seep water once the head space of the seepage meters is flushed. Thus a two-component mixing equation between ground water and lagoon water could be written as:

$$C_{sw} = (1 - f_{gw})C_{lw} + f_{gw}C_{gw}$$
(5-1)

where f_{gw} is the fraction of ground water entering the seepage meter, C_{lw} is the concentration or isotope ratio of the tracer in the lagoon water, C_{gw} is the concentration or isotope ratio of the tracer in the ground water, and C_{sw} is the concentration or isotope ratio measured in the water flowing from the seepage meter.

The similarity in the Cl concentrations of the seep and lagoon waters qualitatively implies that water flowing into the seep meters is mostly composed of water that has a composition similar to the composition in lagoon water. The generally lower Cl concentrations in the seep water than the lagoon water indicates that some additional low-Cl component has mixed with the lagoon water prior to discharge from the sediment. The increase in Cl concentrations of pore waters at depths below 70 cmbsf (Fig. 5-8 and 5-9) implies that the low Cl concentrations are from some component other than ground water. Substituting the fraction of this unidentified additional component, f_a for f_{gw} and rearranging equation 5-1 allows calculation of f_a , according to:

$$f_{a} = \frac{C_{lw} - C_{sw}}{C_{lw} - C_{gw}}$$
(5-2).

In order to use equation 5-2 to determine the fraction of the additional component, assumptions must be made about its Cl concentrations.

The values of C_{lw} and C_{sw} are easily measured (e.g. Appendix D). The largest uncertainty comes from determining the value of C_{gw} . Because the Floridan and Surficial aquifer waters mix across the northern region, average values for concentrations in the two aquifers would have to be used in order to determine the value of C_{gw} . The Cl concentrations in the Floridan aquifer range widely across the northern Indian River Lagoon (e.g., Toth, 1988), however, making precise calculations of the fraction of Floridan aquifer water difficult to determine. If most of the water is derived from the west (i.e. in the region with the greatest recharge potential), then the Cl concentration in ground water from this area could be used to estimate the fraction of water that enters the lagoon. If most of the water is from the east, however, then the Cl concentration in the source water would be elevated (Toth, 1988). The larger recharge area and higher potentiometric surface is to the west (e.g., Fig. 1-1), suggesting that the ground water component contained within the seep water would be derived from that area.

The Cl concentrations in the water supply wells that penetrate the upper Floridan and Surficial Aquifer and measured as part of this study (Appendix D) are significantly lower than the lagoon water. In the northern area, their Cl concentrations increase slightly from May to August 1999 with the average concentrations of these wells ranging from 0.36 g/L and 0.27 g/L. In contrast to the upper Floridan wells, the one well that sampled water from the Surficial Aquifer in the northern area exhibits Cl concentrations greater than the Floridan Aquifer water, but about one quarter the value of the lagoon water (Appendix D). This well is located to the east of the lagoon and thus is located in the region with elevated Cl concentrations (Toth, 1988). All of the wells in the central area have approximately the same Cl concentrations of around 0.5 mg/L regardless if they sample the Floridan or Surficial aquifer.

Assuming that the seep water contains low-Cl water from aquifers, the fraction of ground water contained in the seep water can be calculated using equation 2-2 by

comparing the average concentrations of Cl in the seep water (20.8 g/L) and lagoon water (21.1 g/L), and a range of 0.1 to 7.8 g/L for the values for ground water collected during May 1999 (e.g. Appendix D). These values suggest that the fraction of ground water derived from the Floridan Aquifer ranges from ~1 to 2 %. This small fraction of ground water is also reflected in the values for the Sr isotope ratios between the lagoon and seep water, which are identical within error because of the small difference in the isotopic composition of the aquifer and lagoon water compared with Cl concentrations. Consequently, strontium isotopic compositions cannot be used for a calculation similar to that for the Cl concentrations.

The concentrations of Cl in August 1999 are significantly lower than May 1999, both in the water column and in the seep water. On average, the seep water concentrations decrease by ~3.9%, but the water column samples decrease by ~6.7% from May to August probably because of dilution of the water column from direct precipitation and from surface runoff. The lower Cl concentration values for the lagoon than the seep water implies that there is no low-Cl water from the aquifers discharging from the sediment, although it is possible that high-Cl water from the dry season continues to be flushed from the sediment in August. A comparison of the Cl concentrations of the seep water in August with the Cl concentrations of the lagoon water during May could provide an estimate of the fraction of the ground water in the seep water. This calculation suggests that as much as 5% of the seep water may be ground water. Because of the extensive mixing between the Surficial and Floridan Aquifers in the area (e.g. Toth, 1988), the ground water entering the lagoon through seepage is a combination of water from the two aquifers

The apparently small fraction of ground water in the seep water suggests that the shallow pore waters could be an important source of water for ground water discharge. The increase in Cl concentration at depths below the Cl minimum further indicates that ground water from aquifers are unlikely to be important for reducing the Cl concentrations in the seep water. For all three sampling trips during the second year of the project the multisamplers exhibit lower Cl concentrations than the lagoon water at depths of ~70 cm as exemplified by stations BRL2 and BRL6 (Figs. 5-8 and 5-9). If this low-Cl water is responsible for the slight lowering of the Cl concentration in the seep

water over the lagoon water, it would be reasonable to use the minimum Cl concentration as a constraint for calculating f_a from equation 2. At station BRL2 in August, the Cl concentration at the depth of 80 cmbsf was 329 mM while the Cl concentrations in the lagoon and seep water were 412 mM and 401 mM, respectively (Appendix D). Using these concentrations in equation 5-2 indicates that around 13% of the seep water is composed of water with a Cl concentration similar to that at a depth of 80 cmbsf. Although there is a relatively small fraction of the low Cl water in the seep water, changes in its concentration of reactive solutes, such as nutrients, may be important for control of the chemical composition of the water column. Similarly, the cause or causes of the low Cl concentrations in the sediment is important to determine the origin of this water. The cause of variability in concentration of conservative solutes may be determined using changes in the pore water profiles.

5.4.2 Pore water profiles

5.4.2.1 Conservative solutes

The shape of the pore water profiles are similar between the northern and central study areas. In both places, there are minima in Cl and SO₄ concentrations at depths of 50 to 70 cm, although the limited amount of data in the north does not constrain the shape of the profiles as well as in the central study area. These results differ from those observed by Gu et al. (1987) and Trefry et al. (1992), who found Cl concentration decrease by approximately a factor of 2 with depth in the Eau Gallie River and Turkey Creek, two streams that source the Indian River Lagoon. At these sites, the deepest samples extended to ~40 cmbsf and thus there is no information about variations of the Cl concentrations at greater depths. The decrease in Cl concentration was attributed by Gu et al. (1987) to discharge of fresh ground water to the lagoon. Diffusive mixing with the overlying lagoon water also is an important process, which is likely to contribute to the changes in the shallow sediments.

The origin of the observed solute minima could also be associated with downward mixing of lagoon water into the sediments. Such downward mixing of low-Cl water to create the Cl minima could not occur by gravity because the flow direction would have

been against the density gradient; low density fresher water would have to flow downward and displace more dense water high in Cl. Although the mechanisms causing mixing in shallow lagoonal sediments are unknown, there are several possible ways that it could occur. For example, high winds associated with hurricanes that passed through the area in the fall of 1999 may have resuspended some of the lagoon bottom sediment and pore water. It is unlikely, however, that it was resuspended to a depth of 50 to 70 cm. Large waves formed from the high winds may have pumped water into the sediments. Biota living within the sediment, for example burrowing shrimp, may also pump water through there burrows (e.g. Emerson et al., 1984). If biological factors are important, they would cause water to pass through the sediment constantly. If storms are important, the flow through the sediment would occur only sporadically. Continuous flushing of water by biota could also explain the significantly larger volumes of water that are measure in seep meters than are calculated from numerical models of the ground water discharge. Regardless of the cause of the Cl minimum, the increase of the Cl concentrations below ~70 cm indicates that the decrease in the shallow sediments can not be derived from upward flow from the aquifers.

Another possible source of the observed Cl minima could be from lateral flow. The possibility that low-Cl water flows laterally from onshore can be tested with δ^{18} O values. The low-Cl zone has δ^{18} O values that are significantly lower than the overlying water column, indicating that some other source of water may flow laterally into the sediments. Although there is no data on the δ^{18} O isotopic composition of precipitation in the region it would be expected to be less than zero. The values measured for water from ground water wells average around -1.5% (SMOW). Consequently, the low δ^{18} O values of the low Cl water are consistent with mixing with a meteoric or ground water source.

The lowest δ^{18} O values measured for the Cl minimum average around 1.8‰ at stations BRL2 and BRL6 (Fig. 5-9 and 5-10). The lagoon water varies with time from around 2.1 ‰ in May and December to around 2.7‰ in August. If the low Cl zone results from lateral flow through the sediments, the mixing relationship shown in equation 5-2 can be used for the mixing calculations of lagoon and meteoric water if it is assumed that the δ^{18} O value of 1.8‰ in low Cl zone (C_{sw}) is a result of mixing of meteoric water with δ^{18} O values of -1.5% (C_{gw}) and lagoon water with a concentration

of around 2.1‰ (C_{lw}). With these values, equation 5-2 suggests that the low Cl zone is approximately 8% meteoric water. Assuming that the lagoon water concentration is 2.7‰, such as in August, indicates that the low Cl zone contains as much as 20% meteoric water. The similar values in May and December suggest that the high value measured in August may be anomalous. It will be important to get a measure of the change through time in the δ^{18} O value of the lagoon water and the pore water profiles in order to make precise mixing calculations.

It is more difficult to do a similar calculation using Cl as a constraint because the concentration of Cl in the shallow aquifer is not known and because the Cl concentration of the lagoon water is more variable than the δ^{18} O values. Good measurements of these values, in particular the rate of change with time of the Cl concentration of the lagoon water would be required in order to calculate the extent of mixing with meteoric water in the low Cl zone.

5.4.2.2 Constraints on flow rates

The shape of the pore water profiles can be used to infer vertical flow rates through the sediments. The calculations are based on a one dimensional differential equation which describes changes in concentration of solutes with depth in the sediment caused by diffusion, advection, and reactions (e.g., Berner, 1980):

$$D\frac{d^2C}{dz^2} - v\frac{dC}{dz} - \Sigma R = 0$$
(5-3)

where D represents the diffusion coefficient in the sediment, C represents the solute concentration at depth z, and v represents the upward velocity of flow. The term for v could also represent sedimentation rate, but the lack of information about sedimentation rate in the lagoon makes it impossible to evaluate the relative difference between sedimentation rate and fluid flow rate. Sedimentation rate will be an important constraint to evaluate in future applications of equation 5-3. The third term, ΣR represents changes in concentrations that result from all fluid-solid reactions. For conservative solutes, there are no fluid solid reactions and $\Sigma R = 0$. With $\Sigma R = 0$, the analytical solution to equation 5-3 is

$$C(z) = \frac{1}{1 - \exp(\frac{vL}{D})} \{ C_1 [1 - \exp(\frac{vZ}{D})] + C_0 [\exp(\frac{vZ}{D} - \exp(\frac{vL}{D})] \}$$
(5-4)

In this equation, C_1 is the concentration of the conservative solute at depth L in the sediment and C_0 is the concentration at the sediment water interface. Values of D are well known for various solutes in sandy sediment (e.g., for Cl⁻, D = ~0.05 m²/yr). By measuring the water column values (C_0) and fitting curves to the profiles of conservative solutes, such as Cl, ⁸⁷Sr/⁸⁶Sr, δ^{18} O, and/or δ D, it is possible to calculate values for v (e.g., Fig. 5-11).

If solute concentrations are controlled only by diffusion, the diffusive mixing between the two water bodies will produce a straight line. The concave downward curvature of the Cl profiles at depths below 70 cm at BRL2 suggests there is upward flow of water. Using the measured concentration of Cl at 70 cm (C_o) and 230 cm (C_l) as boundary conditions, and assuming that $D = 0.05 \text{ m}^2/\text{yr}$, the curvature of the Cl concentration indicates there is an upward flow rate of v = 5 cm/yr (Fig. 5-11). This value of upward flow is three to four orders of magnitude slower than the values that are measured using the seepage meters (e.g. Appendix B), and is close to values that are calculated using numerical methods (e.g. Pandit and El-Khazim, 1990). This value thus suggests that ground water flow could be important to the lagoon, but the elevated Cl concentration indicates that water other than ground water contributes to flow. Although little or no ground water appears to discharge, the force for the upward flow may derive from the hydrostatic head on the aquifers onshore.

5.5 Summary and Recommendations

The chemical and isotopic composition of different waters in the Indian River Lagoon suggest that ground water, which herein is defined as freshwater flowing through



Figure 5-12. Measured and calculated Cl concentrations for BRL2. The heavy dashed line represents concentrations that were calculated using assumptions discussed in text and equation 5-4.

the major aquifers in the region, is only a minor component of water discharging from the sediment to the overlying lagoon water. The Cl concentrations of regional ground water and the difference of Cl concentrations of the lagoon water and water discharging from seep meters indicate that at most approximately 5% of the water could have a Cl

concentration similar to ground water, and that the value may be less than 1%. These small amounts of the ground water discharge are consistent with the small amounts of ground water that are calculated to be available for discharge using numerical flow models (Pandit and El-Kazim, 1990) and mass balance considerations (Motz, 2001).

Although the generally lower Cl concentration in the seep water than the lagoon water suggests that some ground water may be discharging from the sediment, the concentration gradients of the pore water imply that the ground water does not reach the sediment water interface. The increase in Cl concentrations below the minima that occur at a depth of \sim 50 to 70 cmbsf indicates that water sources other than ground water may be important for the seep water. Pressure associated with the elevation head of the ground water could influence discharge, and might be associated with the general increase in average seepage rates that are observed between the sampling periods in May at the end of the dry season and in August and December in the middle and following the rainy season.

Regardless of the origin of the seep water, the pore water profiles suggest that there is a significant amount of mixing between the shallow pore fluid and the overlying lagoon water. This mixing is shown by changes through time in the concentrations of conservative solutes at depths between 0 and 70 cmbsf, with little change through time in their concentrations at depths below 70 cmbsf. The curvature of the pore water profiles at depths below 70 cmbsf appears to be a result of upward flow of ~5 cm/y. This flow rate is several orders of magnitude less than found in the seepage meters.

The observation of shallow water cycling in the sediments reflects several important aspects of nutrient cycling in the Indian River Lagoon. First, the apparent small volume of ground water discharge relative to the total volume of discharge suggests that the Indian River Lagoon may not be at great risk for contamination associated with pollution in the ground water flowing from onshore. Only extremely high nutrient concentrations would cause a large flux of nutrients from the apparently small source of water from the aquifers. The extensive remineralization of organic matter that occurs during shallow diagenetic reactions, however, suggests that mixing of lagoon water into the shallow sediments could provide a mechanism to drive a large nutrient load to the lagoon. The physical mechanism that drives this mixing is unknown but will be

important to understand in order to quantify the magnitude of the discharge and its potential influence on nutrient cycling.

Several different approaches could be taken to study the extent of the mixing. High resolution measurements through time of the shallow pore water would provide better constraints on how rapidly the shallow pore water mixes with the overlying lagoon water. These temporal measurements could be made on a monthly or biweekly basis and would have to be associated with the measurements of the lagoon water chemistry. The measurements could be simplified from the work done in this project by measuring the compositions to slightly below the depth of the minimum (e.g. at depths of ~1 m). Obtaining shorter profiles would also allow wider distribution of the measurements to see how the mixing occurs spatially.

In order to better understand the link between ground water, pore water, the mixed zone, and the lagoon water, it will also be important to get deeper samples of the pore water than those available from the multisamplers. Obtaining such deep pore waters will require drilling through the coquina layer that appears to underlie most of the lagoon at shallow depths. Such deep samples will provide information on the mixing zone between the fresh water contained within the aquifers and the overlying salt water of the lagoon and shallow pore waters.

CHAPTER 6 – POTENTIAL NUTRIENT FLUXES ASSOCIATED WITH GROUND WATER DISCHARGE

6.1 Introduction

The potential decline in biological integrity from a macrophyte-based ecosystem to a phytoplankton- or algal-based system of the Indian River and Banana River lagoons (IRL SWIM Plan, 1989; 1984; Sigua et al., 2000) reflects the importance of cycling of nutrients to the water quality of these enclosed water bodies. There are several sources of nutrients surrounding the Indian River lagoon system. One source is from surface water runoff, and the urbanization around the lagoon appears to have increased the load of nutrients from this source. Atmospheric deposition provides another source of nitrogen, and this source has been estimated from direct measurements at a National Atmospheric Deposition Program site on Cape Canaveral (Dreschel et al., 1990). Remineralization of organic matter in the sediment provides another source of nutrients to the coastal water (e.g. Froelich, 1970; Reddy et al., 1999). Previous estimates of the sedimentary source have considered only diffusion as a transportation mechanism (e.g. Trefry et al., 1992; Reddy et al., 1999). If there is a significant large discharge of ground water to the lagoon or if mixing of lagoon and shallow pore water is important as was discussed in Chapter 5, then the total loading of remineralized nutrients could be larger than that provided through diffusion alone and could be an important pathway in the nutrient cycle. Studies in other coastal areas and estuaries suggest that ground water discharge may provide a

mechanism for transportation of nutrients and other dissolved species to lagoon waters (e.g. Gallagher et al., 1996; Rutkowski et al., 1999).

The purpose of this portion of the study is to estimate the nutrient flux to lagoon water that comes from seep water and to compare this estimated value with previously measured diffusive fluxes as well as other parts of nutrient cycling, such as atmospheric deposition and surface water runoff (e.g. Trefry et al., 1992; Reddy et al., 1999). The procedure used is straightforward and relies on sampling concentrations of various nutrient species in the seep water and converting these concentrations to fluxes on the basis of the seepage rates measured with seep meters and radioisotope tracers.

6.2 Analytical Methods

Concentrations of all nutrients were measured using a either a Milton Roy Spectronic model 401 spectrophotometer (e.g. Clesceri et al., 1989) or a Technicon Autoanalyzer II. All samples that were collected after May 1999 were measured using the autoanalyzer. The PO₄ and Si concentrations were measured on the non-acidified filtered water samples, and NH_4 was measured on the acidified filtered water samples. Nitrogen and phosphorous concentrations were measured following Kjeldahl digestion for both the filtered and non-filtered samples. The concentrations of these samples are reported as total soluble nitrogen (TSN) and total soluble phosphorous (TSP) for the filtered samples and total nitrogen (TN) and total phosphorous (TP) concentrations for the unfiltered samples. The Kjeldahl digestion was accomplished by autoclaving the samples in the presence of potassium persulfate reagent (20 g/L of K₂S₂O₈ and 0.75 N NaOH). Concentrations of NO_3 were measured on filtered samples prior to Kjeldahl digestion. A cadmium reduction column converted all NO₂ to NO₃ prior to analysis and thus the values reported are the sum of NO₂ and NO₃. Precisions of the PO₄ and NH₄ analyses were estimated by measuring check standards every fourth sample and calculating the coefficient of variation (standard deviation divided by the mean) of the values for the check standard. Precisions of the TSN, TN, NO₃, TSP, TP, and SiO₂ concentrations were estimated by analyzing duplicate samples every 10th sample.

Solute	Precision (%)
PO ₄	2.6*
$\rm NH_4$	2.5*
NO ₃	2.0**
TSN	1.5**
TN	1.7**
TSP	4.1**
ТР	2.2**
SiO ₂	0.5**

Table 6-1. Estimated precision of various solutes

* Precision is the coefficient of variation, $COV = 1 \sigma/mean$.

** duplicate measured every 10 sample.

6.3 Results

6.3.1 Lagoon and Seep Water

In contrast to the conservative solutes shown in Table 5-2, there is a large variation in concentrations of all of the nutrient species, and this variation is greater in the seep water than in the lagoon water. Table 6-2 reports the average, median and standard deviations of the nutrient concentrations (NO₃, NH₄, TSN, TN, PO₄, TSP, TP, and SiO₂) in seep and lagoon water for both May and August 1999. (See Section 5.1 for a definition of seep and lagoon water). For example, the coefficients of variation of the TSN are 32% and 47% for the seep water in the May and August, 1999, respectively. The coefficients of variation for TSP are even greater than for TSN: 100% and 242% for May and August 1999, respectively. In all cases, the median value is lower than the average indicating that the average values are skewed to high values because of a few high concentrations.

There are several observations that can be made about differences in median values for each of the components. The median concentrations of NO₃ are lower in both seep and lagoon water samples in May than in August and are considerably lower than

	NO ₃	NH₄	TSN	TN	PO_4	TSP	TP	SiO ₂	
	(mg N/L)	(mg N/L)	(mg/L)	(mg/L)	(µM)	(µg/L)	(µg/L)	(mg/L)	
	May 1999								
Seep water									
Average	0.006	2.56	2.62		210	108		5.11	
Median	0.004	2.22	2.50		92	61		4.79	
1σ	0.005	1.44	0.83		238	108		1.79	
Lagoon water									
Average	0.006	0.10	0.92		19	17		0.47	
Median	0.005	0.10	0.93		17	16		0.41	
1σ	0.004	0.02	0.08		3	2		0.31	
		August 1	999						
Seep water									
Average	0.048	4.57	2.97	3.11	345	182	237	5.65	
Median	0.050	3.55	2.74	2.77	219	80	135	5.22	
1 σ	0.027	5.55	1.41	1.92	507	442	494	1.57	
Lagoon water									
Average	0.051	0.13	1.07	1.30	0	16	35	1.51	
Median	0.038	0.10	1.05	1.30	0	16	34	1.43	
1σ	0.024	0.05	0.07	0.05	0	1	4	0.58	

 Table 6-2. Average, median, and standard deviation of conservative tracers for seep

 water and lagoon water.

the ammonia concentrations in the seep meters. The median ammonia, TSN, PO_4 , TSP, and SiO₂ concentrations are greater in the seep than the lagoon water for both May and August 1999. The median concentrations of these solutes in the seep water are also greater in August than in May. Except for NO₃ and silica concentrations, there is little significant difference in the lagoon water concentrations between the dry and rainy season samples. Both median NO₃ and silica concentrations increase in the lagoon water from the dry to the rainy season sampling.

In general, differences between concentrations of the various nutrient species in the central study are similar to the northern study area. Although there are significant variations in Cl concentrations, which reflect evaporation and precipitation (Fig. 5-2), biogeochemical processes are likely to exert a greater control of the nutrient concentrations than evaporation or precipitation. Although there is some variation in the

average concentrations of the nutrients longitudinally in the lagoon, these variations do not mimic those observed by the Cl concentrations (Figs. 6-1 and 6-2). For this reason, and for ease in comparison of the different species, sample collection times, and water samples, the concentrations of all the nutrient samples for the seep water and lagoon water have been averaged and are reported in Table 6-3. These averages are similar to the northern study areas in the differences between the solutes in the seep and lagoon water. For example, NO₃ is slightly enriched in the seep water over the lagoon water and NH₄ is greatly enriched, commonly by more than an order of magnitude in the seep water than in the lagoon water (Table 6-3). The TSN and TN concentrations are greater than the NH₄ concentrations, reflecting the presence of soluble and particulate organic compounds. The PO₄, TSP and TP are also enriched in the seep water over the lagoon water, in most cases by more than an order of magnitude. Most of the phosphorous is in the form of PO₄.

6.3.2 Pore waters

The profiles of nutrient concentrations in the pore waters differ greatly from the profiles of the conservative solutes (Figs. 6-3, 6-4, and 6-5). In the northern study area, they do not exhibit smooth concentration gradients with depth in the sediment. At all stations, the oxygen concentrations are low in the pore waters, and the small amount of oxygen that was measured could represent atmospheric contamination when the samples were being collected. There is little NO₃ in the pore waters as well, suggesting all oxygen should have been utilized during microbial mineralization of organic matter (e.g. Froelich et al., 1979). In contrast to the oxygen and NO3 concentrations, the TSN and TSP concentrations increase with depth in the sediment.

The nutrient profiles in the central study area exhibit smoother depth profiles than in the northern study area, and the profiles also have major inflections in concentrations at depths corresponding to the depth of the minima in Cl concentrations. At BRL2 and BRL6 in the central area, the concentrations of TN, TSN, and NH₄ increase to a depth of approximately 50 cmbsf and then maintain an approximately constant concentration below this depth (Fig. 6-4). The most rapid increase in concentration occurs over the



Figure 6-1. Average TN concentrations at each transect versus distance from the northernmost transect for A. May, B. August, and C. December.



Figure 6-2. Average TP concentrations at each transect versus distance from the northernmost transect for A. May, B. August, and C. December.

· ·		1			1	1		1
	NO ₃	NH ₄	TSN	TN	PO ₄	TSP	TP	SiO ₂
	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L)	(mg/L)
May 2000								
Seep water - IRL	1		1	1			1	
Average	0.009	0.30	0.83	2.55	1.76	1.36	1.37	16.6
Median	0.009	0.26	0.65	0.85	1.90	1.37	1.32	14.5
1 σ	0.003	0.26	0.89	3.52	1.25	0.98	0.86	8.9
Seep water - BRL								
Average	0.004	0.47	0.31	1.56	0.17	0.10	0.22	5.9
Median	0.005	0.43	0.36	0.63	0.12	0.09	0.13	4.9
1 σ	0.002	0.15	0.11	2.01	0.13	0.09	0.23	4.5
Lagoon water - IRL								
Average	0.002	0.02	0.29	0.34	0.07	0.07	0.03	1.5
Median	0.001	0.02	0.30	0.35	0.03	0.02	0.03	1.1
1 σ	0.001	0.02	0.07	0.05	0.16	0.17	0.01	1.6
Lagoon water - BRL								
Average	0.003	0.04	0.33	0.30	0.003	0.01	0.04	1.1
Median	0.002	0.03	0.33	0.30	0.003	0.01	0.04	1.1
1 σ	0.002	0.03	0.02	0.03	0.001	0.01	0.01	0.4
	Augu	ust 2000						
Seep water - IRL								
Average	0.004	0.77	1.65	1.64	0.57	0.48	0.55	9.1
Median	0.004	0.52	1.54	1.46	0.38	0.31	0.36	6.7
1 σ	0.003	0.59	0.67	0.73	0.54	0.45	0.56	5.5
Seep water - BRL								
Average	0.002	0.36	1.49	1.33	0.28	0.24	0.26	8.1
Median	0.001	0.45	1.32	1.27.	0.25	0.23	0.22	7.2
1 σ	0.002	0.24	0.63	0.34	0.27	0.25	0.26	5.6
Lagoon water - IRL								
Average	0.005	0.03	0.38	0.40	0.05	0.06	0.07	2.2
Median	0.002	0.02	0.38	0.36	0.05	0.07	0.08	2.2
1 σ	0.011	0.02	0.06	0.07	0.02	0.02	0.01	0.2
Lagoon water - BRL								
Average	0.001	0.02	0.55	0.61	0.01	0.03	0.04	2.9
Median	0.001	0.02	0.54	0.60	0.01	0.03	0.04	2.7
1 σ	0.001	0.01	0.06	0.07	0.004	0.01	0.01	0.4

 Table 6-3. Average, median and standard deviation of nutrients for seep and lagoon water, central area.

	NO ₃	NH ₄	TSN	TN	PO ₄	TSP	TP	SiO ₂
	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L)	(mg/L)
	Decen	nber 2000						
Seep water - IRL		-			-	-		-
Average	0.006	0.46	1.63	1.69	0.14	0.15	0.15	4.2
Median	0.005	0.43	1.56	1.67	0.08	0.09	0.13	4.3
1 σ	0.007	0.26	0.49	0.55	0.12	0.11	0.09	1.1
Seep water - BRL								
Average	0.000	0.35	1.32	1.46	0.10	0.10	0.13	3.7
Median	0.000	0.27	1.20	1.47	0.06	0.08	0.11	3.9
1 σ	0.000	0.30	0.50	0.46	0.11	0.10	0.09	1.6
Lagoon water - IRL								
Average	0.013	0.04	0.83	0.91	0.01	0.02	0.03	0.8
Median	0.015	0.04	0.82	0.91	0.01	0.02	0.03	0.9
1 σ	0.006	0.02	0.05	0.05	0.004	0.003	0.01	0.4
Lagoon water - BRL								
Average	0.002	0.02	0.74	0.90	0.01	0.01	0.04	0.03
Median	0.002	0.02	0.76	0.89	0.01	0.01	0.04	0.03
1 σ	0.000	0.01	0.03	0.03	0.001	0.001	0.004	0.03

interval where the Cl concentration decreases. The TN and TSN concentrations have approximately similar profiles, while the NH₄ concentrations are significantly less than TN or TSN. The NO₃ concentrations are at or below the detection limit (Appendix D). Consequently, most of the nitrogen is contained as soluble organic compounds and dissolved NH₄. The shapes of the profiles change slightly when normalized to Cl concentrations (Fig. 6-6). In particular, the TSN concentrations increase sharply with depth to ~50 cmbsf and then decrease slightly during May and August. A sharp maximum in TSN concentrations occurs for samples collected in December 2000. In contrast to the nitrogen profiles, the depth profiles of TP and TSP show their largest increase at BRL2 and BRL6 in the central area at depths below 70 cmbsf (Fig. 6-5). At depths above 70 cmbsf, both TP and TSP show only slight increases in concentration with depth. Similar to the nitrogen profiles, the TP and TSP are similar in concentration indicating that most of the phosphorous in the pore water is composed



Figure 6-3. TSP, TSN, and DO versus depth in pore water collected from multisamplers at IRL 4, IRL 5, and IRL 22. The heavy dark line represents the sediment water interface, and the water column samples were collected from the shallowest port of the multisampler.



Figure 6-4. Total nitrogen and total soluble nitrogen versus depth for pore waters at station BRL2. The circles represent samples collected in May 2000, the squares represent samples collected in August 2000, and the triangles represent samples collected in December 2000.



Figure 6-5. Total phosphorous and total soluble phosphorous versus depth for pore waters at station BRL2. The circles represent samples collected in May 2000, the squares represent samples collected in August 2000, and the triangles represent samples collected in December 2000.



Figure 6-6. Total soluble nitrogen and total soluble phosphorous normalized to Cl versus depth at station BRL2. The circles represent samples collected in May 2000, the squares represent samples collected in August 2000, and the triangles represent samples collected in December 2000.

largely of dissolved phosphate. Normalizing the TSP concentrations to Cl concentrations alters the profiles of TSP to increase more or less monotonically with depth in the sediment, suggesting that the low concentrations in the upper 50 to 70 cm of the sediment column results from a dilution effect similar to the Cl concentrations (Fig. 6-6).

6.4 Discussion

6.4.1 Pore Water Profiles

Oxygen and NO₃ are nearly depleted in the pore water which suggests that bacterial SO₄ reduction may have begun at shallow depths in the sediment (Froelich et al., 1979). If SO₄ reduction has begun, then the SO₄ concentrations should be depleted relative to the changes in the Cl concentrations. In general, the shapes of the SO₄ concentration profiles mimic the Cl concentration profiles at station BRL2 and BRL6 (Fig. 5-8 and 5-9). At BRL2, they pass through a minimum at a depth of ~80 cmbsf in the May, August and December samples. Below this minimum, the SO₄ concentrations increase at similar rates for all three sampling times. In addition, the SO₄ concentrations for May and August are slightly greater than the highest measured values in the lagoon water. At BRL6, the SO₄ concentrations decrease from the sediment-water interface to a depth of around 50 cmbsf and remain approximately constant below this depth. The similarity in the shapes of the SO₄ and Cl profiles suggests that SO₄ concentrations are largely controlled by dilution from the low Cl water.

These SO₄ profiles differ greatly from those found by Gu et al. (1987) and Trefry et al. (1992). For example, Gu et al. (1987) showed complete sulfate reduction has occurred by a sub-bottom depth of ~10 cm for fine grained sediment of Eau Gallie River. The rapid sulfate reduction in these profiles imply there may be little exchange between the pore water and overlying lagoon water, unlike the solute profiles observed at station BRL6. The difference between these results and those reported in Gu et al. (1987) may be caused by differences in the physical properties of the sediments at the two locations. Gu et al. (1987) report on pore water composition from muddy sediments, and although no cores were collected from BRL6, the surface sediments are sandy. The ease with which water could be pumped from all multisamplers ports suggests that most of the sediment at depth is also sandy. The differences in lithology and pore water compositions illustrate the importance of determining the physical characteristics of sediments, such as grain size, permeability, mineralogy, and organic carbon content, along with the concentrations of dissolved solutes. These differences also indicate that it is important to gather pore water in several different ways. Gu et al. (1987) and Trefry et al. (1992) rely on squeezing water from the sediments using Reeburgh-type squeezers (Reeburgh, 1967). This technique works quite well for fine grained sediment, but provide little water in sandy sediment. In contrast, the multisamplers used in this study are biased toward extraction of water from sandy sediment.

At station BRL2, the value of the SO₄/Cl ratio in the shallow part of the sediment is approximately uniform with depth with values that range from ~0.048 to 0.050, which are similar to the SO_4/Cl ratio in the overlying lagoon water. These values are slightly lower than the ratio in seawater (0.052). At station BRL6, the SO₄/Cl ratios pass through a slight minimum at a depth of around 50 to 90 cmbsf. The low SO₄/Cl ratios in the pore water could indicate that the low Cl water mixing with the pore water is depleted in SO_4 relative to seawater. Alternatively, the low ratios could reflect bacterial SO₄ reduction. Below the depth of the Cl minimum, the SO₄/Cl ratio increases from average values of between ~ 0.048 and 0.050 to a value of around 0.54. If bacterial SO₄ reduction has begun in the shallow sediment, it should continue with greater depth, thereby decreasing the SO₄ ratios to values lower than those observed at the Cl minimum (Fig. 5-10 and 5-11). Consequently, the low-Cl at depths of ~ 80 cmbsf appears to be depleted in SO₄ relative to seawater and lagoon water, but the high Cl water below the minimum is enriched in SO₄ over seawater values. The SO₄/Cl ratios measured in samples collected from the groundwater wells are generally higher than seawater values suggesting that the elevated SO₄/Cl ratios in ground water may be observed in the high-Cl water below the Cl minimum.

Regardless of the apparently limited amount of SO_4 reduction in the pore waters, the nitrogen and phosphorous species all increase with depth, probably from oxidation and remineralization of the solid organic matter (Fig. 6-4 and 6-5). Oxidation of organic matter is likely to be extensive in the upper 70 cm of the sediment if there is mixing of oxygenated lagoon water into the sediments as suggested by the depth profiles of Cl concentrations (Chapter 5). The dilution shown by Cl concentration makes observation of the increase in nutrients difficult to observe. These complications can be minimized by normalizing the nutrient concentrations to Cl concentrations (e.g. Fig. 6-6). These normalized profiles indicate that most of the N diagenesis occurs in the upper 70 cm of the sediment. At depths below the Cl minimum, the N species reach a constant composition and the TSN/Cl ratios decrease with depth, possibly reflecting uptake reaction such as occurs during clay mineral diagenesis. Unlike the N profiles, the TSP/Cl ratios continue to increase with depth, suggesting there is continuous release of P from the sediments with depth. The extensive diagenesis of organic matter within the shallow sediments could provide a large flux of nutrients to the water column.

Particularly important is the relationship between the concentrations of nutrients in the shallow pore waters and the concentrations in the seep water. The shallow pore waters and seep waters have similar concentrations, supporting the idea that altered pore water flows upward and displaces the lagoon water in the seep meter. Consequently, the concentrations of nutrients in the seep water and the seep rates could provide a first order estimate of the flux and loading rates of nutrients to the Indian River Lagoon.

6.4.2 Nutrient Fluxes

The flux of water from the lagoon sediments appears to be fairly well constrained by consistent values measured on the basis of direct seepage measurements reported in Chapter 2, the short lived Ra isotope ratios reported in Chapter 3, and ²²²Rn and ²²⁶Ra activities reported in Chapter 4. These flux values, when multiplied by the concentrations of nutrients in the seep water, provide a means of estimating the flux of nutrients to the water column. Although concentrations of nutrients have been suggested to increase in the head space in water beneath the seep meters because of *in situ* oxidation of organic matter (e.g. Belanger and Mikutel, 1995), the measured high flow rates from most of the seep meters and the low oxygen concentration in the pore water and seep water suggest that *in situ* oxidation is unlikely to be a significant artifact in the Indian River Lagoon. The average flow rate from the seep meters is 10.9 and 17.6 ml/min. for the May and August 1999 respectively, which indicates that on average the 10 L head space of the seep meter (assuming it is inserted half way into the sediment) is flushed by pore water in ~0.6 days during May 1999 and ~0.4 days during the August 1999. The slower flow rates during the 2000 than the 1999 season (Table 2-1) indicate that there was longer flushing times. For May 2000, the meters would flush in ~0.9 days and in August and December 2000, the meters would flush in ~0.65 days. All meters were deployed for more than 2 days prior to sampling for seep water and thus should be completely flushed of their headspace lagoon water at the time of sampling and the samples should approximate pure seep water.

Some lagoon water may be pushed into the sediments during deployment of the seepage meters, although most water would be expected to flow from the port during deployment. The maximum amount of water that could be pushed into the sediment would be approximately 10 L, assuming that the meters penetrate half way into the sediment and no water escapes from the port. Although the volume of water that vents from the port during deployment of the seep meters has not been quantified, there is always a strong flow of water out of the ports, suggesting that during deployment of the meters most of the water is displaced out of the port rather than into the sediment. The water sampled should represent the concentrations of the pore water and be representative of the concentrations of nutrients entering the lagoon water.

If there is a large amount of mixing in the shallow sediment, then not all of nutrients in the seep water can be considered as a new flux to the lagoon. Some of the nutrients in the seep water would have been brought into the shallow sediment along with the lagoon water prior to flow through the sediment. Some nutrients also might originate from the upward flow of ground water. A new source of nutrients from ground water would be small, however, because the nutrient concentrations in ground water are lower than in the pore water and because ground water appears to be at most ~5% of the seep water but may be considerably less (e.g. Chapter 5). The nutrient pore water profiles suggest that most of the newly generated nutrients come from the remineralization of organic matter in the shallow sediment during mixing of the lagoon and pore water. This source of remineralized nutrients may provide a significant contribution of new nutrients

to the lagoon and constitute a major flux in the nutrient cycle. Therefore, the following calculations estimate possible fluxes of N and P that are measured in the seep meters.

6.4.2.1 N Flux Calculations

Calculations of the nitrogen loading to the lagoon are made assuming average seep rates across the study areas for the seep meter stations (Table 2-2). This assumption is reasonable because the average seepage rates are similar to the seep measurements using radioisotopes, a technique that integrates the seepage rates. Because seep rates and concentrations differ depending on the season the samples were collected, the calculations are divided between the different sample trips. Specifically, for the northern area, the seepage rate averaged 40 and 63 ml/m²/min for May and August 1999, respectively. The seep rates are generally lower in the central area, averaging 28 and 39 $ml/m^2/min$ for May and August 2000, respectively when all measurements from the Banana and Indian River lagoon are combined. These combined rates are essentially identical for August and December 2000 (39.1 ml/m²/min and 38.9 ml/m²/min, respectively). From August to December, there are slight but not systematic differences between the seep rates in the Banana River and Indian River lagoons. The rate decreases from August to December for the Indian River Lagoon, but increase over the same time interval for the Banana River Lagoon (Table 2-2). Although the dry season lasts approximately 8 months from November to May and the rainy season occurs during the remainder of the year (Fig. 1-3), the similarity in seep rate between August and December suggests that seep rates do not exactly correspond to periods of high and low rainfall. Consequently, the nutrient fluxes have been calculated separately for the three sampling periods for the two lagoons assuming the seep rates remain constant for these times.

If much of the seep water that was collected from the seep meters originated as lagoon water circulated through the shallow sediments, the nutrient concentrations of the lagoon water must be subtracted from the nutrient concentrations in the seep water in order to calculate the flux to the lagoon of newly generated nutrients. For example, in the northern study area, the average TSN concentrations in the seep and lagoon water were

2.6 and 0.9 mg/L in May 1999, reflecting a net increase of 1.7 mg/L in the seep water over the lagoon water. In August 1999, the average TN concentrations in the seep and lagoon water were 3.1 and 1.3 mg/L reflecting a net increase of 1.4 mg/L (Table 6-4). Multiplying these increases in nutrient concentrations by the seepage rates indicates the flux of TSN was ~98 mg/m²/day for the May sampling period and 164 mg/m²/day for the August sampling. Assuming that the fluxes measured during May and August 1999 each last approximately half of the year, the net loading of nitrogen to the lagoon water can be calculated for each sample period. Summing these two values provides the total annual load. This calculations indicates that the annual load of TN is 2.3 x 10⁶ kg for the ~48 km² northern study area (Table 6-4). Similar calculations for the central study area suggests that the annual load of TN is 0.85 x 10⁶ kg for the ~29 km² region of the central Indian River Lagoon and is 0.43 x 10⁶ kg for the ~28 km² region of the Banana River Lagoon.

6.4.2.2 Comparison with other N flux calculations

The diffusive flux of ammonium N has been measured previously for three stations in a small region south of Melbourne (Reddy et al., 1999). In order to compare the fluxes for nitrogen calculated here with those of Reddy et al. (1999), the flux of ammonium N was calculated in the same way as for the flux of TN (Table 6-4). For the northern study area, the flux and loading of ammonium N is greater than for the TN. The higher values for ammonium N are caused by the low NH₄ concentrations in the lagoon water. Consequently when these values are subtracted from the concentrations in the seep water, there is greater net increase in NH₄ than for TN. There are similarities between the calculated fluxes of TN and one of its components, ammonium N, for northern and central Indian River Lagoon and the Banana River Lagoon. For example, the fluxes of both measurements of N species are considerably greater in the northern than central area, both because of the higher seepage rates and because of the higher concentrations of N in the northern seep water. The Banana River Lagoon shows the lowest fluxes of N in the region.

The diffusive flux and loading of ammonium N were obtained by Reddy et al. (1999) at two separate times, once in May 1997 and again in June 1998, using two

Location ¹	Date	Duration	TN flux ²	N load	NH ₄ flux	NH ₄ load
		(months)	$(mg/m^2/day)$	$(x10^{6} \text{ kg})$	$(mg/m^2/day)$	$(x10^{6} \text{ kg})$
North IRL	May 1999	6	98	0.86	141	1.24
	Aug. 1999	6	164	1.44	403	3.53
	Total annual:	12		2.30		4.77
Central IRL	May 2000	4	81	0.28	10	0.04
	Aug. 2000	4	113	0.40	67	0.24
	Dec. 2000	4	47	0.17	25	0.09
	Total	12		0.85		0.37
	annual:					
South BRL	May 2000	4	56	0.19	19	0.06
	Aug. 2000	4	51	0.17	20	0.07
	Dec. 2000	4	21	0.07	16	0.06
	Total	12		0.43		0.19
	annual:					

Table 6-4. Estimates of nitrogen fluxes and loading.

¹ Locations are: (1) North IRL = northern study area,~48km²; Central IRL – central study area of Indian River Lagoon, ~29 km²; South BRL = central study area of Banana River Lagoon, ~28 km²

² Calculated using values for TN except for May 1999 when TSN values are used.

techniques. One technique calculated diffusive flux on the basis of pore water concentration gradients that were measured using pore water equilibrators and modeled with Fick's first law of diffusion. The second technique relied on laboratory measurements of nutrient concentrations in water that was flowed over the tops of intact sediment cores. The pore water profiles typically showed lower fluxes than those measured for cores and range from 2.7 to 12.9 mg/m²/day. The fluxes measured from the cores ranged from 4.0 to 66.0 mg/m²/day, and the overall average of the two techniques was found to be 19 mg/m²/day. This value is similar to the ammonium N flux for the Banana River Lagoon, and is approximately twice the magnitude of the flux measured in

May for the central Indian River Lagoon. The average of the measured fluxes for the three sample times of this study, however, indicate that the ammonium-N fluxes measured for the central Indian River Lagoon are ~80% greater and for the northern Indian River Lagoon are nearly 700% greater than those measured by Reddy et al. (1999). Although there is large uncertainty in all of these measurements and calculations, the generally higher flux calculated here may reflect nutrient loading from advective processes that would have been missed in calculations that only considered diffusive transportation.

Fluxes of nitrogen to coastal waters caused by ground water discharge have also been measured in other regions. For example, Rukowski et al. (1999) found that N loading into an ~10 km² portion of the Gulf of Mexico was ~5.4 mg/m²/day along the Florida panhandle. Gallagher et al. (1996) found the flux of nitrate-N to the tidal water around the Chesapeake Bay was ~60.2 mg/m²/day. Although the causes of the differences between regions is unknown, the lower values in the Gulf of Mexico may result from lower organic carbon content in the sandy carbonate sediments of the region. Similarly, high organic carbon content in the Chesapeake Bay may contribute to the high flux there. The concentration of organic matter in the Indian River Lagoon sediments may be important to nutrient fluxes and should be included in further studies of flux nutrients that originate from remineralized organic matter.

6.4.2.3 P flux calculations and comparisons with other calculations

The flux of P to the Indian River Lagoon resulting from ground water discharge can be calculated with a procedure similar to that used to calculate the flux of N. For this calculation the same rates of ground water discharge are used (Table 2-2). The P fluxes are made on the basis of the increase in TP of the seep water over the lagoon water for all of the sampling times except for May 1999 when these data are unavailable. In order to compare with fluxes measured by Reddy et al. (1999), the flux of TSP is also calculated for all of the sampling times. Multiplying the advective flux of water from Table 2-2 with the difference between the TP concentrations in the seep and lagoon water indicates that the average flux of TP ranges from ~ 4.5 mg/m²/day to a high of 49.4 mg/m²/day

(Table 6-5). The average flux of TSP is similar, but slightly lower than the flux of TP and ranges from 4.5 to 47.6 mg/m²/day. Total phosphorous loads have also been calculated for the different regions assuming that the fluxes measured in May and August last approximately half the year in the northern region, and that the fluxes measured in May, August and December last approximately one third of the year in the central region. These calculations indicate that the annual loads of TSP are 0.18 x 10^6 kg of TSP for the northern region and 0.5 x 10^6 kg for the central region of the Indian River Lagoon and is 0.10 x 10^6 kg for the Banana River Lagoon.

In generally the highest fluxes of P occur in the central study. The values are \sim 4 to 8 time greater in the central than the northern area, a result that differs from the nitrogen fluxes which show values \sim 3 to 10 greater in the northern area than in the central area. Because the same ground water discharge rates are used in the calculations in the two regions, the observed differences result from differences between the two regions in their nutrient concentrations. The origin of the difference thus may reflect difference in the composition of the sediment and detrital organic material in the two regions, again emphasizing the need to determine sediment composition and properties. Regardless of its origin, the magnitude of the difference in fluxes of the two nutrients between the two regions may be important for controlling the particular limiting nutrient in the water column.

Neither Rutkowski et al. (1999) nor Gallagher et al. (1996) measured the advective flux of P to the Gulf of Mexico and Chesapeake Bay along with their measurements of the fluxes of N. Reddy et al. (1999) did measure the flux of soluble P (similar to TSP) in the same locations and using the same techniques as for N flux measurements. Similar to the N measurements, the flux measured from pore water equilibrators are less than those measured with intact sediment cores. The overall average from two separate measurement times and from both techniques was 1.2 mg/m²/day (Reddy et al., 1999), which is substantially lower than the values measured in this study. Similar to the differences observed between this study and Reddy et al. (1999), the differences in the two estimates of the P flux may represent differences between the diffusive and advective fluxes. Smaller diffusive flux rates were obtained by Zimmerman et al. (1985) and Montgomery et al. (1979) for a few hundred square meter

Location ¹	Date	Duration	TP flux ²	TP load	TSP flux ²	TSP load
		(months)	$(mg/m^2/day)$	$(x10^{6} \text{ kg})$	$(mg/m^2/day)$	$(x10^{6} \text{ kg})$
North IRL	May 1999	6			5.2	0.05
	Aug. 1999	6	18.4	0.16	15.1	0.13
	Annual:	12				0.18
Central IRL	May 2000	4	49.4	0.17	47.6	0.16
	Aug. 2000	4	43.6	0.15	38.2	0.13
	Dec. 2000	4	7.2	0.03	7.8	0.03
	Annual:	12		0.35		0.32
South BRL	May 2000	4	8.0	0.03	4.0	0.01
	Aug. 2000	4	12.8	0.04	12.3	0.04
	Dec. 2000	4	4.5	0.02	4.5	0.02
	Annual:	12		0.09		0.07

Table 6-5. Estimates of phosphorous fluxes and loading.

¹ Locations are: (1) North IRL = northern study area,~48km²; Central IRL – central study area of Indian River Lagoon, ~29 km²; South BRL = central study area of Banana River Lagoon, ~28 km²

² Calculated using values for TP except for May 1999 when TSP values are used.

area of the lagoon, although the exact locations of the study sites are not reported. Diffusive flux was calculated to range between 0.05 to $0.08 \text{ mg/m}^2/\text{day}$ on the basis of pore water profiles. Unpublished calculations that are reported in Zimmermann et al. (1985) indicate higher diffusive rates of .16 to .3 mg/m²/day.

In addition to the diffusive flux calculations made by Zimmermann et al. (1985), advective flux of P were measured using discharge rates measured by seep meters combined with the concentrations of P in the pore water. This technique is thus similar to the one used in this study expect for the method for determining the concentrations of P in the seep water. The advective flux reported by Zimmermann et al. (1985) is 7.8 mg/m2/day, which is of the same order of magnitude as the values reported here (Table 6-5). Zimmermann et al. (1985) note that of the total flux of P (both diffusive and advective) more than 99% results from the advection of water from the sediment.

6.4.3 Comparison with nitrogen loading from other nutrient sources

A few studies have attempted to estimate the total flux of nitrogen to the Indian River Lagoon from sources such as atmospheric deposition and surface water runoff (Table 6-6). In order to compare previous estimates of total nitrogen flux to the Indian River Lagoon system, the nitrogen flux data have been extrapolated to the Banana and Indian River lagoons, which have surface areas of ~582 km² and ~179 km² respectively. Mosquito Lagoon is excluded from these calculations because of the lack of data from that region. The extrapolations over the entire lagoon surface areas are made using assuming that the flow rates and concentrations measured in the northern and central Indian River Lagoon field areas and the Banana River Lagoon field area are constant across both lagoons. Thus, three separate calculations are made of the potential nitrogen flux to the lagoon. The results of these calculations are listed in the rows labeled IRL (N), IRL (C), and BRL in Table 6-6, reflecting calculations on the basis of data from northern Indian River Lagoon, central Indian River Lagoon, and Banana River Lagoon, respectively.

The data presented in Table 6-6 illustrate variations in estimates of the different sources of nitrogen as well as differences for estimates from an individual source depending on the technique used to make the estimates. In all cases, these data presented in Table 6-6 have been converted to represent fluxes from the combined Indian River and Banana River lagoons, but exclude the Mosquito Lagoon. Atmospheric deposition for the Indian River and Banana River lagoons is estimated to range from 0.19 to 0.36 x 10^6 kg N/yr (Dreschel et al., 1990; Castro et al., 2001). Two separate studies suggest that N loading from surface water runoff range between 2.6 and 5.6 x 10^6 kg N/yr (Woodward and Clyde, 1994; Castro et al., 2001). Monitoring of 10 rivers flowing in the north central and south central lagoon appear to provide 0.86 x 10^6 kg N/yr (Steward, pers. comm.). This lower flux value may represent stream flow measurements during drought times, or that additional streams contribute to the P flux, but have not been measured. The diffusive flux of ammonium N alone has been calculated to be 2.4 x 10^6 kg N/yr (Reddy et al., 1999). This value is considerably less than that calculated using data from this study.

Several factors could contribute to the higher values of N loading calculated from the seep meter results compared with the diffusion of ammonium-N. Ammonium-N does not include other forms of nitrogen such as dissolved organic species, and thus the total

Location	Source of N	Mass	Reference
		$(x \ 10^{6} \text{kg})$	
IRL (N)*	Sediment	27.9	This study
IRL (C)*	Sediment	10.5	This study
BRL*	Sediment	14.0	This study
IRL**	Rivers	0.86	Steward (pers. comm.)
IRL	Water shed	5.57	Castro et al., 2001
IRL	Water shed	2.21	Woodward & Clyde, 1994
IRL	Atmospheric [#]	0.19	Dreschel et al., 1990
IRL	Atmospheric [#]	0.36	Castro et al., 2001
IRL ^{##}	Sediment	2.35	Reddy et al., 1999

 Table 6-6. Annual Nitrogen Loading to the Indian River and Banana River lagoons

* Location represents the study area that provided data used to calculate the P loading: IRL (N) = northern Indian River Lagoon, IFL (C) = central Indian River Lagoon, and BRL = Banana River Lagoon.

** Includes 10 streams between Horse Creek and South Vero Beach Canal.

[#] Atmospheric deposition directly to surface of lagoon.

^{##} Diffusive flux of ammonium-N

flux of N, as calculated here, should be greater than the flux of ammonium N which represents only a single dissolved species of N. In addition, the diffusive flux of ammonium N neglects the potential additional N contributed from advective transport. The high values of N loading calculated from the data presented in this report reflect the critical nature of determining the advective flux of water from the sediments, as well as accurate measurements of the N concentrations in the water.

Extrapolations of nutrient loads to the entire lagoon are tenuous at best because the northern and study areas cover only small fractions of the entire lagoon system, specifically 48 km² for the north and 29 km² for the central Indian River Lagoon and 28 km² for the Banana River Lagoon. These extrapolations, however, provide the best technique for comparing results of studies that were conducted in different sections of the lagoon. The extrapolations also provide the beginnings of the development of nutrient cycling for the entire lagoon. These extrapolations do stress the importance of nutrient fluxes from the sediment. Both of these studies indicate that nutrient loading of nitrogen from the sediment is at least of the same order of magnitude as that from surface water runoff and atmospheric deposition, and may be a factor of 2 to 10 greater than the flux from surface water runoff. These natural sources of nutrients must be understood and quantified before alteration to the system through addition of anthropogenic nutrients can be determined.

6.4.4 Comparison of P loading from diffusive and advective fluxes

The estuary-wide phosphorous cycle in the Indian River Lagoon has not previously been described, but it is possible to extrapolate various measurements of phosphorous fluxes to the entire lagoon for comparative purposes. For data from this study, the total P flux is calculated following the same techniques that were used to calculate N fluxes. Three calculations were made on the basis of data from the northern and central Indian River Lagoon study sites and the Banana River Lagoon study site. The total flux for each of these study sites was then scaled to the combined surface areas of the Banana and Indian River lagoons, estimated to be 761 km². Using these values, the total annual load of P to the lagoons is calculated to range between 1.9 and 8.4 x 10⁶ kg (Table 6-7). The P loads fall within the range of values measured by Zimmermann et al. (1985) for his advective flux calculations. The estimated annual flux from 10 rivers in the north central and south central region is 0.094 x 106 kg P (Steward, pers. comm.). This value is smaller than the estimates for advective fluxes from the sediments, similar to the comparison that was made for the N fluxes from the sediments and from the rivers.

Diffusive flux calculations are 1 to 3 orders of magnitude smaller than the advective fluxes (Table 6-7). Although there may be numerous errors resulting from the extrapolation of the data from small study areas to the entire lagoon, these difference between the measurements of diffusive and advective fluxes again indicate the importance to P cycling in the lagoon of discharge of water from the sediment. This source of P again emphasizes the significance of knowing the flow rate of water from the sediments, the mechanisms driving this flow rate, and the concentration of P in the water.
6.5 Summary and Recommendations

The elevated concentrations of nutrients in the seep water are similar to their concentrations in pore water that are less than a couple of meters below the sediment water interface. The nutrient pore water profiles increase sharply within the zone of decreasing Cl concentrations which is interpreted to represent mixing between lagoon and pore waters. The sharp increase likely reflects remineralization of detrital organic

 Table 6-7. Annual Phosphorous Loading to the Indian River and Banana River lagoons

Location	Flux mechanism	Mass	Reference
		$(x \ 10^{6} \text{ kg})$	
IRL (N)*	Advective	2.8	This study
IRL (C)*	Advective	8.4	This study
BRL*	Advective	1.9	This study
IRL	Advective	2.1	Zimmermann et al., 1985
IRL	Diffusive	0.019	Zimmermann et al., 1985
IRL	Diffusive	0.00021	Montgomery et al., 1979
IRL	Diffusive	0.31	Reddy et al., 1999
IRL**	Rivers	0.094	Steward (pers. comm.)

* Location represents the study area the provided data used to calculate the P loading: IRL(N) = northern Indian River Lagoon, IFL(C) = central Indian River Lagoon, and BRL = Banana River Lagoon.

** Includes 10 streams between Horse Creek and South Vero Beach Canal.

matter. The similarity between seep water and pore water concentrations suggests that much of the nutrients in the seep water derive from remineralization of organic matter in the sediment.

The nutrients contained in the seep water are not a new source, however, if some of the water in that comprise the shallow pore water originates from mixing with the lagoon water as suggested in Chapter 5. In this model, some of the nutrients of the seep water would have originally been dissolved in the lagoon water. Subtracting the concentration of nutrients of the lagoon water from that in the seep water provides an estimate of the concentration of newly generated nutrients. Combining this concentration with the measured ground water discharge from the seep meters provides a first order estimate of the flux of nutrients.

The results of these flux calculations reflect higher rates than were measured on the basis of the diffusive flux alone that were made by Reddy et al. (1999). The flux calculations are made for small regions of the lagoon and thus extrapolation to the entire lagoon is tenuous. These extrapolations are important, however, because they serve as a measure of the potential magnitude of the flux of nutrients from sediments. These calculations indicate that sediments, coupled with ground water discharge, could provide approximately the same order of magnitude as atmospheric deposition or surface runoff of nitrogen. Similar estimates of surface water sources of phosphorous are not available.

The extent of the potential nutrient loading from sediments reflects the importance of quantifying this flux in the nutrient cycle of the Indian River Lagoon system. Perturbations to the natural nutrient cycle, such as increases due to anthropogenic sources, can not be remediated without having a good understanding of the magnitude of the natural system. The observed heterogeneity of flow rates and the differences in the concentrations of nitrogen and phosphorous between the northern and central study areas indicate that it will be important to sample ground water discharge and nutrient fluxes from a variety of locations within the lagoon. The variations between locations make lagoon-wide extrapolations somewhat speculative.

CHAPTER 7 SUMMARY AND RECOMMENDATIONS

7.1 Summary

Ground water discharge appears to be an important process in the hydrologic and nutrient budgets of the Indian River Lagoon. The *in situ* measurements of ground water discharge using seep meters reflect point discharge rates that are several orders of magnitude greater than those calculated using numerical modeling of discharge from the Surficial aquifer or were calculated on the basis of mass balance of available on-shore recharge. Measurements of U-series radioisotope activities in the water column appear to corroborate the high rates of discharge measured using seep meters. Although there is uncertainty in all of the flux measurements, as well as in the modeling of discharge, the wide discrepancy between modeled rates and those measured *in situ* implies that different processes are being measured with these two techniques. The modeled rates reflect a source of water that is derived solely from on-shore recharge with subsequent discharge to the lagoon from major regional aquifers. The elevated rates that were measured *in situ* suggests that there may be additional sources of water discharging from the sediments. It will be critical to identify this additional source of water in order to accurately assess the hydrologic and nutrient budgets of the lagoon.

Some evidence about its identity comes from comparison of the chemical and isotopic composition of conservative tracers in the seep and lagoon water. Compositions of conservative tracers in these two waters are nearly identical, implying that much of the seep water may originate from the lagoon. Their compositions are not identical, however; for example, their Cl concentrations are commonly 1 to 5 % lower in the seep water than the lagoon water, although in a few cases the seep water is enriched in Cl

relative to the lagoon water. Because there are no fluid-solid reactions in the Indian River Lagoon sediments that would change the Cl concentrations, the differences between lagoon and seep water must result from mixing of different water sources. Although low Cl concentrations might be interpreted to represent fresh ground water discharging from the Floridan or Surficial aquifers, profiles of Cl concentrations in the pore waters contradicts this interpretation. These profiles show Cl concentrations are elevated above the lagoon water concentrations at depth ~2 m below the sediment water interface. If fresh water was flowing upward from aquifers, then a continuous decrease in Cl concentrations would be expected if ground water flow.

The gradients of various conservative solutes and isotope ratios in the shallow pore waters provide some information about the origin of the additional component of seep water. These profiles show changes in concentration in the uppermost 70 cm that mimic changes in concentrations of the lagoon water. These changes in the shallow pore water suggest that lagoon water mixes with pore water to depths in the sediment of around 70 cm. Mixing must take place on a time scale of at most a few months, which is the shortest time interval between sampling in this project. Mixing could also occur more rapidly than over several months, although this rate can not be determined from the data that are available. Mixing may also be responsible for the slight differences observed in the compositions of seep and lagoon water because of the time lag required for lagoon water to circulate through the sediment. For example, pore water may remain fresher than the lagoon water as Cl concentration increases from evaporation. Higher frequency sampling of the pore waters during times when the lagoon water salinity changes rapidly would be required in order to determine the time required to mix the two water sources.

The mechanisms driving mixing are also unknown, but could involve physical mixing caused by head differences from tides and waves, or through biological pumping. Regardless of the mechanisms controlling the mixing, the magnitude of the process should be important for nutrient fluxes because of the increased organic matter regeneration that would occur in shallow sediments from cycling of oxygenated water through the sediments. Mixing of lagoon and pore water would also be important for nutrient fluxes because of water and associated nutrients discharged from the sediments by advective rather than by diffusive processes.

183

Although ground water discharge appears to have a major impact on nutrient cycling, the lagoon-wide flux is difficult to quantify from the data included here because the fluxes measured for the two study areas differ from each other by factors of about 2 to 5. These differences would cause widely different calculations of the lagoon-wide flux, depending on which area was chosen to represent basin-wide flux. In order to get an accurate measure of the lagoon-wide nutrient fluxes, it will be important to determine the range of ground water discharge across the entire lagoon. It will also be important to determine what causes the heterogeneous nature of the flux. The most likely controls on the nature of the flux are the chemical composition of the bottom sediment, which would control the source of the nutrients, and the physical properties of the sediment, which would control the rate of flow through the sediments.

Regardless of the poorly constrained nature of all of the nutrient flux calculations, the advective flux of nitrogen and phosphorous species from the sediment appears to be significantly larger than the diffusive flux. The advective flux also appears to be approximately the same order of magnitude as the flux from surface water runoff and as atmospheric deposition of nitrogen. These flux calculations indicate that seep water is a major but previously undocumented part of the nutrient cycle in the lagoon. If excess nutrients are carried to the lagoon, for example from anthropogenic sources such as agricultural runoff or from septic tanks, the remediation of such a problem requires good information on the complete nutrient cycle in the lagoon. Development of this nutrient cycle will require extensive and detailed data on the nutrient source for ground water discharge.

7.2 Additional Questions

This work provides some preliminary information about ground water discharge to the Indian River Lagoon, processes controlling the discharge, and nutrient fluxes associated with the discharge. Many additional questions are raised by the results, and answers to these questions will be important in order to gain a complete understanding of the magnitude of nutrient fluxes to the Indian River Lagoon from ground water discharge. Some of these broad questions include:

- How do the ground water discharge rates compare with the physical properties (e.g. porosity, permeability, bioturbation) of shallow sediments?
- What is the rate of exchange and the magnitude of shallow pore waters and lagoon water?
- What are the sedimentation rates in the lagoon, and how do they compare with discharge rates?
- Do ground water discharge and the associated nutrient fluxes decrease systematically from the northern to middle reaches of the Indian River Lagoon?
- How do ground water discharge and the associated nutrient fluxes in the southern portion of the lagoon compare to the previously measured fluxes in the central and northern reaches of the lagoon?
- How do the chemical compositions of shallow sediments compare with measured nutrient fluxes within areas of the lagoon that have not previously been sampled?
- How far and at what depths beneath the Indian River Lagoon does fresh water in major regional aquifers extend?
- How sharp is the interface between fresh and salty water beneath the lagoon.

Answers to these questions should provide better constraints on the lagoon-wide flux of nutrients from ground water discharge. For example, determining the relationship between the sediment and the fluxes would allow better basin-wide mapping of the ground water-derived fluxes of nutrients. Knowing the distribution of these fluxes, and mapping the sediment composition of the lagoon, could provide a simple tool that would allow good regional extrapolations of the fluxes into areas of the lagoon that have not been sampled. Such calculation of the ground water nutrient fluxes will be important to relate to other pathways in the lagoon-wide nutrient cycle. If ground water sources of nutrients are as large as surface water run off and atmospheric deposition, it is critical to determine the magnitude of the flux in order to identify pollutant nutrient loading from anthropogenic sources. In addition, remediation of pollutant nutrients would require knowing all pathways and magnitude of fluxes in the natural nutrient cycle in the lagoon.

7.3 Recommendations for Future Work

Future work should focus on three aspects of the questions outlined above. First, the mechanism, magnitude, and controls of advective mixing between pore water and lagoon water need to be determined. Second, the distribution of this mixing needs to be better constrained for the lagoon as a whole in order to refine the basin-wide flux of nutrients. Third, the physical and chemical relationships between lagoon water and water in the aquifers underlying the lagoon need to be refined. This future work could draw from the results of this project, utilize similar techniques, and focus on some of the established field areas.

Measurements of mixing between pore water and lagoon water could be achieved through observations of the changes in the shallow (i.e. < 1 m) chemical and isotopic composition of pore water over periods when the lagoon water compositions changed rapidly. The initial focus should be on previously established stations with widely different seep and sediment characteristics. Tracking the temporal changes in composition of the pore water with the corresponding changes in the overlying lagoon water would reveal the rate at which the water is exchanged. This rate, coupled with the porosity of the sediment would indicate the volume of water being exchanged. Measuring porosity would require collecting intact cores from the lagoon, but these cores would provide much additional useful information. For example, these cores could be used to determine the extent of bioturbation through the use of X-radiographs. The cores could also provide measurements of other important sedimentary properties, such as grain size distribution, organic matter concentrations and compositions, and possibly permeability. These data would provide information about the extent of activity of the benthic biota such as burrowing shrimp, the amount of material that might provide a source of nutrients to the lagoon, and the ease with which water could pass through the sediments.

186

In terms of the lagoon-wide distribution of the ground water discharge, the best technique to make this determination would be to choose a few additional areas along the length of the lagoon where observations could be made of the range of discharge rates and the relationship between the discharge rates and sediment properties. For example, small regions located between the northern and central study areas could be mapped in order to determine the distribution of ground water discharge, as well as the sediment composition and physical properties. Newly developed study areas should be smaller than the two already established in order to better focus the studies of ground water discharge. It is clear from the results of this study that ground water discharge is heterogeneous on meter wide scale, and thus study areas concentrated within at most a few square kilometers would provide good information on the average discharge from a particular region. An additional advantage would be that field logistics would be simplified, thus increasing the amount of data that could be gathered within the field trips. More sampling stations located within the small study areas would likely provide better estimates of the average rate of ground water discharge, and the extent of the nutrient fluxes.

Finally, the nature of the salt water-fresh water interface should be explored. Although there appears to be little ground water (i.e. water from aquifers) discharging to the lagoon, there may be a link between the hydrostatic head of the ground water and the upward flow of water through the sediment. Furthermore, the interface between the ground water and the lagoon water is important for problems including salt water intrusion. Studying the salt water-fresh water interface is difficult, however, because it requires obtaining deep water samples from below the lagoon. Much preliminary work on this problem can be achieved through studies of wells surrounding the lagoon, but it will be important to eventually gather information or the composition of water located beneath the lagoon. Such samples would require development of drilling techniques that could be used offshore. Such drilling techniques are currently available and are not difficult to use to obtain water samples from depths of tens of meters. These depths should be sufficient for sampling water in the Surficial aquifer where the Floridan aquifer is confined and sampling water mixed between the Floridan and Surficial aquifer where the Floridan aquifer is unconfined.

187

Ground Water Discharge and Nutrient Loading - Indian River Lagoon

REFERENCES CITED

- Aller, R.C., 1980, Quantifying solute distributions in the bioturbated zone of marine sediments by defining an average micro-environment: Geochim. Cosmochim. Acta, v. 44, p. 1955-1965.
- Asikainen, M., 1981, Radium content and the ²²⁶Ra/²²⁸Ra activity ratio in ground water from bedrock: Geochim. Cosmochim. Acta, v. 45, p. 1375-1381.
- Baliela, I., Teal, J.M., Volkmann, S., Shafer, D., and Carpenter, E.J., 1978, Nutrient and particulate fluxes in a salt marsh ecosystem: tidal exchanges and inputs by precipitation and groundwater: Limnol. and Oceanogr., v. 23, p. 798-812.
- Belanger, T.V., and Kirkner, R.A., 1994, Groundwater/surface water interaction in a Florida augmentation lake: Lake and Reserv. Manage., v. 8, p. 165-174.
- Belanger, T.V., and Mikutel, D.F., 1985, On the use of seepage meters to estimate groundwater nutrient loading to lakes: Water Resources Bull., v. 21, p. 265-272.
- Belanger, T.V., and Montgomery, M.T., 1992, Seepage meter errors: Limnol. Oceanogr., v. 37, p. 1787-1795.
- Belanger, T.V., and Walker, R.B., 1990, Groundwater seepage in the Indian River Lagoon, Florida. *in* (eds.), Tropical Hydrology and Caribbean Water Resources: , Proc. Int. Symp. Am. Water Resour. Assoc., 367-375.
- Beneš, P., Obdrzalek, M., and Cejchanova, M., 1982, The physico-chemical forms of traces of radium in aqueous solutions containing chlorides, sulfates and carbonates: Radiochem. Radioanal. Lett., v. 50, p. 227-242.
- Bermes, B.J., 1958, Interim report on geology and groundwater resources of Indian River County, Florida: , Bur. of Geol., Inf. Circ. No. 18, 75 p.
- Berner, R.A., 1980, Early Diagenesis: A Theoretical Approach: Princeton, NJ, Princeton Univ. Press, 241 p.
- Bokuniewicz, W., 1965, The application of natural radon to problems in ocean circulation. *in* T. Ichiye (eds.), Symposium on Diffusion in Oceans and Fresh Waters: Palisades, N.Y., Lamont-Doherty Geol. Observatory, 116-145.
- Bollinger, M.S., and Moore, W.S., 1993, Evaluation of salt marsh hydrology using radium as a tracer: Geochim. Cosmochim. Acta, v. 57, p. 2203-2212.

- Boudreau, B., 1998, The diffusive tortuosity of fine-grained unlithified sediments: Geochim. Cosmochim. Acta, v. 60, p. 3139-3142.
- Bouwer, H., Asce, M., and Rice, C., 1963, Seepage meters in seepage and recharge measurements: Am. Soc. of Civil Eng., v. 89, p. 18-42.
- Boynton, W.R., Hagy, J.D., Murray, L., Stokes, C., and Kemp, W.M., 1995, Modeling the effect of salinity on the desorption of radium from sediments.: Geochim. Cosmochim. Acta, v. 59, p. 2469-2476.
- Bradner, L.A., 1998, Potentiometric surface of the upper Floridan aqifer in the St. Johns River Water Management District and vicinity, Florida: , USGS, Open File Report 99-100, p.
- Bradner, L.A., and Knowles, L., Jr., 1999, Potentiometric surface of the upper Floridan aquifer in the St. Johns River Water Management District and vicinity, Florida: , USGS, p.
- Broecker, W.S., 1965, The application of natural radon to problems in ocean circulation. *in* T. Ichiye (eds.), Symposium on Diffusion in Oceans and Fresh Waters: Palisades, N.Y., Lamont-Doherty Geol. Observatory, 116-145.
- Broecker, W.S., and Peng, T.-H., 1974, Gas exchange rates between air and sea: Tellus, v. 26, p. 21-35.
- Broecker, W.S., and Peng, T.-H., 1982, Tracers in the Sea: Palisades, N.Y., Eldigio, 690 p.
- Bugna, G.C., Chanton, J.P., Cable, J.E., Burnett, W.C., and Cable, P.E., 1996, The importance of groundwater discharge to the methane budgets of nearshore and continental shelf waters of the northeastern Gulf of Mexico: Geochim. Cosmochim. Acta, v. 60, p. 4735-4746.
- Bush, P.W., and Johnston, R.H., 1988, Ground-waer hydraulics, regional flow, and ground-water development of the Floridan Aquifer system in Florida and in parts of Georgia, South Carolina and Alabama: , U.S. Geological Survey, USGS Professional Paper 1403-C, 80 p. p.
- Cable, J.E., Bugna, G.C., Burnett, W.C., and Chanton, J.P., 1996a, Application of ²²²Rn and CH₄ for assessment of ground water discharge to the coastal ocean: Limnology and Oceanography, v. 41, p. 1347-1353.
- Cable, J.E., Burnett, W.C., and Chanton, J.P., 1997a, Magnitude and variations of groundwater seepage along a Florida marine shoreline: Biogeochemistry, v. 38, p. 189-205.

- Cable, J.E., Burnett, W.C., Chanton, J.P., Corbett, D.R., and Cable, P.H., 1997b, Field evaluation of seepage meters in the coastal marine environment: Esturine, Coastal and Shelf Science, v. 45, p. 376-375.
- Cable, J.E., Burnett, W.C., Chanton, J.P., and Weatherly, G.L., 1996b, Estimating groundwater discharge into the northeastern Gulf of Mexico using radon-222: Earth Planet. Sci. Lett., v. 144, p. 591-604.
- Clesceri, L.H., Greenberg, A., Trussell, R.R., and Franson, M.A., 1989, Standard methods for the examination of water and wastewater: Washington DC, American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1289 p.
- Cochran, J.K., 1980, The flux of ²²⁶Ra from deep-sea sediments.: Earth Planet. Sci. Lett., v. 49, p. 381-392.
- Creschel, T.W., Madsen, B.C., Maull, L.A., Hinkle, C., and Knott, W.M., III, 1990, Precipitation Chemistry: Atmospheric loadings to the surface waters of the Indian River Lagoon Basin by rainfall: Environ. Chem., v. 53, p. 184-188.
- Dickson, B.L., Meakins, R.L., and Bland, C.J., 1983, Evaluation of radioactive anomalies using radium isotopes in ground waters: J. Geochem. Exploration, v. 19, p. 195-205.
- Dreschel, T.W., Madsen, B.C., Maull, L.A., Hinkle, C.R., and Knott, W.M.I., 1990, Precipitation chemistry: Atmospheric loadings to the surface waters of the Indian River Lagoon Basin by rainfall: Environmental Chemistry, v. 53, p. 184-188.
- Drever, J.I., 1988, The Geochemistry of Natural Waters: Englewood Cliffs, NJ, Prentice Hall, 437 p.
- Ellins, K.K., Roman Mas, A., and Lee, R., 1990, Using ²²²Rn to examine groundwater/surface discharge interaction in the Rio Grande de Manati in Puerto Rico: Jour. of Hydro., v. 115, p. 319-341.
- Faure, G., 1986, Principles of Isotope Geology: New York, John Wiley & Sons, 589 p.
- Fleisher, R.L., 1982, Alpha-recoil damage and solution effects in minerals: Uranium isotopic disequilibrium and radon release: Geochim. Cosmochim. Acta, v. 46, p. 2191-2201.
- Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., P., D., Hammond, D., Hartman, B., and Maynard, V., 1979, Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis: Geochim. Cosmochim. Acta, v. 43, p. 1075-1090.

- Gallagher, D.L., Dietrich, A.M., Reay, W.G., Hayes, M.C., and Simmons, G.M., 1996, Ground water discharge of agricultural pesticides and nutrients to estuarine surface water: Ground Water, Ground Water Monitoring and Remediation, v. p. 118-129.
- Ghose, S., Alam, M.N., and Islam, M.N., 2000, Concentrations of ²²²Rn, ²²⁶Ra and ²²⁸Ra in the surface seawater of the Bay of Bengal: J. Environ. Radioactivity, v. 47, p. 291-300.
- Goldberg, E.D., 1963, Geochronology with lead-210. *in* (eds.), Radioactive Dating: Vienna, Austria, Atomic Energy Agency, 121-131.
- Gordon, S.L., 1998, Surface and Ground Water Mixing in an Unconfined Karst Aqufier, Ichetucknee River Ground Water Basin, Florida. Gainesville, Fl, University of Florida, M.S., 121 p.
- Groszos, M., Ceryak, R., Allison, d., Cooper, R., Weinberg, M., Macesich, M., Enright, M.M., and Rupert, F., 1992, Carbonate units of the Intermediate Aquifer system in the Suwannee River Water Management District, Florida: , Florida Geological Survey, Open file report #54, 22 p.
- Gu, D., Iricanin, N., and Trefrey, J.H., 1987, The geochemistry of interstitial water for a sediment core from the Indian River Lagoon, Florida: Florida Scientist, v. 50, p. 99-110.
- Hammond, D.E., Giordani, P., Berelson, W.M., and Poletti, R., 1999, Diagenesis of carbon and nutrients and benthic exchange in sediments of the Northern Adriatic Sea: Marine Chem., v. 66, p. 53-79.
- Hammond, D.E., Marton, R.A., Berelson, W.M., and Ku, T.-L., 1990, .Ra-228 distribution and mixing in San Nicholas and San Pedro Basins, Southern California Borderland: J. Geophys. Res., v. 95, p. 3321-3335.
- Hanckock, G.J., in press, Estimating the flux of Ra into a shallow esturine lagoon; implications for biogeochemical processes. Gechim. Cosmochim. Acta.
- Hancock, G.J., and Murray, A.S., 1996, The source and distribution of dissolved radium in the Bega River estuary, southeastern Australia: Earth Planet. Sci. Lett., v. 138, p. 145-155.
- Hancock, G.J., Webster, I.T., Ford, P.W., and Moore, W.S., in press, Using radium isotopes to examine trasport porcesses controlling benthic fluxes into a shallow estuarine lagoon.: v. p. .

- Hartmann, G., and Hammond, D., 1985, Gas exchange in San Francisco Bay: Hydrobiologia, v. 129, p. 59-68.
- Harvey, J.W., and Odum, W.E., 1990, The influence of tidal marshes on upland groundwater discharge to estuaries: Biogeochemistry, v. 10, p. 217-236.
- Israelson, O.W., and Reeve, R.C., 1944, Canal lining experiments in the delta area, Utah: Utah Agricultural Experiment Station Technical Bulletin #313, v. p. 52.
- Ivanovich, M., and Harmon, R.S., 1982, Uranium Series Disequilibrium: Applications to Environmental Problems: Oxford, Clarendon Press, 901 p.
- Kadko, D., Cochran, J.K., and Mitchell, L., 1987, The effect of bioturbation and adsorption gradients on solid and dissolved radium profiles in sediments from the eastern equatorial Pacific: Geochim. Cosmochim. Acta, v. 38, p. 703-714.
- Key, R., Brewer, R., Stockwell, J., Guinass, N., and Schink, D., 1979, Some improved techniques for measuring radon and radium in marine sediments and in seawater: Marine Chem., v. 7, p. 251-264.
- Krest, J., Moore, W.S., Gardner, L.R., and Morris, J.T., 2000, Marsh nutrient export supplied by groundwater discharge: evidence from radium measurements: Global Biogeochemical Cycles, v. 14, p. 167-176.
- Krupa, S.L., Belanger, T.V., Heck, H.H., Brock, J.T., and Jones, B.T., 1998, Krupaseep -The next generation seepage meter. Proceedings of the Iternational Coastal Symposium (ICS 1998), Lawrence, KS, Coastal Education Research Foundation.
- Lee, D.R., 1977, A device for measuring seepage flux in lakes and estuaries: Limnol. Oceanogr., v. 22, p. 140-147.
- Li, L., Barry, D.A., Stagnitti, F., and Parlange, J.-Y., 1999, Submarine groundwater discharge and associated chemical input to a coastal sea: Water Resources Res., v. 35, p. 3253-3259.
- Li, Y.-H., and Gregory, S., 1974, Diffusion of ions in seawater and in deep-sea sediments: Geochim. Cosmochim. Acta, v. 38, p. 703-714.
- Li, Y.-H., Mathieu, G.G., Biscaye, P., and Simpson, H.J., 1977, The flux of Ra-226 from estuarine and continental shelf sediments: Earth Planet. Sci. Lett., v. 37, p. 237-241.
- Macintyre, S., Wanninkhof, R., and Chanton, J.P., 1995, Trace gas exchange across the air-water interface in fresh water and coastal marine environments. *in* P. A. Matson and R. C. Harriss (eds.), Biogenic Trace Gases: Measuring Emissions from Soil and Water: Cambridge, Mass., Blackwell Science Ltd., p. 52-97.

- Martens, C.S., Kipphut, G., and Klump, J., 1980, Sediment-water chemical exchange in the coastal zone traced by in situ radon-222 flux measurements: Science, v. 208, p. 285-288.
- Martin, J.B., Kastner, M., Henry, P., Le Pichon, X., and Lallemant, S., 1996, Chemical and isotopic evidence for sources of fluids in mud volcano field seaward of the Barbados accretionary wedge: J. Geophys. Res., v. 101, p. 20,325-20,345.
- Martin, J.B., Orange, D.L., Lorensen, T.D., and Kvenvolden, K.A., 1997, Chemical and isotopic evidence of gas-influenced flow at a transform plate boundary: Monterey Bay, California: J. Geophys. Res., v. 102, p. 24,903-24,915.
- Mathieu, G., Biscayne, P., Lupton, R., and Hammond, D., 1988, System for measurement of ²²²Rn at low levels in natural waters: Health Physics, v. 55, p. 989-992.
- McBride, M.S., and Pfannkuch, H.O., 1975, The distribution of seepage within lake beds: USGS J. Res., v. 3, p. 505-512.
- Miller, J.A., 1986, Hydrogeologic framework of the Floridan aquifer system in Florida and parts of Georgia, Alabama, and South Carolina: , U.S. Geological Survey, 91 p. p.
- Moore, W.S., 1996, Large groundwater inputs to coastal waters revealed by ²²⁶Ra enrichments: Nature, v. 380, p. 612-614.
- Moore, W.S., and Arnold, R., 1996, Measurement of ²²³Ra and ²²⁴Ra in coastal waters using a delayed coincidence counter: J. Geophys. Res., v. 101, p. 1321-1329.
- Osmond, J.K., and Cowart, J.B., 1982, Ground water. *in* (eds.), Uranium Series Disequilibrium, Application to Environmental Problems: Oxford, Clarendon Press, .
- Pandit, A., and El-Khazen, C.C., 1990, Groundwater seepage into the Indian River Lagoon at Port St. Lucie: Florida Scientist, v. 53, p. 169-179.
- Pin, C., and Bassin, C., 1992, Evaluation of a Sr-specific extraction chromatographic method for isotopic analysis in geologic materials: Anal. Chim. Acta, v. 269, p. 249-255.
- Rama, and Moore, W.W., 1996, Using the radium quartet for evaluating groundwater input and water exchage in salt marshes: Geochim. Cosmochim. Acta, v. 60, p. 4645-4652.

- Reddy, K., Fisher, M.M., Pant, H., and Inglett, P., 1999, Indian River Lagoon Hydrodynamics and Water Quality Model: Nutrient Storage and Transformations in Sediments: Palatka, FL, St. Johns River Water Management District, p.
- Rutkowski, C.M., Burnett, W.C., Iverson, R.L., and Chanton, J.P., 1999, The effect of groundwater seepage on nutrient delivery and seagrass distribution in the northeastern Gulf of Mexico: Estuaries, v. 22, p. 1033-1040.
- Santschi, P., Hohener, P., Benoit, G., and Buchholtz-ten Brink, M., 1990, Chemical processes at the sediment-water interface: Marine Chem., v. 30, p. 269-315.
- Sarmiento, J., Feely, H., Moore, W., Bainbridge, A., and Broecker, W., 1976, The relationship between vertical eddy diffusion and buoyancy gradient in the deep sea: Earth Planet. Sci. Lett., v. 32, p. 357-370.
- Scott, T.M., 1988, The lithostratigraphy of the Hawthorn Group (Miocene of Florida): , Florida Geological Survey Bulletin, 147 p.
- Scott, T.M., 1992, A Geological Overview of Florida: , Florida Geological Survey, 78 p.
- Sigua, G.C., Steward, J.S., and Tweedale, W.A., 2000, Water-quality monitoring and biological integrity assessment in the Indian River Lagoon, Florida: Status, trends, and loadings (1988-1994): Environmental Management, v. 25, p. 199-209.
- Smith, N.P., 1992, The intertidal volume of Florida's Indian River Lagoon: Florida Scient., v. 55, p. 209-218.
- Smith, N.P., 1993, Tidal and nontidal flushing of Florida's Indian River Lagoon: Estuaries, v. 16, p. 739-746.
- Sonzogni, W.C., Larsen, D.P., Malueg, K.W., and Scult, M.D., 1977, Use of large submerged chambers to measure sediment-water interactions: Water REsearch, v. 11, p. 461-464.
- Sun, H., and Semkow, T.M., 1998, Mobilization of thorium, radium, and radon radionuclides in ground water by successive alpha recoils: J. Hydrology, v. 205, p. 126-136.
- Swarzenski, P.W., 1999, Examining freshwater-saltwater interface processes with four radium isotopes: , USGS, Open File Report, FS-065-99 unpginated.
- Torgersen, T., DeAngelo, E., and O'Donnell, J., 1997, Calculations of horizontal mixing rates using ²²²Rn and the controls on hypoxia in western Long Island Sound, 1991: Estuaries, v. 20, p. 328-345.

- Toth, D.J., 1988, Salt water intrusion in coastal areas of Volusia, Brevard, and Indian River Counties: Palatka, FL, St. Johns River Water Management District, Technical Publication SJ 88-1, 160 p.
- Trefry, J.H., Feng, H., Trocine, R.P., Metz, S., Gruguric, G., Vereecke, R., and Cleveland, S., 1992, Concentrations and benthic fluxes of nutrients from sediments in the Indian River Lagoon, Florida (Project Muck, Phase II): Palatka, FL, St. Johns River Water Management District, Final Report, 47 p.
- Upchurch, S.B., 1992, Quality of water in Florida's aquifer systems. *in* (eds.), Florida's Ground Water Quality Monitoring Program: Tallahassee, FL, Florida Geological Survey, 12-51.
- Valiela, I., Costa, J., Foreman, K., Teal, J.M., Howes, B., and Aubrey, D., 1990, Transport of groundwater-borne nutrients from watersheds and their effects on coastal waters: Biogeochemistry, v. 10, p. 177-197.
- Wanninkhof, R., 1992, Relationship between wind speed and gas exchange over the ocean: J. Geophys. Res., v. 97, p. 7373-7382.
- Webster, I.T., Hancock, G.T., and Murray, A.S., 1994, On the use of radium isotopes to examine pore water exchange in an estuary: Limnology and Oceanography, v. 39, p. 1917-1927.
- Webster, I.T., Hancock, G.T., and Murray, A.S., 1995, Modeling the effect of salinity on the desorption of radium from sediments: Geochim. Cosmochim. Acta, v. 59, p. 2469-2476.

Appendix A. Seep meter measurements of seep rates.

	Dry Season Sampling (May 1999)								Wet Season Sampling (August 1999)						Change from
Station	Date		Flux	4		Rate	•	Date	I	Flux	[1	Rate	e	Dry to Wet
	Collected	(ml/r	n²/m	in)	(0	cm/da	iy)	Collected	(ml/m ²	/mii	n)	(ci	m/d	lay) (%)	
Big Flound	ler Transect														
IRL 1	5/4/99	23.5	±	14.2	3.39	±	2.04	8/14/99	43.0	±	14.5	6.20	±	2.1	83
IRL 2	5/4/99	21.6	±	0.3	3.11	±	0.04	8/14/99	55.3	±	18.7	7.96	±	2.7	156
IRL 3	5/4/99	27.7	±	5.0	3.99	±	0.72	8/14/99	43.7	±	5.6	6.29	±	0.8	58
IRL 4	5/4/99	28.3	±	2.9	4.08	±	0.42	8/14/99	46.4	±	11.6	6.68	±	1.7	64
IRL 5	5/4/99	36.7	±	5.2	5.28	±	0.75	8/14/99	35.5	±	5.9	5.11	±	0.9	-3
IRL 6	5/4/99	49.7	±	8.4	7.16	±	1.20	8/14/99	102.8	±	13.9	14.81	±	2.0	107
IRL 7	5/4/99	18.1	±	0.6	2.61	±	0.08	8/14/99	144.4	±	10.8	20.80	±	0.0	697
IRL 8	5/4/99	47.0	±	7.2	6.77	±	1.04	8/14/99	100.9	±	9.40	14.52	±	1.4	115
Turnbull Tı	ransect														
IRL 9	5/6/99	44.8	±	1.2	6.45	±	0.18	8/15/99	65.7	±	14.6	9.46	±	2.1	47
IRL 10	5/6/99	21.9	±	2.5	3.15	±	0.36	8/15/99	50.6	±	6.5	7.28	±	0.9	131
Shiloh Trai	nsect														
IRL 12	5/6/99	92.1	±	4.7	13.26	±	0.67	8/15/99	74.3	±	12.7	10.71	±	1.8	-19
IRL 13	5/6/99	38.6	±	2.3	5.56	±	0.34	8/15/99	51.0	±	16.1	7.34	±	2.3	32
IRL 14	5/6/99	54.7	±	4.6	7.87	±	0.67	8/15/99	58.1	±	25.7	8.37	±	3.7	6
IRL 15	5/6/99	26.6	±	3.0	3.84	±	0.43	8/15/99	23.4	±	4.3	3.36	±	0.6	-12
Tower Trar	nsect														
IRL 17	5/7/99	19.5	±	1.5	2.81	±	0.22	8/15/99	31.3	±	3.3	4.51	±	0.5	61
IRL 18	5/7/99	50.9	±	6.7	7.33	±	0.97	8/15/99	43.7	±	1.2	6.29	±	0.2	-14
IRL 19	5/7/99	33.4	±	5.8	4.80	±	0.84	8/15/99	74.0	±	14.8	10.66	±	2.1	122
IRL 20	5/7/99	26.5	±	4.0	3.81	±	0.57	8/15/99	37.1	±	1.5	5.34	±	0.2	40
Duckroost	Cove Transect														
IRL 21	5/8/99	30.5	±	3.4	4.33	±	0.67	8/14/99	40.9	±	2.9	5.89	±	0.4	34
IRL 22	5/8/99	50.1	±	2.3	7.08	±	0.34	8/14/99	84.3	±	9.2	12.13	±	1.3	68
IRL 23	5/8/99	103.7	±	10.4	14.93	±	2.12	8/14/99	89.9	±	3.5	12.94	±	0.5	-13
IRL 24	5/8/99	50.6	±	6.9	7.79	±	0.68	8/14/99	72.7	±	20.5	10.47	±	3.0	44
Deep wate	r sites														
IRL 11	5/8/99	54.0	±	7.1	7.19	±	0.09	8/15/99	79.7	±	4.7	11.48	±	0.7	48
IRL 16	5/8/99	52.4	±	4.6	7.55	±	0.67	8/15/99	139.1	±	12.5	20.03	±	1.8	166
IRL 25	5/8/99	2.9	±	0.3	0.40	±	0.04	8/14/99	22.0	±	9.3	3.16	±	1.3	652
IRL 26	5/8/99	15.5	±	1.3	2.29	±	0.24	8/15/99	66.3	±	3.1	9.54	±	0.4	328
IRL 27	5/8/99	41.2	±	2.0	5.82	±	0.30	8/14/99	39.4	±	0.5	5.67	±	0.1	-4
IRL 28	5/8/99	55.1	±	7.7	8.43	±	0.97	8/14/99	50.8	±	5.8	7.32	±	0.8	-8

Appendix A.1. Seepage Rates, 1999.

* Errors represent variation in the triplicate seepage measurement at each station

Appendix A.2. Seep water fluxes and rates, 2000.

	Dry Seas	on Sam	(May 2	000)	Det		Wet Season Sampling (August 2000)							
Station	Date Collect	(1001)	Flux	(,	e e		Date Collect	(-	Flux			Rate (cm/d	a
-	ea	(mi/i	m /mi	n)	(cm/da	iy)	ea	(r	ni/m /i	min)		y)	-
Transec	t 1	40.4		40.0				0144100			11.0	4.00		4.00
BRL1A	5/15/00	43.1	±	16.9	6.2	±	2.44	8/14/00	30.3	±	11.3	4.36	±	1.63
BRL1B	5/15/00	40.1	±	8.7	5.78	±	1.25	8/14/00	56	±	38.4	8.06	±	5.53
BRL2	5/15/00	44.5	±	12	6.41	±	1.73	8/14/00	48.1	±	3.2	6.93	±	0.47
BRL3A	5/15/00	13.1	±	5.4	1.89	±	0.78	8/14/00	8.8	±	9	1.27	±	1.3
BRL3B	5/15/00	23	±	9.4	3.31	±	1.36	8/14/00	15	±	10.3	2.16	±	1.49
BRL4	5/15/00	42	±	15.1	6.05	±	2.17	8/14/00	26.6	±	18.5	3.82	±	2.66
BRL5	5/15/00	22.5	±	14.2	3.24	±	2.05	8/14/00	41.6	±	11.4	5.99	±	1.64
Transec t 2	;													
BRL6	5/15/00	18.7	±	12.6	2.69	±	1.81	8/14/00	35.3	±	10.2	5.09	±	1.47
BRL7	5/15/00	23.2		11.2	3.34		1.61	8/14/00	47.1		10.1	4.52		4.05
BRL8	5/15/00	36.5	±	14.6	5.25	±	2.11		96	±	44.7	13.82	±	6.44
Transec t 1	:													
IRL29		14.5	±	11.5	2.1	±	1.7		49.9	±	8.3	7.2	±	1.2
IRL30		14.7	±	1.8	2.12	±	0.26		28.6	±	4.9	4.11	±	0.71
IRL31		15.3	±	11.4	2.2	±	1.65		13	±	6.5	1.88	±	0.94
Transec t 2	:													
IRL32		26	±	7	3.74	±	1.01		62.1	±	32.6	8.95	±	4.69
IRL33		26.9	±	4.1	3.87	±	0.59		43.1	±	51.2	6.21	±	7.37
IRL34		14.7	±	18.1	2.12	±	2.6				meter			
Transec t 3	:													
IRL35	5/14/00	42.4	±	4.4	6.11	±	0.63	8/16/00	42.8	±	3.4	6.16	±	0.49
IRL36	5/14/00	19.7	±	1.8	2.84	±	0.25	8/16/00	15	±	0.7	2.16	±	0.1
IRL37	5/17/00	14.2	±	5.6	2.05	±	0.81	8/16/00	36.5	±	7.1	5.26	±	1.03
IRL38	5/14/00	37.4	±	15	5.39	±	2.17	8/16/00	26.2	±	5.4	3.77	±	0.77
Transec t 4	:													
IRL39		30.4	±	11.1	4.37	±	1.61	8/16/00	94.3	±	12.7	13.58	±	1.83
IRL40		57.7	±	25.4	8.31	±	3.65		Turneo	d over -	– lost equ	ilibrium		
IRL41		10.1	±	21.2	1.46	±	3.05	8/16/00	16.6	±	2.4	2.39	±	0.34
IRL42		34	±	12.9	4.89	±	1.86	8/16/00	27.6	±	22.2	3.97	±	3.2
Transec	t 1													
Blank														
(BRL1)	5/8/99	7.7	±	5.2	1.11	±	0.75	8/14/99	6.3	±	7.2	0.91	±	1.04

* Errors represent variation in the triplicate seepage measurement at each station.

Appendix A.2 (cont.)

	Wet Season	Sampling	(De	cember 2000)					
Station	Date		I	Rate					
	Collected	(ml/ı	m²/m	in)	(cm	(cm/day)			
Transect 1									
BRL1A		27.82	±	13.64	4.01	±	1.96		
BRL1B				No duplicate	s				
BRL2		25.06	±	15.01	3.61	±	2.16		
BRL3A		49.06	±	25.81	7.06	±	3.72		
BRL3B		No duplicates							
BRL4		47.3	±	17.65	6.81	±	2.54		
BRL5		32.06	±	14.22	4.62	±	2.05		
Transect 2									
BRL6		27.99	±	3.63	4.03	±	0.52		
BRL7		30.07		13.3	2.89		2.84		
BRL8		34.84	±	21.09	5.02	±	3.04		
Transect 1									
IRL29	12/10/00	14.34	±	4.32	2.07	±	0.62		
IRL30	12/10/00	34.31	±	9.49	4.94	±	1.37		
IRL31	seep meter malfunction								
Transect 2									
IRL32	12/10/00	62.08	±	18.39	8.94	±	2.65		
IRL33	12/10/00	24.28	±	6.02	3.5	±	0.87		
IRL34	12/10/00	9.08	±	12.43	1.31	±	1.79		
Transect 3									
IRL35	12/9/00	58.4	±	15.27	8.41	±	2.2		
IRL36	12/9/00	37.73	±	16.93	5.43	±	2.44		
IRL37	12/9/00	71.92	±	6.76	10.36	±	0.97		
IRL38	12/9/00	34.01	±		4.9	±			
Transect 4									
IRL39	12/9/00	45.25	±	21.31	6.52	±	3.07		
IRL40	12/9/00	98.98	±	11.58	14.25	±	1.67		
IRL41	12/9/00	35.69	±	21.36	5.14	±	3.08		
IRL42	12/9/00	17.05	±		2.45	±			
Transect 1									
Blank (BRL1)				No blanks					

Appendix B. ²²³Ra and ²²⁴Ra activities.

Station	²²³ Ra (dpm/L)	ex ²²⁴Ra (dpm/L)	²²⁸ Th (dpm/100L)	223/226	224/223
Big Flounder transec	t				
IRL 1	0.08 ± 0.01	0.12 ± 0.01	3.42 ± 0.34	0.03	1.50
IRL 3	0.13 ± 0.01	0.11 ± 0.01	2.45 ± 0.25	0.06	0.85
IRL 5	0.14 ± 0.01	0.07 ± 0.01	5.83 ± 0.58	0.07	0.50
IRL 8	0.14 ± 0.01	0.10 ± 0.01	2.89 ± 0.29	0.07	0.71
Palm Tree/Shiloh tra	nsect				
IRL 13	0.07 ± 0.01	0.06 ± 0.01	5.68 ± 0.57	0.04	0.86
IRL 15	$0.08 \hspace{0.2cm} \pm \hspace{0.2cm} 0.01$	0.05 ± 0.01	5.76 ± 0.58	0.03	0.63
Tower transect					
IRL 17	$0.09 \hspace{0.2cm} \pm \hspace{0.2cm} 0.01$	0.13 ± 0.01	2.1 ± 0.21	0.04	1.44
IRL 18	$0.08 \hspace{0.2cm} \pm \hspace{0.2cm} 0.01$	0.09 ± 0.01	3.23 ± 0.32	0.04	1.13
IRL 20	$0.09 \hspace{0.2cm} \pm \hspace{0.2cm} 0.01$	0.08 ± 0.01	5.77 ± 0.58	0.05	0.89
Duckroost Cove					
IRL 21	$0.07 \hspace{0.2cm} \pm \hspace{0.2cm} 0.01$	0.12 ± 0.01	2.76 ± 0.28	0.04	1.71
IRL 22	$0.10 \hspace{0.1in} \pm \hspace{0.1in} 0.01$	0.11 ± 0.01	2.61 ± 0.26	0.05	1.10
IRL 23	$0.11 \hspace{0.1in} \pm \hspace{0.1in} 0.01$	0.10 ± 0.01	2.82 ± 0.28	0.06	0.91
IRL 24	$0.15 \hspace{0.1 in} \pm \hspace{0.1 in} 0.02$	0.08 ± 0.01	3.76 ± 0.38	0.09	0.53
Deep water sites					
IRL 11	$0.11 \hspace{0.1in} \pm \hspace{0.1in} 0.01$	0.13 ± 0.01	5.77 ± 0.58	0.05	1.18
IRL 16	$0.10 \hspace{0.1in} \pm \hspace{0.1in} 0.01$	0.07 \pm 0.01	4.73 ± 0.47	0.05	0.70
IRL 25	$0.07 \hspace{0.2cm} \pm \hspace{0.2cm} 0.01$	0.10 ± 0.01	3.61 ± 0.36	0.04	1.43
IRL 26	0.12 ± 0.01	0.06 ± 0.01	3.54 ± 0.35	0.07	0.50
IRL 27	0.08 ± 0.01	0.08 ± 0.01	3.21 ± 0.32	0.04	1.00
IRL 28	0.09 ± 0.01	0.09 ± 0.01	3.43 ± 0.34	0.04	1.00
Ground water sites					
GW-1	1.59 ± 0.16	$4.39 \hspace{0.2cm} \pm \hspace{0.2cm} 0.44$	23.25 ± 2.33	0.75	2.76
GW-2	1.14 ± 0.11	11.04 ± 1.10	24.23 ± 2.42	0.24	9.68
GW-3	0.39 ± 0.04	3.38 ± 0.34	24.21 ± 2.42	0.06	8.67
GW-4	0.66 ± 0.07	10.64 ± 1.06	23.87 ± 2.39	0.17	16.12
GW-5	0.18 ± 0.02	3.74 ± 0.37	23.65 ± 2.37	0.38	20.78
GW-6	$4.34 \hspace{0.2cm} \pm \hspace{0.2cm} 0.43$	7.96 ± 0.80	23.42 ± 2.34	1.14	1.83
Endmember sites					
НОС	0.04 ± 0	0.06 ± 0.01	3.26 ± 0.33	0.02	1.50
TBC	0.11 ± 0.01	0.21 ± 0.02	3.01 ± 0.30	0.04	1.91
		Average Values <u>+</u> 1	σ		
Lagoon waters	0.10 ± 0.03	0.09 ± 0.02	3.86 ± 1.29	0.05	0.98
Ground water	1.38 ± 1.54	6.86 ± 3.49	23.77 ± 0.41	0.46	9.97
Creek/inlet water	0.08 ± 0.05	0.14 ± 0.11	3.14 ± 0.18	0.03	1.70

Appendix B.1. Water column radium activities (May 1999).

Station	²²³ Do	ox ²²⁴ Do	228 _T	h		
Station	ка (dpm/L)	(dpm/L)	(dpm	n /L)	223/226	224/223
D:- El d 4						
BIG Flounder tran	sect 0.10 ± 0.01	0.12 ± 0.01	2 4 2 +	0.34	0.03	1.2
IKL I	0.10 ± 0.01	0.12 ± 0.01	$3.42 \pm 2.45 \pm 100$	0.34	0.03	1.2
IRL 5	0.11 ± 0.01 0.13 + 0.01	0.13 ± 0.01	$2.43 \pm 3.56 \pm 3.55 \pm 3.56 \pm $	0.25	0.04	0.02
IRL 5	0.13 ± 0.01	0.12 ± 0.01	3.50 ± 2.61	0.30	0.05	0.92
	0.12 ± 0.01	0.11 ± 0.01	$3.01 \pm 2.00 \pm 100$	0.30	0.05	0.92
IKL o	0.14 ± 0.01	0.10 ± 0.01	2.89 ±	0.29	0.03	0.71
i ui iibuii ti ansect						
IRL 10	0.09 ± 0.01	0.10 ± 0.01	1 2.67 ±	0.27	0.03	1.11
Palm Tree/Shiloh	transect					
IRL 13	0.06 ± 0.01	0.08 ± 0.01	4.24 ±	0.42	0.02	1.33
IRL 14	0.07 ± 0.01	0.08 ± 0.01	1 3.13 ±	0.31	0.03	1.14
Tower transect						
IRL 17	0.11 ± 0.01	0.10 ± 0.01	1 2.92 ±	0.29	0.04	0.91
IRL 18	0.09 ± 0.01	0.08 ± 0.01	1 3.09 ±	0.31	0.04	0.89
IRL 20	0.08 ± 0.01	0.14 ± 0.01	4.53 ±	0.45	0.03	1.75
Duckroost Cove						
IRL 21	0.08 ± 0.01	0.13 ± 0.01	2.65 ±	0.27	0.04	1.63
IRL 23	0.08 ± 0.01	0.12 ± 0.01	2.61 ±	0.26	0.04	1.5
IRL 24	0.08 ± 0.01	0.13 ± 0.01	2.83 ±	0.28	0.03	1.63
Deep water sites						
IRL 11	0.12 ± 0.01	0.12 ± 0.01	5.77 ±	0.58	0.05	1
IRL 16	0.10 ± 0.01	0.08 ± 0.01	3.56 ±	0.36	0.04	0.8
IRL 25	0.07 ± 0.01	0.10 ± 0.01	3.61 ±	0.36	0.03	1.43
IRL 28	0.10 ± 0.01	0.08 ± 0.01	3.52 ±	0.35	0.05	0.8
Ground water site	S					
GW-1	1.02 ± 0.10	3.61 ± 0.36	5 23.25 ±	2.33	-	3.54
GW-3	0.66 ± 0.07	4.61 ± 0.46	5 23.80 ±	2.38	-	6.98
GW-4	0.70 ± 0.07	10.06 ± 1.01	1 23.98 ±	2.40	-	14.37
GW-5	0.63 ± 0.06	4.09 ± 0.41	24.10 ±	2.41	-	6.49
GW-6	1.34 ± 0.13	4.01 ± 0.40) 24.23 ±	2.42	-	2.99
Endmember sites						
HOC	0.06 ± 0.01	0.07 ± 0.01	2.34 ±	0.23	0.02	1.17
TBC	0.13 ± 0.01	0.20 ± 0.02	2 2.78 ±	0.28	0.04	1.54
		Average	Values <u>+</u> 1 σ			
Lagoon water	$0.10 \ ^{\pm} \ 0.02$	0.11 ± 0.02	2 3.39 [±]	0.82	0.04	1.16
Ground water	0.87 ± 0.31	5.28 [±] 2.70) 23.87 [±]	0.38		6.88
Creek/inlet waters	0.10 ± 0.05	0.14 ± 0.09) 2.56 [±]	0.31	0.03	1.35

Appendix B.2. Water column radium activities (August 1999).

Transect	Station	Salinity	Conductivity	Oxygen	pН	Temperature	²²³ Ra	²²⁴ Ra
			(mS/cm)	(mg/L)		(°C)	(dpm/100L)	(dpm/100L)
Transect 1	IRL29WC	20.3	32.4	7	8.4	28.8	3.89	50.13
	IRL30WC	20.4	32.6	7.2	8.1	27.9	2.86	36.95
	IRL31WC	20.4	N/A	7.3	8.1	26.9	5.34	73.03
Transect 2	IRL32WC	20.4	32.4	7.9	8.4	29.3	4.23	61.20
	IRL33WC	20.3	32.3	7.8	8.3	28.1	4.67	49.93
	IRL34WC	20.2	32.2	7.5	8.2	27.3	4.09	49.16
Transect 3	IRL35WC	21.8	34.6	9.2	8.4	28.9	4.32	40.21
	IRL36WC	21.6	34.3	7.1	8.3	28.9	4.02	38.10
	IRL37WC	22.5	35.2	N/A	8.3	28.1	3.46	31.79
	IRL38WC	22.6	35.7	N/A	8.3	28	3.35	28.95
Transect 4	IRL39WC	24.3	37.8	6.5	8.3	28.1	6.63	47.99
	IRL40WC	26.8	41.1	6.7	8.3	28.2	5.97	44.41
	IRL41WC	25.2	39.4	7	8.3	27.6	5.88	51.63
	IRL42WC	24.8	38.9	6.8	8.4	27.6	5.28	55.45
Transect 1	BRL1WC	19.7	31.5	7.2	8.8	29.2	3.59	68.13
	BRL2WC	19.3	30.9	6.7	8.6	28.2	1.99	29.18
	BRL3WC	19.2	30.8	6.4	8.5	28	1.42	24.53
	BRL4WC	19	30.7	6.7	8.5	28	3.07	40.01
	BRL5WC	19.6	31.4	6.4	8.5	27.1		
Transect 2	BRL6WC	20.6	32.9	7.6	8.7	27.2	2.06	42.42
	BRL7WC	19.3	31	6.1	8.6	27.1	1.67	22.45
	BRL8WC	20.6	32.9	5.5	8.5	27.2	3.70	50.01

Appendix B.3. Water column radium activities (May 2000).

Transect	Station	Port*	Depth	Salinity	Conductivity	Oxygen	рН	Temp.	²²³ Ra	²²⁴ Ra
			(cm)		(mS/cm)	(mg/L)		(0C)	(dpm/100L)	(dpm/100L)
Transect 1	IRL31	7	157	22.4	35.6	0.8	7.5	24.8	-	-
		8	197	22.6	36.8	4.5	7.6	27.2		-
	IRL32	6	34	19.4	32.7	0.6	7.6	28	-	-
		7	74	20.9	34.7	5.5	7.7	27.2	-	-
		8	114	18.6	30.8	1.3	7.6	26.6	-	_
Transect 1	BRL1	3	30	19.6	31.3	3.4	8.1	28	28.73	254.62
		5	110	19.7	31.4	1.8	7.6	29.2	39.07	523.96
		6	150	21.8	34.6	1.6	7.6	27.5	113.20	1126.38
		7	190	19.6	31.4	2.3	7.8	28.5	-	-
	BRL2	1	10	19.2	30.9	1.3	7.6	26.7	11.61	257.08
		2	30	18.1	30.1	1.4	7.7	26.9	21.57	266.85
		3	50	18.1	29.2	0.5	7.7	26.5	34.53	556.57
		5	110	22	34.9	0.5	7.6	25.7	86.82	753.52
		6	150	24.7	38.8	0.6	7.6	25.8	102.13	1393.61
		7	190	25.3	39.9	0.6	7.4	25.5	60.50	1193.61
		8	230	27.1	42.3	0.7	7.5	24.8	150.11	2326.86
	BRL5	5	20	19.1	30.6	0.7	7.6	27	-	-
		8	130	31.2	47.9	1.2	7.5	25.9	-	_
Transect 2	BRL6	4	18	20.9	34.3	1.3	7.5	26.5	-	-
		5	48	20.1	33.4	1.6	7.9	27.2	-	-
		6	88	19.5	32.9	3.5	7.9	28	-	-
		8	168	20.6	32.9	1.2	7.7	27	-	-
	BRL7	3	14	21.6	36.3	3.1	7.7	28.5	-	-
		4	44	20.7	34.6	4.6	7.9	27.5	-	-
		5	74	19.8	32.4	1.8	7.8	26.3	-	-
		6	114	21.4	34.7	2.1	7.8	25.7	-	-
		7	154	25	39.9	0.6	7.8	26.1	-	-

Appendix B.4. Multi-sampler radium activities (May 2000).

* Port number of multi-sampler.** Depth below the sediment-water interface.

Station	Salinitv	Conductivity	Oxvgen	рH	Temperature	²²³ Ra (dnm/100L)	²²⁴ Ra (dnm/1001)
		(ms/cm)	(mg/L)		(C)	(apm/100L)	(apm/100L)
BHSpring	2	3.8	0.6	7.8	24.8	97.67	170.20
GW331	1.4	2.7	0.2	7.5	25.2	93.98	122.61
GW921	1.9	3.5	0.3	7.9	26	19.90	61.84
GW1472	0.1	0.2	0.4	4.3	24.5	3.30	203.16
GW1580	1.1	2.1	2.3	7.6	25.6	13.81	62.57
GW1647	1.1	2.2	0.1	7.6	31.5	22.51	40.73
GW1473	0.3	0.6	0.7	6.9	24.7	3.58	29.01
SEB. INLET	36	56.3	7.3	8.3	26.6	2.38	23.44
SEB. RIVER	27.8	48.1	6.1	8.3	29.8	10.93	79.84
EAU GALLIE	18	32.6	7.3	8.4	28.8	16.69	133.53
TURKEYCREEK	23.7	40.6	5.5	8.1	29.2	11.32	127.52
CRANE CREEK	20.6	36.5	6	8.2	30.4	8.90	72.94

Appendix B.5.	Well and	surface water	radium	activities	(May	2000).
---------------	----------	---------------	--------	------------	------	--------

Transect	Station	Salinity	Conductivity	Oxygen	pН	Temperature	²²³ Ra	²²⁴ Ra
			(mS/cm)	(mg/L)		(°C)	(dpm/100L)	(dpm/100L)
Transect 1	IRL29	29.5	45.3	8.2	8.4	28.6	8.22	73.30
	IRL30	29.2	45.0	7.4	8.2	29.0	7.78	52.20
	IRL31	28.9	44.5	7.1	8.2	29.0	6.72	55.74
Transect 2	IRL32	29.6	45.5	8.3	8.3	28.6	-	-
	IRL33	29.8	45.8	6.2	8.1	29.1	7.01	52.27
	IRL34	29.8	45.8	7.9	8.2	29.1	4.78	46.99
Transect 3	IRL35	28.6	44.0	7.5	8.1	29.3	6.35	42.07
	IRL36	28.5	44.0	6.0	8.0	29.3	6.36	44.58
	IRL37	28.7	44.1	6.2	8	29.3	-	-
	IRL38	28.2	43.6	29.1	8.1	6.6	5.27	37.11
Transect 4	IRL39	26.6	41.4	6.3	8.1	28.5	-	-
	IRL40	26.5	41.3	5.7	8.1	29.0	6.29	44.20
	IRL41	26.2	40.9	5.8	8.0	28.1	-	-
	IRL42	25.8	40.3	6.5	8.1	27.2	5.59	55.54
Transect 1	BRL1	28.6	44.5	4.2	8.5	27.3	7.54	108.92
	BRL2	29	45.1	6.7	8.6	29	4.88	44.68
	BRL3	28.4	44.2	5.4	8.4	28.5	6.79	64.43
	BRL4	28.5	44.2	6.8	8.6	28.9	5.60	66.35
	BRL5	28.6	44.5	6.9	8.6	29.1	3.69	35.74
Transect 2	BRL6	29.8	46.2	5.9	8.6	27.9	6.12	63.65
	BRL7	29.5	45.7	5.3	8.6	28.5	4.74	40.60
	BRL8	29.5	45.6	4.4	8.4	27.3	6.21	54.74

Appendix B.6. Water column radium activities (August 2000).

Appendix	B.7 .	Multi-san	apler rad	lium activ	vities (A	agust 2000).
11			1		(

Transect	Station	Port	Depth*	Salinity	Cond.	Oxygen	pН	Temp.	²²³ Ra	²²⁴ Ra
			(cm)		(mS/cm)	(mg/L)		(°C)	(dpm/100L)	(dpm/100L)
Transect 1	IRL29	4	80	20.6	35.5	1.1	7.4	30.1	-	-
		5	110	20.7	35.6	1.9	7.6	29.8	-	-
		6	150	N/A	N/A	N/A	N/A	N/A	-	-
Transect 1	BRL1	1	10	26.7	34.9	1	7.6	29.9	51.72	562.35
		5	110	20.6	35.1	0.8	7.4	29.1	51.85	548.16
		6	150	22.1	37.7	0.7	7.2	29.7	97.53	1734.73
	BRL2	1	10	26.7	44.5	0.6	7.9	29.4	7.52	200.01
		2	30	25.1	42.2	0.8	7.8	29.3	38.24	231.45
		3	50	23.1	39	0.2	76	29.4	58.66	599.11
		1	80	19.9	34	0.2	7.6	29.1	64.20	599.64
		-	110	27.5	26.2	0.2	7.0	29.1	92.26	646.33
		5	110	27.5	50.5	0.2	7.4	28.9	93.61	1142.13
		6	150	23.9	40	0.4	1.3	28.8	128.37	1134.73
		7	190	26	42.6	0.3	7.2	28.2	-	-
		8	230	26.5	44	N/A	7.5	28.9	28 60	572 21
	BRL5	2	20	26.4	43.8	0.4	8	29.1	28.09	575.21
		3	40	24.9	41.7	0.3	7.5	29.1	-	-
		4	70	24.2	40.8	0.3	7.5	29.3	73.11	547.40
		5	100	27.5	45.7	0.6	7.4	29.3	158.88	1241.28
Transect 2	BRL6	1	10	26.9	45.8	2.1	8.1	31.1	31.37	420.93
		2	30	26	43.9	0.3	7.7	29.9	46.28	422.22
		3	50	21.6	37.6	0.5	7.6	31	30.88	299.52
		4	80	20.9	36.5	14	76	31.1	-	-
		6	150	21.3	36.7	0.4	7.6	30.1	28.28	363.74
		2	14.5	26.0	27.2	1.1	7.0	20.2	-	-
	DKL/	2	14.5	20.9	57.5	1.1	7.8	20.4	-	-
		4	44.5	27.6	44.8	2.2	1.1	29.4	-	-
		7	154.5	27.2	45.4	3.9	8.6	29.7		

Station	Salinity	Conductivity	Oxygen	рН	Temperature	²²³ Ra	²²⁴ Ra
		(mS/cm)	(mg/L)		(°C)	(dpm/100L)	(dpm/100L)
BHSpring	1.8	3.5	1.8	7.6	26.6	83.14	71.65
GW1647	0.9	2.1	2.1	7.7	32.4	39.87	32.51
GW331	1.2	2.5	0.5	7.5	27.1	77.02	49.79
GW1580	0.9	2.1	1.6	7.6	25.7	36.75	63.57
GW1473	0	0.6	0.3	6.7	25.7	3.41	20.23
GW921	1.6	3.3	2.1	7.8	27.6	23.86	45.74
CRANE CREEK	23	36.3	6.5	7.9	30.3	7.47	46.99
HORSE CREEK	26.9	41.7	3.9	7.5	32.4	9.32	101.46
EAU GALLIE	26.1	40.5	8.3	8.1	30.8	7.04	57.98
SEB. INLET	33.7	51	8.6	8.2	29.5	-	-
TURKEY CREEK	0.2	0.9	8.2	7.7	30.2	3.77	23.30
SEB. RIVER	21.6	34.1	7.7	8.1	31.1	6.63	40.05

Appendix B.8. Well and surface water radium activities (August 2000).

Transect	Station	Salinity	Conductivity	Oxygen	PH	Temperature	²²³ Ra	²²⁴ Ra
			(mS/cm)	(mg/L)		(°C)	(dpm/100L)	(dpm/100L)
Transect 1	IRL29WC	30.5	47.6	7.87	8.45	16.4	3.89	50.13
	IRL30WC	30.7	47.7	7.34	8.39	16.4	2.86	36.95
	IRL31WC	29.9	46.9	7.31	8.46	16.5	5.34	73.03
Transect 2	IRL32WC	29.5	46	7.54	8.47	16.1	4.23	61.20
	IRL33WC	29.2	45.9	7.41	8.43	16.8	4.67	49.93
	IRL34WC	29	45.6	7.32	8.38	16.5	4.09	49.93
Transect 3	IRL35WC	27.5	43.4	9.14	8.66	17	4.32	40.21
	IRL36WC	27.2	43.1	8.08	8.53	17	4.02	38.10
	IRL37WC	27.1	42.8	7.71	8.43	17	3.46	31.79
Transect 4	IRL38WC	27.2	43	7.82	8.44	17.3	3.35	28.95
	IRL39WC	-	-	-	-	-	6.63	47.99
	IRL40WC	-	-	-	-	-	5.97	44.41
	IRL41WC	-	-	-	-	-	5.88	51.63
	IRL42WC	24.7	39.4	10.69	8.39	17.3	5.28	55.45
Transect 1	BRL1WC	23.7	37.9	10.97	8.74	16.7	3.59	68.13
	BRL2WC	23.9	38.3	11.26	8.78	16.8	1.99	29.18
	BRL3WC	23.9	38	8.26	8.63	16.8	1.42	24.53
	BRL4WC	24.1	38.4	10.53	8.7	16.4	3.07	40.00
	BRL5WC	24.3	38.7	10.27	8.77	16.6	-	-
Transect 2	BRL6WC	23.9	38.2	10.36	8.77	16.7	2.06	42.42
	BRL7WC	23.9	38.2	9.84	8.69	16.3	1.67	22.45
	BRL8WC	23.7	38	9.7	8.6	16.1	3.70	50.01

Appendix B.9. Water column radium activities (December 2000).

Appendix B.10. Multi-sampler radium activities (December 2000).

Transect	Station	Port	Denth (cm)	Salinitv	Conductivitv (mS/cm)	Oxvgen (mg/L)	рН	Temperature (°C)	²²³ Ra (dpm/100L)	²²⁴ Ra (dpm/100L)
Transect 1	IRL29	2	30	26.8	42.61	4.2	7.97	26.4	-	-
		4	80	21.2	33.7	3.32	7.42	28.1	-	-
		5	110	23.7	37.07	0.46	8.08	23.3	-	-
	IRL31	1	10	32.5	39.6	2.33	8.29	20.8	-	-
Transect 2	IRL32	1	10	29.2	45.19	2.49	8.34	22.4	-	-
		2	30	25.4	39.74	0.58	8.11	21.3	-	-
		3	50	23.2	36.67	1.89	8.13	24.4	-	-
		4	80	23.3	36.08	0.55	8.22	22.4	-	-
Transect 1	BRL1	1	10	-	-	-	-	-	-	-
		2	30		-	-	-	-	-	-
		5	110	-	-	-	-	-	-	-
		6	150	-	-	-	-	-	-	-
	BRL2	1	10	26.4	41.04	2.25	8.51	20.6	11.61	257.08
		2	30	25.6	39.89	1	8.07	21.6	21.57	266.85
		3	50	23.2	21.9	0.9	8.21	21.9	65.26	427.43
		4	80	23.4	21.2	0.49	8.17	21.2	75.23	673.23
		5	110	24.1	21.6	0.39	8.11	21.6	86.82	753.52
		6	150	26.4	21.8	0.36	8.02	21.8	102.13	1393.88
		7	190	27.7	22.3	0.5	8.06	22.3	113.24	1393.61
		8	230	28.2	22.6	0.97	8.02	22.6	150.11	2326.86
	BRL5	1	10	26.8	41.66	10.86	9.29	18.1	-	-
		2	30	26.7	41.61	0.56	8.66	18.4	-	-
		3	50	26.5	41.32	0.43	8.42	18.7	-	-
		4	80	28.7	44.34	0.42	7.99	19.5	-	-
		5	110	31.8	48.63	0.26	7.94	20.2	-	-
Transect 2	BRL6	1	10	26.4	40.8	3.12	8.81	20.1	-	-
		2	30	25.9	40.4	0.31	8.48	20.3	-	-
		3	50	24.9	39.16	0.33	8.21	21.5	-	-
		4	80	24.8	38.92	0.52	8.16	21.5	-	-
		6	150	23.3	36.81	0.25	8.08	22.6	-	-
	BRL7	3	50	-	-	-	-	-	-	-
		4	80	-	-	-	-	-	-	-
		5	110	-	-	-	-	-	-	-
		6	150	-	-	-	-	-	-	-

Station	Salinity	Conductivity	Oxygen	рН	Temperature	²²³ Ra	²²⁴ Ra
		(mS/cm)	(mg/L)		(°C)	(dpm/100L)	(dpm/100L)
BHSpring						97.67	170.20
GW1647	0.9	1.823	0.48	7.47	31.3	22.51	40.73
GW331	1.5	2.837	1.05	8.08	25	93.98	122.61
GW1473						3.58	29.01
GW1561						-	-
GW921						19.90	61.84
CRANE CREEK						8.90	72.94
HORSE CREEK						-	-
EAU GALLIE RIVER	25.9	40.56	7.36	8.61	23.7	16.69	133.53
SEB. INLET	35.6	53.9	8.25	8.6	22.8	2.38	23.44
SEB. RIVER	16.1	26.1	8.19	8.59	22.6	10.93	79.84

Appendix B.11. Well and surface water radium activities (December 2000).

Appendix C. ²²²Rn and ²²⁶Ra activities

Appendix C.1. ²²²Rn and ²²⁶Ra activities in lagoon waters for northern site, May 1999.

			Station and Transect Inventories				
	²²⁶ Ra	ex ²²² Rn	²²⁶ Ra	ex ²²² Rn	Σ^{226} Ra	$\Sigma ex^{222}Rn$	
Station	(dpm/L)	(dpm/L)	(dpm/m ²)	(dpm/m^2)	(10^4 dpm/m)	(10 ⁴ dpm/m)	
Big Flounder T	ransect, 6 May 199	9			· ·		
IRL 1	$2.36~\pm~0.16$	$2.55 ~\pm~ 0.22$	1084	1175	245	293	
IRL 2	$2.32 \ \pm \ 0.36$	$1.79 ~\pm~ 0.45$	1415	1094			
IRL 3	$2.28~\pm~0.35$	1.85 ± 0.43	1389	1131			
IRL 4	$2.46~\pm~0.08$	$2.03 ~\pm~ 0.14$	1695	1399			
IRL 5	$2.12 ~\pm~ 0.09$	$3.23 ~\pm~ 0.45$	1612	2454			
IRL 6	$2.05 ~\pm~ 0.05$	$2.52 \ \pm \ 0.12$	1867	2293			
IRL 7	2.01 ± 0.14	$2.44 \ \pm \ 0.20$	3373	4093			
IRL 8	$2.04 \ \pm \ 0.38$	$2.80~\pm~0.46$	3726	5119			
Palm Tree/Shile	oh Transect, 6-7 Ma	ıy 1999					
IRL 13A	1.99 ± 0.14	3.64 ± 0.20	1767	3237			
IRL 13B	1.84 ± 0.18	$2.53 ~\pm~ 0.40$	1641	2250			
IRL 14A	2.41 ± 0.28	1.75 ± 0.34	2264	1647			
IRL 14B	2.22 ± 0.33	2.53 ± 0.40	2087	2374			
IRL 15	$2.46 ~\pm~ 0.43$	$2.67 ~\pm~ 0.52$	1574	1708			
Tower Transect	t, 7 May 1999						
IRL 17	2.20 ± 0.54	1.10 ± 1.12	1343	674	68	27	
IRL 18	1.91 ± 0.13	$0.99 ~\pm~ 0.29$	1411	729			
IRL 19	$2.09 ~\pm~ 0.09$		1585	0			
IRL 20	1.98 ± 0.23	1.14 ± 0.59	1507	864			
Duckroost Cove	e, 8 May 1999						
IRL 21	1.68 ± 0.16	2.50 ± 0.33	1632	2423	320	463	
IRL 22	$2.08 \ \pm \ 0.33$	1.53 ± 0.69	2480	1819			
IRL 23	1.86 ± 0.23	3.21 ± 0.47	2030	3499			
IRL 24	1.67 ± 0.29	4.37 ± 0.51	1708	4457			
Deep Water Site	es, 6-8 May 1999						
IRL 11	2.06 ± 0.04	$3.48 \ \pm \ 0.07$	4072	6896	2392	2111	
IRL 16	1.96 ± 0.30	$2.70 \ \pm \ 0.78$	3584	4947			
IRL 25	1.63 ± 0.09	$0.79 ~\pm~ 0.26$	3116	1508			
IRL 26	$1.82 \ \pm \ 0.23$	$0.63~\pm~0.41$	3603	1254			
IRL 27	1.93 ± 0.21	$2.12 \ \pm \ 0.39$	2888	3176			
IRL 28	$2.06~\pm~0.28$	1.06 ± 0.48	3932	2033			

					Station and Transect Inventories				
	²²⁶ R	a	ex ²²²	Rn	²²⁶ Ra	ex ²²² Rn	Σ^{226} Ra	Σ ex ²²² Rn	
Station	(dpm/	′L)	(dpm	/L)	(dpm/m^2)	(dpm/m^2)	(10^4 dpm/m)	(10^4 dpm/m)	
Big Flounder T	^r ransect, 1	6 August	1999						
IRL 1	$3.01 \pm$	0.11	2.66 ±	0.13	1385	1222	295	495	
IRL 2	$2.94\pm$	0.32	$2.93 \ \pm$	0.35	1350	1347			
IRL 3	$2.77\pm$	0.18	$3.53 \pm$	0.20	1688	2151			
IRL 4	$2.66 \pm$	0.04	$5.81 \pm$	0.08	1620	3546			
IRL 6	$2.66 \pm$	0.04	6.74 ±	0.15	2025	5119			
IRL 7	$2.61 \pm$	0.04	$4.15 \pm$	0.12	4389	6971			
IRL 8	$2.87\pm$	0.04	$4.86 \ \pm$	0.13	5249	8892			
Turnbull Trans	ect, 15 Au	gust 1999							
IRL 9	$2.97\pm$	0.05	$3.15 \pm$	0.14	3177	3370	66	72	
IRL 10	$2.77\pm$	0.28	$3.13 \pm$	0.35	1688	1910			
Palm Tree/Shil	oh Transe	ct, 15 Aug	ust 1999						
IRL 12	$2.44\pm$	0.01	2.85 \pm	0.11	1808	2112	380	373	
IRL 13	$3.06 \pm$	0.10	2.87 \pm	0.13	2724	2550			
IRL 14	$2.53\pm$	0.18	1.70 ±	0.23	2379	1601			
IRL 15	$2.84\pm$	0.12	0.57 \pm	0.15	1815	366			
Tower Transec	t, 15 Augu	ist 1999							
IRL 17	$2.74\pm$	0.22	1.82 ±	0.27	1674	1109	85	56	
IRL 18	$2.52\pm$	0.08	$1.85 \pm$	0.13	1839	1352			
IRL 19	$2.72 \pm$	0.16	$1.68 \pm$	0.22	1878	1157			
IRL 20	$2.47\pm$	0.11	1.05 \pm	0.15	2005	850			
Duckroost Cov	e, 14 Augi	ust 1999							
IRL 21	$2.09\pm$	0.20	3.29 \pm	0.26	1901	2996	362	529	
IRL 22	$2.43 \pm$	0.09	3.18 \pm	0.17	2645	3467			
IRL 23	$2.18 \pm$	0.03	$3.14 \pm$	0.12	2223	3199			
IRL 24	$2.47\pm$	0.08	$4.07 \pm$	0.15	2249	3707			
Deep Water Sit	es, 14-15	August 19	99						
IRL 11	$2.43\pm$	0.11	$1.39 \pm$	0.16	4451	2544	3087	2306	
IRL 16	$2.82\pm$	0.31	$3.66 \pm$	0.38	5167	6690			
IRL 25	$2.76 \pm$	0.30	$3.29\pm$	0.36	5687	6768			
IRL 26	$2.72 \pm$	0.19	$1.03 \pm$	0.25	4974	1877			
IRL 27	$2.37\pm$	0.01	$1.78 \pm$	0.10	3985	2987			
IRL 28	$2.11 \pm$	0.06	$1.83 \pm$	0.11	3853	3345			

Appendix C.2. ²²²Rn and ²²⁶Ra activities in lagoon waters for northern site, August 1999.

			Station Activities		Station Inv	entories
Sample Location	Collection Date/Time	Depth (m)	Ra-226 dpm/L	ex Rn-222 dpm/L	²²⁶ Ra (dpm/m ²)	ex ²²² Rn (dpm/m ²)
Indian River	Lagoon					
IRL 29 dry	5/14/00 12:02	1.6	2.77 ± 0.17	$0.92\pm\ 0.26$	4475	1480
IRL 30 dry	5/14/00 11:04	3.4	2.30 ± 0.04	$0.55\pm\ 0.09$	7723	1861
IRL 31 A	5/14/00 10:05	2.4	2.08 ± 0.05		5083	
IRL 31 B	5/17/00 16:45	2.4	2.51 ± 0.02	$0.56\pm\ 0.47$	6129	1374
IRL 32 dry	5/14/00 13:06	1.4	2.58 ± 0.37	0.79 ± 0.67	3535	1088
IRL 33 dry	5/14/00 13:32	3.0	2.58 ± 0.37		7856	
IRL 34 dry	5/14/00 14:04	2.7	2.58 ± 0.37	0.25 ± 0.46	6913	666
IRL 35 dry	5/14/00 15:02	2.3	2.92 ± 1.38	0.70 ± 1.69	6674	1607
IRL 36 A	5/14/00 15:32	3.2	3.23 ± 1.00		10335	
IRL 36 B	5/17/00 12:00	3.2	2.36 ± 0.03	0.20 ± 0.15	7563	647
IRL 37 dry	5/14/00 15:56	3.7	2.58 ± 0.37	1.21 ± 0.54	9427	4436
IRL 38 dry	5/14/00 16:34	2.7	2.58 ± 0.37	0.72 ± 0.51	7070	1978
IRL 39 dry	5/15/00 10:11	1.8	2.58 ± 0.37	1.01 ± 0.47	4713	1843
IRL 40 dry	5/15/00 10:45	3.7	2.58 ± 0.37		9427	
IRL 41 dry	5/15/00 11:11	2.6	2.44 ± 0.05	0.74 ± 0.15	6310	1926
IRL 42 dry	5/15/00 11:44	1.5	2.58 ± 0.37	1.00 ± 0.45	3928	1521
Banana River	· Lagoon					
BRL 1 dry	5/15/00 16:10	1.8	3.33 ± 1.58		6091	
BRL 2 dry	5/15/00 16:35	1.5	3.25 ± 1.00		4954	
BRL 3 dry	5/15/00 17:00	2.7	2.61 ± 0.04		7167	
BRL 4 dry	5/15/00 17:30	3.4	2.68 ± 0.07		8974	
BRL 5 dry	5/15/00 18:00	1.5	2.81 ± 0.21	0.12 ± 0.30	4283	185
BRL 6 dry	5/16/00 12:15	0.9	2.22 ± 0.14		2031	
BRL-7 dry	5/16/00 11:40	2.7	2.46 ± 0.15		6756	
BRL-8 dry	5/16/00 11:05	1.2	2.62 ± 0.19		3193	

Appendix C.3. ²²²Rn and ²²⁶Ra activities in lagoon waters for central sites, May 2000.

			Station A	Station Inventories		
Sample Location	Collection Date	Depth (m)	Ra-226 dpm/L	ex Rn-222 dpm/L	²²⁶ Ra (dpm/m ²)	ex ²²² Rn (dpm/m ²)
Indian I	River Lagoon					
IRL 29 wet	8/13/00 16:56	2.4	4.4 ± 1.5		10609	
IRL 30 wet	8/13/00 17:54	3.4	$3.94 \ \pm \ 0.77$		13216	
IRL 31 wet	8/13/00 19:00	2.4	$3.04 \ \pm \ 0.12$		7411	
IRL 32 wet	8/13/00 13:21	1.5	3.188 ± 0.030	$3.10~\pm~0.40$	4916	4787
IRL 33 wet	8/13/00 14:05	3.0	3.062 ± 0.085		9333	
IRL 34 wet	8/13/00 15:15	2.7	2.805 ± 0.028		7433	
IRL 35 wet	8/13/00 15:54	2.1	$2.76 ~\pm~ 0.22$	$0.91 ~\pm~ 0.32$	5787	1906
IRL 36 wet	8/13/00 12:44	3.2	$2.46 ~\pm~ 0.22$		7887	
IRL 37 wet		3.8				
IRL 38 wet	8/13/00 11:57	2.7	2.51 ± 0.19		6690	
IRL 39 wet	8/13/00 11:26	1.5	2.72 ± 1.29	7.2 ± 1.6	3972	10463
IRL 40 wet	8/13/00 10:42	3.6	2.267 ± 0.050	$0.13 \ \pm \ 0.12$	8160	463
IRL 41 wet	8/13/00 10:16	2.6	1.716 ± 0.086	0.8 ± 1.0	4447	2179
IRL 42 wet	8/13/00 9:05	1.4	2.088 ± 0.026		2964	
Banana	River Lagoon					
BRL1 wet	8/13/00 11:32	1.8	3.478 ± 0.047	$0.23 ~\pm~ 0.28$	6360	416
BRL 2 wet	8/13/00 12:34	1.5	$2.93 ~\pm~ 0.22$		4463	
BRL 3 wet	8/13/00 13:00	2.7	3.332 ± 0.063		9141	
BRL 4 wet	8/13/00 15:40	3.4	$3.39 ~\pm~ 0.31$		11352	
BRL 5 wet	8/13/00 16:09	1.5	$2.56 ~\pm~ 0.19$		3907	
BRL 6 wet	8/13/00 10:55	0.9	4.3 ± 1.3		3934	
BRL 7 wet	8/13/00 10:22	2.7	2.755 ± 0.089		7559	
BRL 8 wet	8/13/00 9:32	1.2	2.913 ± 0.065		3552	

Appendix C.4. ²²²Rn and ²²⁶Ra activities in lagoon waters for central sites, August 2000.

Sample Location	Collection Date	Depth (m)	Activities Ra-226 dpm/L	Station Inventories ²²⁶ Ra (dpm/m ²)
Indian River Lagoon IRL-36	12/10/00 18·08	32	6.93 + 0.63	22176
Banana River Lagoon	12/10/00 15 45	1.5		45(1
BKL-2	12/10/00 15:45	1.5	3.040 ± 0.069	4561

Appendix C.5. ²²²Rn and ²²⁶Ra activities in lagoon waters for central sites, December 2000.

Appendix C.6. Surface water creek and canal ²²²Rn and ²²⁶Ra activities for northern site, 1999.

Date	Creek/Canal	²²⁶ Ra (dpm/L)	ex ²²² Rn (dpm/L)
8-9 May 1999	Haulover Canal	2.00 ± 0.09	1.78 ± 0.19
	Turnbull Creek (upstream)	3.13 ± 0.12	1.53 ± 0.26
	Turnbull Creek (mouth)	2.85 ± 0.47	4.59 ± 0.82
16 August 1999	Haulover Canal	2.49 ± 0.28	0.98 ± 0.42
	Turnbull Creek (upstream)	3.53 ± 0.36	
Collection		Ra-226	ex Rn-222
---------------	---------------------------	-----------------	-----------------
Date	Rivers	(dpm/L)	(dpm/L)
Dry Season: M	<i>Iay 2000</i>		
16-May-00	Sebastian Inlet	0.40 +/- 0.02	1.17 +/- 0.09
16-May-00	St. Sebastian River	0.69+/- 0.05	3.40 +/- 0.10
16-May-00	Turkey Creek	2.90+/- 0.07	5.85 +/- 0.34
16-May-00	Crane Creek	4.45 +/- 0.04	16.35 +/- 2.63
16-May-00	Eau Gallie River	6.19+/- 2.93	8.24 +/- 3.91
Rainy Season:	August 2000		
15-Aug-00	Sebastian Inlet	0.49 +/- 0.01	11.64 +/- 4.24
15-Aug-00	St. Sebastian River	1.34 +/- 0.06	1.28 +/- 0.13
15-Aug-00	Turkey Creek	2.76+/- 0.02	313.99 +/- 7.03
16-Aug-00	Crane Creek	2.29 +/- 0.08	7.66 +/- 0.43
16-Aug-00	Horse Creek	3.17+/- 0.04	6.91 +/- 0.23
16-Aug-00	Eau Gallie River	2.76+/- 0.04	10.28 +/- 0.75
16-Aug-00	Blue Heaven Spring	10.63 +/- 0.18	515 +/- 183
Rainy/Transit	ional Season: December	2000	
11-Dec-00	Crane Creek	3.53 +/- 0.38	
08-Dec-00	Horse Creek	3.405 +/- 0.065	
11-Dec-00	Eau Gallie River	3.657 +/- 0.075	

Appendix C.7. Surface water river ²²²Rn and ²²⁶Ra activities for central site, 2000.

Appendix C.8. G	roundwater activities of ²²² Rn and ²²⁶ Ra in wells surrounding
northe	rn site.

Well ID	Latitude	Longitude	Depth (m)	²²⁶ Ra (dpm/L)	ex ²²² Rn (dpm/L)
					. . .
5-8 May 1	1999				
GW-1	28°41.481'	80° 51.505'	38.1	2.114 ± 0.046	351 ± 39
GW-2	28°45.954'	80° 52.638'	36.3	4.79 ± 0.42	$775~\pm~64$
GW-3	28°39.966'	80° 56.907'	1.5-4.6	6.37 ± 1.00	150 ± 28
GW-4	28°46.147'	80° 52.266'	39.0	3.99 ± 0.90	2145 ± 47
GW-5	28°38.511'	80°43.281'	24.4 (?)	0.476 ± 0.042	236 ± 21
GW-6	28°42.377'	80°43.611'	n/a	3.80 ± 0.15	207.7 ± 5.6
16-18 Au	gust 1999				
GW-1	28°41.481'	80° 51.505'	38.1		$159.0\pm~7.6$
GW-2	28°45.954'	80° 52.638'	36.3	4.44 ± 0.96	622 ± 32
GW-3	28°39.966'	80° 56.907'	1.5-4.6		41.8 ± 3.8
GW-4	28°46.147'	80° 52.266'	39.0		283 ± 69
GW-5	28°38.511'	80°43.281'	24.4 (?)		377 ± 41
GW-6	28°42.377'	80°43.611'	n/a		$47\pm$ 45

Well ID	Depth (m)	Ra-226 (dpm/L)	Rn-222 (dpm/L)
May 2000		(,)	(
Surficial A	auifer Wells, 1	8 May 2000	
GW-921	10.7	7.104 +/- 0.094	58.52 +/- 10.34
GW-1472	5.9	1.550 +/- 0.022	9.06 +/- 6.91
GW-1580	18.3	3.66 +/- 0.15	52.86 +/- 10.50
Floridan Aquifer W	ells, 18-19 May 2	2000	
GW-331	73.2	9.38 +/- 0.38	66.31 +/- 11.13
GW-1473	84.7	1.932 +/- 0.028	115.60 +/- 35.04
GW-1647	106.7	6.69 ± 0.17	85.61 +/- 12.35
Merritt Island Sprin	g, 18 May 2000		
Blue Heaven Sprin	ig spring mouth	8.53 +/- 0.20	53.76+/- 11.06
August 2000			
Surficial Aquifer We	ells, 16 August 20	000	
GW-921	10.7	7.32 +/- 0.04	92.70 +/- 16.72
GW-1472	5.9		no sample
GW-1561	18.3	6.06 +/- 0.04	247.71 +/- 38.99
Floridan Aquifer W	ells, 16 August 20	000	
GW-331	73.2	10.59 +/- 0.18	176.15 +/- 19.65
GW-1473	84.7	2.19 +/- 0.19	373.86 +/- 25.26
GW-1647	106.7	9.66 +/- 0.10	258.81 +/- 16.25
Merritt Island Sprin	g, 16 August 200	00	
Blue Heaven Sprin	g spring mouth	10.63 +/- 0.18	123.56 +/- 19.84
December 2000			
Surficial Aquifer We	ells, 8 December	2000	
GW-921	10.7		17.61 +/- 2.28
GW-1472	5.9		no sample
GW-1561	18.3	5.6483 +/- 0.47	5 31.60 +/- 1.04
Floridan	Aquifer Wells,	8 & 11 December 20	000
GW-331	73.2	11.50 +/-0.39	79.02 +/- 0.17
GW-1473	84.7		39.70 +/- 3.37
GW-1647	106.7	7.4835 +/- 0.709	9 no sample
Merritt Island Sprin	g, 8 December 2	000	-
Blue Heaven Sprin	ng mouth		9.66 + - 0.84

Appendix C.9. Groundwater activities of ²²²Rn and ²²⁶Ra in wells central site, 2000.

Station	Date	Depth in th Sediment	²²⁶ Ra (dpm/L)	ex ²²² Rn (dpm/L)
		(cm)		
	12/12/00	20	2.21 ± 0.2	74.2 + 1.2
IKL 4	12/13/99	39	2.21 ± 0.2	74.2 ± 1.3
		64	2.53 ± 1.2	53.1 ± 4.9
		95	2.82 ± 0.2	329.5 ± 4.0
		124	3.13 ± 0.8	389.3 ± 5.8
		156	3.20 ± 0.2	484.9 ± 4.6
		185	$3.93~\pm~0.0$	308.2 ± 4.0
IRL 5	12/13/99	-39	1.67 ± 0.4	7.3 ± 1.9
		1	1.67 ± 0.4	12.2 ± 2.0
		31	1.58 ± 0.1	$8.7~\pm~0.7$
		60	3.10 ± 0.1	104.6 ± 2.2
		89	3.43 ± 0.1	361.2 ± 3.5
IRL 6	12/13/99	-69	1.79 ± 0.0	105.5 ± 2.3
		-14	1.35 ± 0.1	8.8 ± 0.9
		47	1.59 ± 0.4	98.3 ± 2.5
		.,		
IRL 22	12/12/99	-29	1.59 ± 0.1	$43.0~\pm~2.0$
		4	2.29 ± 0.5	76.9 ± 3.6
		32	34.44 ± 3.3	150.5 ± 19.5
		123	1.49 ± 0.1	1265.1 ± 8.8

Appendix C.10. Pore water activities in multisamplers in the northern site, December 1999.

Station	Collection Date	Port No.	Depth in Sediments (cm)	Ra-226 (dpm/L)
IRL-4	12-Dec-00	water column	0	3.69 ± 0.13
		1	10	3.196 ± 0.061
		2	30	1.69 ± 0.24
		3	50	$2.94 \ \pm \ 0.28$
		4	80	$2.36~\pm~0.10$
IRL-22	12-Dec-00	water column	0	8.01 ± 0.33
		1	10	2.221 ± 0.050
		2	30	2.431 ± 0.057
		3	50	3.66 ± 0.15
		4	80	$10.53 \ \pm \ 0.27$
		6	150	5.33 ± 0.17
		8	230	12.95 ± 0.15

Appendix C.11. Pore water activities in multisamplers in the northern site, December 2000.

Station	Collection Date	Port No.	Depth in Sediments (cm)	Ra-226 (dpm/L)		Rn-222 (dpm/L)		
					,			
BRL-1	17-May-00	1	1	$5.08 \pm$	0.20	bd	l	
		3	10	$9.23 \pm$	0.36	$14.55 \pm$	4.65	
		5	70	$4.86 \pm$	0.10	$32.70 \pm$	7.71	
		6	110	$10.51 \pm$	0.09	$65.15 \pm$	14.06	
		8	190	$3.90 \pm$	0.07	$6.07 \pm$	1.29	
BRL-2	18-May-00	1	10			7.61±	3.84	
		2	30			$16.03 \pm$	4.07	
		3	50	$17.87 \pm$	0.79	$30.62 \pm$	3.60	
		5	110	$5.42 \pm$	0.06	$46.18 \pm$	8.84	
		6	150	$8.07 \pm$	0.14	$103.73 \pm$	10.95	
		7	190	$9.95 \pm$	0.85	$53.18 \pm$	8.22	
		8	230	$45.20\pm$	6.07	$92.54 \pm$	11.01	
BRL-5	18-May-00	5	50	5.38±	0.34	31.37±	4.21	
		8	130	$2.47 \pm$	0.10	$21.54 \pm$	6.99	
BRL-6	18-May-00	4	18			$2.89 \pm$	1.19	
		5	48			$6.11 \pm$	2.40	
		6	88			$9.72 \pm$	3.73	
		8	168	$6.75 \pm$	0.20	$6.77 \pm$	1.55	
BRL-7	18-May-00	3	14			$7.47 \pm$	4.79	
	2	4	44	$22.14 \pm$	1.70	$16.03 \pm$	6.95	
		5	74			$29.59\pm$	6.86	
		6	114			$36.14 \pm$	3.69	
		7	154	$11.85 \pm$	0.16	$75.10 \pm$	13.82	
IRL-29	19-May-00	6	57			17.33±	3.60	
IRL-31	19-May-00	7	157	$4.10 \pm$	0.05	53.79±	10.72	

Appendix C.12. Pore water activities in multisamplers in the central site, May 2000.

Station	Collection Date	Port No.	Depth in Sediments (cm)	Ra-226 (dpm/L)	Rn-222 (dpm/L)
BRL-1	15-Aug-00	3	10	3.06 ± 0.23	18.07 ± 4.90
		5	110	50.92 ± 2.04	112.22 ± 12.08
		6	150	10.07 ± 0.19	248.18 ± 60.95
BRL-2	15-Aug-00	1	10	5.10 ± 0.21	7.91 ± 1.34
		2	30	4.81 ± 1.49	27.33 ± 3.54
		3	50	5.50 ± 1.70	41.70 ± 14.05
		4	80	4.542 ± 0.085	63.82 ± 15.06
		5	110	8.747 ± 0.082	88.74 ± 8.85
		6	150	10.52 ± 0.27	160.65 ± 37.51
		7	190	12.81 ± 0.23	84.57 ± 22.35
BRL-5	15-Aug-00	2	20	3.90 ± 0.35	27.24 ± 7.68
		3	40	4.74 ± 0.10	48.02 ± 15.81
		4	70	7.50 ± 0.11	87.55 ± 1.29
		5	100	4.715 ± 0.074	47.47 ± 3.38
BRL-6	15-Aug-00	1	10	3.71 ± 0.34	2.16 ± 2.17
	C	2	30	3.65 ± 0.044	13.60 ± 2.54
		3	50	5.42 ± 0.079	29.43 ± 6.40
		4	80	4.20 ± 0.082	37.23 ± 8.90
		6	150	$2.45~\pm~0.12$	30.26 ± 3.87
IRL-29	16-Aug-00	4	80	2.59 ± 0.27	72.97 ± 16.07
	e	5	110	3.47 ± 0.14	58.42 ± 19.52

Appendix C.13. Pore water activities in multisamplers in the central site, August 2000.

Station	Collection Date	Port No.	Depth in Sediments (cm)	Ra-226 (dpm/L)	Rn-222 (dpm/L)
RDI 1	9-Dec-00	1	10	3.025 ± 0.093	bd
DRL-1	9-Dee-00	2	30	7.21 ± 0.095	552 ± 1.08
		5	110	7.21 ± 0.10 4.942 ± 0.083	10.01 ± 3.04
		5	150	5.12 ± 0.085	19.01 ± 3.94 33.75 + 3.66
		0	150	5.12 ± 0.14	55.75 ± 5.00
BRL-2	10-Dec-00	1	10	2.97 ± 0.27	bd
		2	30	3.076 ± 0.055	15.04 ± 1.58
		3	50		24.99
		4	80	3.91 ± 0.18	13.29 ± 0.03
		5	110	5.51 ± 0.49	13.16 ± 0.03
		6	150	9.19 ± 0.42	13.03 ± 0.03
		7	190	2.92 ± 0.14	49.10 ± 1.79
		8	230	9.33 ± 0.30	$17.00 \pm$
BRL-5	9-Dec-00	1	10	13.64 ± 0.46	bd
		2	30	2.62 ± 0.24	3.02 ± 1.43
		3	50	2.83 ± 0.27	5.24 ± 1.09
		4	80	3.66 ± 0.15	17.69 ± 4.83
		5	110	3.24 ± 0.29	6.84 ± 1.03
BRL-6	9-Dec-00	1	10	3.54 ± 0.10	bd
		2	30	2.74 ± 0.11	$1.46 \pm$
		3	50	2.89 ± 0.11	3.94 ± 0.01
		4	80	3.41 ± 0.12	9.74 ± 1.34
		6	150	3.554 ± 0.073	6.17 ± 0.01
BRL-7	9-Dec-00	3	50	2.27 ± 0.14	11.67 ± 0.87
		4	80	4.913 ± 0.076	11.46 ± 0.03
		5	110	5.83 ± 0.19	$28.05 \pm$
		6	150		32.60 3.23
IRL-29	12-Dec-00	2	30	5.16 ± 0.20	
		4	80	2.12 ± 0.14	31.27 ± 18.01
		5	110	3.73 ± 0.15	33.89 ± 10.04
IRL-31	12-Dec-00	1	10	3.86 ± 0.13	bd
IRL-32	12-Dec-00	1	10	3.76 ± 0.11	
		2	30	4.16 ± 0.11	
		3	50	2.80 ± 0.25	
		4	80	2.571 ± 0.077	22.18 ± 2.33

Appendix C.14. Pore water activities in multisamplers in the central site, December 2000.

Appendix C.15. ²²²Rn diffusive fluxes in northern IRL, Florida (1999), measured on sediment grab samples. The radon diffusion coefficient (D_m) = 5.76 x 10⁻⁶ cm²/sec; porosity (ϕ) = 0.44; and wet bulk sediment density (ρ_{wet}) = 1.86 g/cm³. Fluxes range from 175 to 857 dpm/m²/day (mean (±1 σ) = 253±134 dpm/m²/day) and a coefficient of variation = 53%.

Station ID	Wet Sediment Mass (g)	Rn-2 Cec (dpm	22 1 /L)	Rn Bottor (dp	-22 n v m/	2 vater L)	Diff F (dpm/	usi lux m2	ive (//day)
Big Flounder	Transect								
IRL-1	50.06	114 ±	17	4.489	±	0.084	185	±	27
IRL-2	50.17	94 ±	16	3.814	±	0.078	153	±	26
IRL-3	50.26	101 ±	16	3.836	±	0.081	164	±	26
IRL-4	50.23	60 ±	15	4.155	±	0.082	97	±	25
IRL-5	50.82	68 ±	15	5.015	±	0.098	110	±	25
IRL-6	49.99	69 ±	15	4.144	±	0.087	112	±	25
IRL-7	50.59	309 ±	17	4.052	±	0.081	508	±	28
IRL-8	50.34	287 ±	16	4.406	±	0.083	473	±	27
Turnbull Tra	nsect								
IRL-9	50.79	271 ±	16	5.653	±	0.105	444	±	26
IRL-10	50.35	207 ±	11	5.439	±	0.092	339	±	18
Deep Center	Sites								
IRL-11	50.85	254 ±	12	4.435	±	0.034	417	±	19
IRL-16	50.76	207 ±	15	3.099	±	0.139	339	±	25
Shiloh/Palm 7	Free Transec t								
IRL-12	50.28	120.1 ±	8.5	4.884	±	0.092	196	±	14
IRL-13	50.12	133.8 ±	9.0	4.087	±	0.078	219	±	15
IRL-14	50.51	130.2 ±	8.6	4.141	±	0.089	212	±	14
IRL-15	50.79	89.2 ±	7.6	4.704	±	0.089	145	±	13
Tower Site									
IRL-17	50.70	168 ±	10	2.741	±	0.070	276	±	16

Appendix C.16. ²²²Rn diffusive fluxes in IRL/BRL, Florida (2000), measured on sediment grab samples. The radon diffusion coefficient (D_m) is 5.76 x 10⁻⁶ cm²/sec; porosity (ϕ) is 0.37; and wet bulk sediment density (ρ_{wet}) is 1.96 g/cm³. Fluxes range from x to x dpm/m²/day (mean (±1 σ) of x±x dpm/m²/day) and a coefficient of variation of X%.

Station ID	Wet Sediment Mass (g)	Rn-222 Ceq (dpm/L)	Ex Rn-222 Bottom water (dpm/L)	Diffusive Flux (dpm/m²/day)
Indian River Lagoon		· - ·	· - ·	
IRL-31	50.52	81.6 ± 7.5	$0.56~\pm~0.47$	135 ± 12
IRL-32	50.26	280.2 ± 8.6	$0.79 \hspace{0.1in} \pm \hspace{0.1in} 0.67$	$463~\pm~14$
IRL-39	50.52	401 ± 36	$0.56 ~\pm~ 0.47$	663 ± 60
IRL-29 0-20 cm	42.65	153.5 ± 4.4	0.92 ± 0.26	253.6± 7.3
IRL-29 20-40 cm	44.26	333 ± 29	0.92 ± 0.26	550 ± 48
IRL-29 40-60 cm	50.14	139.4 ± 8.4	0.92 ± 0.26	230 ± 14
IRL-29 60-73 cm	44.22	157.7 ± 4.3	$0.92 ~\pm~ 0.26$	260.6 ± 7.1
Banana River Lagoon	n			
BRL-1	49.83	97.5 ± 8.4	-1.8 ± 1.8	162 ± 14
BRL-2	49.24	196 ± 21	-1.5 ± 1.2	325 ± 35
BRL-5	42.79	264 ± 25	0.12 ± 0.30	436 ± 42
BRL-6	41.12	131 ± 19	-0.79 ± 0.35	218 ± 31
BRL-7	50.19	162.3 ± 8.8	-0.72 ± 0.24	269 ± 15

Appendix C.17: ²²² Rn-222 benthic fluxes measured during the rainy season (199	9)
in northern IRL and during the dry season (2000) in BRL.	

Sample ID	Hour of Sampling	Collection Date/Time	Ra-226 (dpm/L)	Rn-222 (dpm/L)	Flux Time (min)	Rn-222 Flux (dpm/m2/day)
August 1999), Northern I	ndian River La	igoon			
Chamber A						
IRL2-6 A	initial $(t=0)$	8/17/99 10:24	2.341 ± 0.434	5.95 ± 0.57		
IRL2-6 A	t = 8	8/17/99 18:09	2.926 ± 0.171	6.571 ± 0.246	463	$856~\pm~572$
Chamber B						
IRL2-6 B	initial $(t = 0)$	8/17/99 10:40	2.457 ± 0.098	6.938 ± 0.198	3	
IRL2-6 B	t = 4	8/17/99 14:43	2.499 ± 0.137	8.944 ± 0.230) 243	$3725~\pm~518$
IRL2-6 B	t = 8	8/17/99 18:05	2.652 ± 0.312	7.492 ± 0.398	3 445	$867~\pm~425$
May 2000, E	Banana River	r Lagoon				
BRL-1	initial $(t=0)$	5/17/00 11:31	2.757 ± 0.026	-1.114 ± 0.103		
Chamber A						
BRL-1A	t = 4	5/17/00 14:54	2.359 ± 0.214	0.054 ± 0.276	203	$2290~\pm~599$
BRL-1A	t = 24	5/18/00 9:15	3.032 ± 1.435	1.314 ± 1.700	1304	$756~\pm~619$
BRL-1A dup	t = 24	5/18/00 9:15	2.573 ± 0.059	2.290 ± 0.693	1304	$1083~\pm~255$
Chamber B						
BRL-1B	t = 4	5/17/00 14:58	2.573 ± 0.345	-0.325 ± 0.450	207	$1498~\pm~920$
BRL-1B	t = 24	5/18/00 9:25	$2.143\pm\!0.059$	3.490 ± 0.247	1314	$1473~\pm~97$

					²³² Th		
	Mass	Date	²¹⁰ Pb*	²³⁸ U*	(²²⁸ Th)	²²⁶ Ra	²²⁸ Ra
Station No.	(g)	Counted	(dpm/g)	(dpm/g)	(dpm/g)	(dpm/g)	(dpm/g)
IRL-11	2.64	9/21/99	bd	bd	0.48 ± 0.11	0.54 ± 0.14	0.81 ± 0.38
IRL-21	2.69	9/1/99	bd	bd	0.17 ± 0.09	0.45 ± 0.15	0.55 ± 0.29
IRL-22	2.63	9/24/99	0.53 ± 0.51	bd	0.13 ± 0.09	0.29 ± 0.14	0.37 ± 0.15
IRL-23	2.56	9/28/99	bd	0.52 ± 0.48	0.27 ± 0.09	0.32 ± 0.12	0.35 ± 0.09
IRL-24	2.54	10/1/99	bd	bd	0.13 ± 0.09	0.19 ± 0.12	0.28 ± 0.07
IRL-25	2.51	10/4/99	0.83 ± 0.59	0.39 ± 0.53	0.47 ± 0.12	0.43 ± 0.16	0.71 ± 0.03
IRL-26	2.63	10/6/99	bd	bd	0.45 ± 0.11	0.55 ± 0.15	0.77 ± 0.35
IRL-27	2.63	10/8/99	bd	bd	0.11 ± 0.08	0.22 ± 0.12	1.65 ± 0.64
IRL-28	2.59	10/13/99	bd	bd	0.23 ± 0.09	0.21 ± 0.12	0.39 ± 0.24

Appendix C.18. Dry sediment activities for uranium series nuclides in northern IRL 1999.

Appendix D. Concentrations and isotope ratios of conservative solutes and nutrients

Ground Water Discharge and Nutrient Loading – Indian River Lagoon Appendix D.1. Chemical composition of seep water during dry season (May 1999)

Station	Salinity	Cond.	Oxygen	рН	SO₄	CI	Sr	NO ₃	NH₄	TSN	PO ₄	TSP	SiO ₂	δ ¹⁸ Ο	δD	⁸⁷ Sr/ ⁸⁶ Sr
	(ppt)	(mS/cm)	(mg/L)		(mg/L)	(g/L)	(µg/g)	(mgN/L)	(mg N/L)	(mg/L)	(µg/L)	(µg/L)	(mg/L)	(‰)		
Big Flound	der Transect															
IRL 1	40.6	63.3	3.3	7.3	3015	21.1	11.91	0.001	2.76	3.78	401	201	5.44	3.9	17.4	0.709079
IRL 2	39.6	61.1	1.2	7.2	2934	20.5	11.80	0.002	6.31	3.72	209	146	N/A	4.5		0.709123
IRL 3	39.8	61.1	2.5	7.3	2982	20.6	11.55	0.002	2.24	1.83	42	39	3.28	3.4		0.709105
IRL 4	39.1	60.1	3.6	7.3	2901	20.2	12.26	0.001	4.73	4.02	793	412	6.17	4.3	15.3	0.709126
IRL 5	38.7	59.4	4.2	7.3	2917	20.0	11.49	0.003	2.64	3.59	209	130	4.32	4.0	13.8	0.709092
IRL 6	39.6	61.7	3.9	7.4	3008	20.7	11.69	0.001	1.39	1.47	42	26	3.00	4.1	11.6	0.709130
IRL 7	38.5	59.3	4.6	7.4	2942	20.7		0.002	2.20	1.97	59	60	3.35	3.8		
IRL 8	39.3	59.5	3.3	7.4	2962	20.4		0.003	2.94	2.75	493	207	7.87	3.8		
Turnbull C	reek Transect															
IRL 9	40.3	59.1		7.5	3038	21.1	11.65	0.016	2.84	2.40	51	24	6.37	3.9		0.709114
IRL 10	40.2	57.8		7.6	3029	20.6		0.002	1.63	2.06	26	17	4.52	3.9		
Shiloh Trar	nsect															
IRL 12	40.2	63.4	3.3	7.3	3025	20.8	12.07	0.011	2.19	2.79	67	49	5.46	3.6		0.709114
IRL 13	40.8	63.3	4.5	7.6	3054	21.2		0.007	0.93	1.81	34	17	3.98	4.4	9.6	
IRL 14	41.3	63.4	4.7	7.5	3072	21.5	12.08	0.002	2.74	3.14	151	131	4.99	3.8		0.709178
IRL 15	41.4	60.6		7.4	3076	21.9		0.017	3.49	3.43	0	71	6.34	4.4	8.9	
Tower Tran	isect															
IRL 17	38.3	61.7	4.6	7.4	2836	20.1		0.010	3.36	3.58	51	35	5.58	3.7		
IRL 18	38.2	60.8	2.9	7.4	2831	20.3	11.69	0.008	1.94	2.58	26	21	2.72	3.6		0.709109
IRL 19	37.5	60.0	4.2	7.5	2789	19.9		0.003	1.88	2.42	34	28	3.46	3.5		
IRL 20	38.2	61.1	4.8	7.5	2871	20.2		0.004	2.87	2.79	92	47	6.20	3.9		
Duckroost	Cover Transe	ct														
IRL 21	41.2	51.2	9.8	7.6	3094	21.7		0.004	5.79	3.74	735	339	4.72	3.7		
IRL 22	40.8	47.7	9.4	7.6	3074	21.4	12.35	0.016	3.78	3.30	460	163	4.79	3.3		0.709290
IRL 23	40.9	61.7	3.5	7.5	3083	21.5	11.79	0.003	1.67	2.27	92	53	3.72	3.6		0.709118
IRL 24	40.8	62.0	4.9	7.5	3090	21.4		0.004	2.07	2.36	134	61	4.22	3.1	9.9	
Deep Wate	r Sites															
IRL 11	39.5	59.7	1.6	7.4	2958	20.0	11.55	0.007	4.42	3.54	735	344	6.43	3.3		0.709111
IRL 16	40.2	59.0		7.8	3003	21.2		0.001	0.69	1.38	26	17	3.67	3.8		
IRL 25	Seep rate too	o slow for suff	ficient samp	ole	3075	n/a	11.83	0.009	1.32	1.97	226	100	10.10	3.3		0.709158
IRL 26	39.3	62.2	6.5	7.6	3013	20.9	11.70	0.016	1.13	1.68	284	122	5.31	3.1	6.1	0.709130
IRL 27	40.7	61.5	6.0	7.6	3064	21.4	11.88	0.004	0.80	1.52	34	18	3.27	3.3		0.709118
IRL 28	40.3	61.6	3.5	7.5	3043	21.2	12.00	0.013	1.00	1.61	384	149	8.72	3.4		0.709126

Station	Salinity	Cond.	Oxygen	рН	SO₄	CI	Sr	NO ₃	NH₄	TSN	PO₄	TSP	SiO ₂	d ¹⁸ O	dD	⁸⁷ Sr/ ⁸⁶ Sr
	(ppt)	(mS/cm)	(mg/L)		(mg/L)	(g/L)	(µg/g)	(mgN/L)	(mg N/L)	(mg/L)	(µg/L)	(µg/L)	(mg/L)	(‰)		
Big Flounder 1	Fransect															
IRL 6WC		59.7	10.8		3070	21.4	12.28	0.001	0.13	0.83	26	22.0	0.31	3.9		0.709140
Turnbull Creek	k Transect															
IRL 9WC	39.8	61.2	9.9	8.3	3006	20.8		0.010	0.09	0.93	17	15.0	1.39	3.9		
Shiloh Transe	ct															
IRL 13WC	40.6	60.5	8.2	8.2	3025	21.0		0.006	0.07	0.98	17	15.0	0.60	3.6		
IRL 14WC	41.2	63.1	10.6	8.4	n/a	21.6		0.001	0.11	0.99	26	20.0	0.25	3.8		
Tower Transec	ct															
IRL 18WC	38.0	58.7	8.9		2819	20.1		0.006	0.08	1.04	17	16.0	0.30	4.0		
Duckroost Cov	ve Transeo	ct														
IRL 23WC	40.7	61.7	8.5		3062	21.2	11.41	0.005	0.11	0.79	17	15.0	0.38	3.4		0.709402
Deep Water Si	tes															
IRL 11WC	39.6	58.6	9.6		n/a	20.7		0.002	0.12	0.93	17	16.0	0.44	3.7		
IRL 16WC	40.2	59.9	10.4	8.3	2984	21.2	11.71	0.011	0.10	0.97	17	15.0	0.37	3.6		0.709145
IRL 25WC	41.4	61.4	9.5		n/a	21.2	11.86	0.004	0.10	0.97	17	16.0	0.52	3.5		0.709144
IRL 26WC	40.1	59.8	9.4		3036	21.0	11.83	0.005	0.08	0.89	17	16.0	0.15	3.3	10.3	0.709122
IRL 27WC	40.8	61.2	9.8		3119	21.4	11.84	0.013	0.11	0.83	17	15.0	0.46	3.3		0.709128
IRL 28WC	40.5	59.7	8.3		3089	21.3		0.005	0.10	0.90	17	17.0	0.45	3.4		
Ground waters	5															
GW-1	1.2		1.0	6.9	9	0.6		0	0.60	0.30	42	0.3	0.02	-2.3	-17.2	0.709053
GW-2	0.4		0.3	6.8	0	0.1		0.001	0.46	0.45	59	0.5	0.03	-2.1		0.709035
GW-3	9.2	15.7	0.3	7.5	957	5.4		0	0.67	0.60	526	0.6	0.01	-1.1		
GW-4	<1	1.0		7.4	0	0.2		0	0.59	0.62	42	0.6	0.03	-2.2		0.709027
GW-5		0.1		6.9	0	0.1		0	0.92	1.20	919	1.2	0.01	-2.7		
GW-6	14.5			6.8	773	7.8		0.01	0.56	2.19	59	2.2	0.01	-1.2		
Surface waters	S															
твс	33.0			7.0	2640	18.2		0.016	0.13	1.41	42	1.4	0.01	3.5		
нос	36.9			7.8	3086	21.3		0.007	0.10	0.84	17	0.8	0.00	3.1		

Appendix D.2. Chemical composition of water from water column (WC samples), ground water (GW samples), and surface water during dry season (May 1999)

									~		0							
Station	Salinity	Cond.	Oxygen	pН	SO₄	CI	Sr	NO ₃	NH4	TSN	TN	PO ₄	TSP	ТР	SiO ₂	d ¹⁸ O	dD	⁸⁷ Sr/ ⁸⁶ Sr
	(ppt)	(mS/cm)	(mg/L)		(mg/L)	(g/L)	(µg/g)	(mg N/L)	(mg N/L)	(mg/L)	(mg/L)	(µg/L)	(µg/L)	(µg/L)	(mg/L)	(‰)		
Big Flounde	er Transect																	
IRL 1	39.1	66.9	0.8	7.1	2891	20.6	9.98	0.041	2.79	2.84	2.08	259	110	175	5.80	3.7		0.709728
IRL 2	37.9	63.7	1.3	7.1	2709	20.0	9.85	0.05	4.08	2.84	2.48	269	153	148	8.85	3.6		0.709104
IRL 3	38.6	63.4	2.3	7.2	2834	20.3	10.32	0.044	3.92	2.92	2.25	69	80	144	6.21	3.5		0.709057
IRL 4	38.7	63.7	2.4	7.3	2872	20.4	10.02	0.072	1.83	2.15	2.23	9	20	77	4.66	3.5		0.709137
IRL 5	38.7	62.4	2.3	7.3	2767	20.4		0.06	6.52	3.68	3.92	719	254	358	4.45	3.3		
IRL 6A	38.3	62.1	0.9	7.5	2882	20.1	10.08	0.028	1.51	1.98	1.97	119	34	81	2.99	3.5		0.709055
IRL 7	38.3	62.1	0.9	7.5	2891	20.3		0.01	0.76	1.51	1.72	169	50	101	4.43	3.5		
IRL 8	38.2	62.4	0.5	7.5	2872	20.3		0.032	2.58	2.54	2.74	229	65	149	4.13	3.5		
Turnbull Cre	eek Transeo	t																
IRL 9	40	64.5	1.2	7.4	2997	21.1	12.20	0.061	2.68	2.32	2.47	289	70	112	6.84	3.6		0.70906
IRL 10	39.6	65.2	0.7	7.2	2939	20.5	12.46	0.054	3.89	3.05	3.30	629	179	210	4.88	3.7		0.70908
Shiloh Tran	sect																	
IRL 12	38.7	63.8	4.6	7.2	2872	20.4	12.19	0.055	3.36	2.84	2.91	369	104	135	6.36	3.8	12.4	0.709078
IRL 13	38.7	63.8	1.7	7.3	2891	20.3		0.055	2.71	2.71	2.79	79	61	98	5.80	3.5		
IRL 14	40.6	66.5	1.0	7.6	3045	21.4	12.58	0.07	2.58	2.73	2.77	19	50	74	5.22	3.5		0.709079
IRL 15	41.9	67.8	1.2	7.1	2968	22.0		0.113	8.21	2.77	2.30	109	86	120	6.96	4.0	17.0	
Tower Trans	sect																	
IRL 17	35.8	61.3	3.4	7.5	2680	19.1		0.028	6.60	3.34	3.23	559	162	170	4.70	3.7		
IRL 18	35.7	60.7	3.1	7.6	2690	19.0	11.52	0.101	2.92	2.74	2.98	179	68	142	3.86	3.3	23.7	0.709069
IRL 19	35.8	60.9	2.4	7.5	2680	18.9		0.03	4.70	2.66	2.86	119	41	93	5.44	3.5		
IRL 20	35.8	60.7	3.3	7.5	2690	19.0		0.046	3.80	3.21	3.09	279	89	190	6.84	3.6		
Duckroost C	Cover Trans	ect																
IRL 21	37.8	63.2	1.4	7.4	2815	20.1		0.019	5.03	2.50	2.75	99	79	103	5.46	3.7		
IRL 22	36.1	61.1	1.1	7.2	2786	19.2	9.85	0.027	3.55	2.94	3.36	139	116	148	5.77	3.7		0.709023
IRL 23	35.9	60.6	1.1	7.3	2699	19.0		0.099	4.40	2.71	2.68	19	60	108	4.44	3.7		
IRL 24	35.6	60.5	2.3	7.0	2584	18.9		0.053	4.47	3.79	4.01	229	81	93	4.43	3.8		
Deep Water	Sites																	
IRL 11	38.5	64.3	1.7	7.4	2853	20.3	12.07	0.008	4.51	3.78	3.51	939	385	399	4.97	3.9	9.9	0.709045
IRL 16	39.9	65.2	1.2	7.6	2988	21.0		0.05	1.80	2.00	2.25	9	33	108	4.13	3.5		
IRL 25	37.5	61.3	0.2	7.6	2459	19.6	10.24	0.057	30.62	9.36	12.18	2509	2318	2635	10.27	3.5		0.709052
IRL 26	37	62.3	2.5	7.5	2795	19.5	11.46	0.025	3.10	2.80	3.01	219	70	121	5.11	3.4		0.709064
IRL 27	37	60.8	1.3	7.3	2776	19.6	10.08	0.028	2.55	2.30	2.61	739	152	159	6.31	3.2	22.3	0.709098
IRL 28	36.8	60.5	1.2	7.3	2719	19.3		0.03	2.49	2.28	2.54	289	116	184	8.90	3.1	18.8	

Ground Water Discharge and Nutrient Loading – Indian River Lagoon Appendix D.3. Chemical composition of seep water during rainy season (August 1999)

Station	Salinity	Cond.	Oxygen	pН	SO₄	CI	Sr	NO₃	NH₄	TSN	TN	PO₄	TSP	TP	SiO2	d ¹⁸ O	dD	⁸⁷ Sr/ ⁸⁶ Sr
	(ppt)	(mS/cm)	(mg/L)	-	(mg/L)	(g/L)	(µg/g)	(mg N/L)	(mg N/L)	(mg/L)	(mg/L)	(µg/L)	(µg/L)	(µg/L)	(mg/L)	(‰)	(‰)	
Big Flounder Tran	sect																	
IRL 6WC	38.6	62.7	4.3	8.1	2882	20.2	10.47	0.077	0.17	1.12	1.36	0	15	45	1.31	3.4		0.709089
Turnbull Creek Tra	ansect																	
IRL 9WC	40.3	65.5	4.0	8.1	3045	n/a		0.074	0.16	1.24	1.47	0	17	44	4.00	3.6		
Shiloh Transect																		
IRL 12WC	38.6	63.7	1.3	8.1	2891	20.2		0.1	0.25	1.25	1.38	0	16	35	2.25	3.3		
Tower Transect																		
IRL 18WC	35.5	60.7	8.2	8.6	2632	18.7		0.043	0.10	1.10	1.24	0	15	33	0.80	3.2	23.3	0.709043
Duckroost Cove T	ransect																	
IRL 22WC	36	60.6	5.6	8.0	2699	19.0	9.88	0.102	0.23	1.14	1.36	0	15	35	2.01	3.3		0.709043
Deep Water Trans	ect																	
IRL 11WC	38.6	64.1	7.1	8.2	2920	20.2	11.95	0.039	0.08	1.08	1.33	0	17	45	1.09	3.3		0.709054
IRL 16WC	38.2	62.5	4.6	8.0	2843	19.9	10.31	0.035	0.13	1.03	1.28	0	14	33	0.66	3.2	20.7	0.709073
IRL 25WC	37.8	61.9	5.8	8.0	2843	19.7		0.039	0.12	1.00	1.23	0	16	33	1.78	3.4		
IRL 26WC	37.2	61.9	6.4	8.1	2795	19.6		0.036	0.11	1.07	1.33	0	16	38	1.02	3.6		
IRL 27WC	37.1	60.9	6.2	8.1	2786	19.4	10.22	0.035	0.04	0.93	1.31	0	17	36	1.85	3.4		0.709186
IRL 28WC	36.8	60.8	6.1	8.0	2757	19.3		0.027	0.10	1.02	1.28	0	15	31	2.10	3.4		
Ground waters																		
GW-1	1.2	22.0		7.3	10	0.7	1.14	0.059	0.48	0.352	0.346	9	0.02	0.019	0.02	-2.1	-16.8	0.709029
GW-2					0	0.2		0.01	0.54	0.444	0.397	9	0.01	0.014	0.03	-2.1		
GW-3	9.1	15.6		9.5	874	5.5		0.001	0.74	0.651	0.721	0	0	0	0.01	-1.1		
GW-4	0.5	1.1		7.3	0	0.3	1.10	0.015	0.60	0.604	0.615	69	0.04	0.027	0.03	-2.2		0.708909
GW-5	0.4	0.9		6.7	0	0.2		0.05	1.32	1.336	1.57	1299	0.66	0.622	0.01	-3.4		
GW-6	17.1	28.0		6.9	0	10.0		0.009	2.47	2.646	2.794	19	0.01	0.089	0.01	-0.8		
Surface waters																		
твс					2767	19.2		0.052	0.22	1.344	1.995	29	0.05	0.179	N/A	3.7		
НОС					2988	20.6		0.069	0.11	1.096	1.274	0	0.02	0.033	0.00	3.8		

Appendix D.4. Chemistry of water from water column, ground water, and surface water rainy season (August 1999)

Transect	Station	Salinity	Cond.	Oxygen	рΗ	Temp.	SO4	CI	Sr	NO3+NO2	NH4	TSN	TN	PO4	TSP	TP	SiO2	δ ¹⁸ Ο	⁸⁷ Sr/ ⁸⁶ Sr
		(ppt)	(mS/cm)	(mg/L)		(oC)	(mg/L)	(g/L)	(ppm)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mg/L)	(mgP/L)	(mgP/L)	(mg/L)		
Transect 1	IRL29	22.2	33.3	1.2	7.5	N/A	1399	12.1		0.004	0.39	0.442	0.866	1.44	N/A	N/A	2.6		
	IRL31	22.5	37	0.3	7.8	27.5	1449	12.1	8.23	0.01	0.07	0.335	0.365	0.435	1.37	1.27	12.1	8.23	0.70888
Transect 2	IRL32	21.8	31	0.3	7.3	N/A	1407	11.9		0.01	0	0.003	5.269	2.345	0.72	0.67	9.1		
	IRL33	21.9	31.6	2.3	7.4	N/A	1361	11.8		0.006	0.82	0.46	0.638	2.739	1.98	2.01	25.1		
	IRL34	22	36	0.3	7.9	26.4	1264	12.0		0.008	0.26	0.837	0.333	4.18	3.11	3	31.1		
Transect 3	IRL36	23	38.3	0.1	7.3	N/A	1424	12.4		0.009	0.26	0.13	11.358	2.391	2.23	1.58	24.3		
	IRL38	23.7	39.3	0.2	7.3	28	1577	12.7		0.014	0.26	0.995	0.837	0.561	0.4	0.7	16.8		
Transect 4	IRL39	24.7	39.5	0.1	7.2	N/A	1679	13.4		0.01	0	0.901	3.809	0.658	0.38	N/A	12.2		
	IRL41	26.5	43.3	0.1	7.3	N/A	2435	14.0		0.007	0.36	1.075	0.216	2.318	1.64	1.37	22.5		
	IRL42	26.4	43.6	3	7.4	28.4	2017	14.2		0.007	0.57	3.143	1.851	0.441	0.37	0.32	10.4		
Transect 1	BRL1B	19.8	31.7	0.5	7.7	27.1	1481	11.6		0.007	0.52	0.367	2.279	0.036	0.09	0.1	3.6		
	BRL2	19.3	31	0.2	7.5	28.4	1436	11.3		0.005	0.28	0.253	0.02	0.059	0.04	0.02	3.3		
	BRL3	19	30.6	1.3	7.9	27.7	1394	11.1		0.003	0.43	0.365	0.075	0.403	N/A	0.31	N/A		
	BRL4	19.2	30.7	0.7	7.4	27.4	1426	11.3		0.005	0.47	0.104	3.248	0.285	0.25	0.12	15.1		
	BRL5	19.3	30.9	0.3	7.7	27.9	1434	11.3		0.007	0.43	0.41	0.025	0.201	0.15	0.13	7		
Transect 2	BRL6	19.4	31.1	2.7	7.7	28.6	1465	11.3	8.44	0.001	0.4	0.214	0.594	0.104	0.11	N/A	6.1	8.44	0.70883
	BRL7	19.3	31	0.3	7.7	27.8	1435	11.2	8.45	0.004	0.8	0.38	0.673	0.123	0	0.18	1	8.45	0.70882
	BRL8	20.5	32.7	0.2	7.4	28.2	N/A	11.9		0.003	0.42	0.349	5.594	0.108	0.03	0.71	4.9		

Appendix D.5. Seep water chemistry data, May 2000

Transect	Station	Salinity	Cond.	Oxygen	pН	Temp.	SO4	CI	Sr	NO3+NO2	NH4	TSN	TN	PO4	TSP	TP	SiO2	δ ¹⁸ Ο	⁸⁷ Sr/ ⁸⁶ Sr
		(ppt)	(mS/cm)	(mg/L)		(oC)	(mg/L)	(g/L)	(ppm)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mg/L)	(mgP/L)	(mgP/L)	(mg/L)		
Transect 1	IRL29WC	20.3	32.4	7	8.4	28.8	N/A	11.8		0.002	0.06	0.081	0.395	0.602	0.63	N/A	6.5		
	IRL30WC	20.4	32.6	7.2	8.1	27.9	1557	11.8		0.006	0.06	0.379	0.3575	0.005	0.01	0.02	0.2		
	IRL31WC	20.4	N/A	7.3	8.1	26.9	1536	11.9	8.27	0.001	0.01	0.311	0.368	0.007	0.01	0.02	0.6	8.27	0.70888
Transect 2	IRL32WC	20.4	32.4	7.9	8.4	29.3	1561	11.8		0.002	0.03	0.331	0.385	0.016	0.02	0.03	1		
	IRL33WC	20.3	32.3	7.8	8.3	28.1	1550	11.8		0.002	0.02	0.38	0.43	0.017	0.02	0.03	1.2		
	IRL34WC	20.2	32.2	7.5	8.2	27.3	1551	11.7		0.001	0.03	0.296	0.386	0.015	0.02	0.03	1.1		
Transect 3	IRL35WC	21.8	34.6	9.2	8.4	28.9	1680	12.6		0.003	0.02	0.284	0.326	0.028	0.03	0.04	1		
	IRL36WC	21.6	34.3	7.1	8.3	28.9	1675	12.5		0.001	0.02	0.299	0.391	0.032	0.03	0.04	1		
	IRL37WC	22.5	35.2	N/A	8.3	28.1	1760	12.9		0.001	0.01	0.32	0.31	0.025	0.02	0.03	0.6		
	IRL38WC	22.6	35.7	N/A	8.3	28	1778	13.2		0.001	0.02	0.298	0.309	0.028	0.02	0.03	0		
Transect 4	IRL39WC	24.3	37.8	6.5	8.3	28.1	1845	13.7		0.001	0.01	0.301	0.338	0.031	0.03	0.04	1.5		
	IRL40WC	26.8	41.1	6.7	8.3	28.2	2076	15.2		0.001	0.01	0.251	0.284	0.021	0.02	0.03	1.7		
	IRL41WC	25.2	39.4	7	8.3	27.6	1985	14.6		0	0.03	0.235	0.25	0.036	0.03	0.04	2.1		
	IRL42WC	24.8	38.9	6.8	8.4	27.6	1959	14.3		0.001	0.01	0.259	0.277	0.03	0.03	0.03	2.1		
Transect 1	BRL1WC	19.7	31.5	7.2	8.8	29.2	1523	11.5	8.65	0.006	0.01	0.298	0.336	0.004	0	0.03	1	8.65	0.70882
	BRL2WC	19.3	30.9	6.7	8.6	28.2	1442	11.1	8.39	0.002	0.04	0.338	0.298	0.003	0.01	0.04	1	8.39	0.70884
	BRL3WC	19.2	30.8	6.4	8.5	28	1499	11.3		0.003	0.02	0.32	0.345	0.003	0.01	0.05	1.1		
	BRL4WC	19	30.7	6.7	8.5	28	1483	11.3		0.001	0.02	0.325	0.284	0.003	0.01	0.04	1.5		
	BRL5WC	19.6	31.4	6.4	8.5	27.1	1494	11.5	8.27	0.002	0.02	0.328	0.298	0.004	0.01	0.04	1.5		0.708800
Transect 2	BRL6WC	20.6	32.9	7.6	8.7	27.2	1515	11.3	8.46	0.004	0.07	0.355	0.294	0.003	0	0.02	0.2	8.46	0.70882
	BRL7WC	19.3	31	6.1	8.6	27.1	1487	11.2	7.97	0.001	0.09	0.357	0.26	0.001	0.01	0.05	0.9	7.97	0.70883
	BRL8WC	20.6	32.9	5.5	8.5	27.2	1586	12.1		0.001	0.04	0.307	0.311	0.003	0.01	0.04	1.4		

Appendix D.6. Lagoon water chemistry data, May 2000.

Transect	Station	Port*	Depth**	Salinity	Cond.	Oxygen	pН	Temp.	SO₄	CI	Sr	NO ₃	NH₄	TSN	TN	PO4	TSP	ТР	SiO2	δ ¹⁸ Ο	⁸⁷ Sr/ ⁸⁶ Sr
			(cm)	(ppt)	(mS/cm)	(mg/L)		(oC)	(mg/L)	(g/L)	(ppm)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L)	(mg/L)		
Transect 1	IRL31	7	157	22.4	35.6	0.8	7.5	24.8	1850	13.1	9.2	0.003	0.06	2.225	2.801	0.217	0.08	0.06	14.5	1.7	0.70891
		8	197	22.6	36.8	4.5	7.6	27.2	1789	13.3	9.37	0.005	0.29	N/A	2.55	0.247	0.13	0.12	11.3	1.8	0.70892
	IRL32	6	34	19.4	32.7	0.6	7.6	28	1505	11.4		0.004	0.72	1.128	0.955	0.133	0.04	0.03	4.8	1.3	
		7	74	20.9	34.7	5.5	7.7	27.2	1444	11.1		0.004	0.72	0.916	1.008	0.127	0.14	0.14	9.5	1.0	
		8	114	18.6	30.8	1.3	7.6	26.6	1466	11.1		0.007	0.59	0.608	0.659	0.164	0.16	0.31	10.7	0.7	
Transect 1	BRL1	3	30	19.6	31.3	3.4	8.1	28	1473	11.3	8.47	0.008	0.88	0.52	0.156	0.146	0.16	0.19	4.9	2.1	0.70881
		5	110	19.7	31.4	1.8	7.6	29.2	1566	11.4		0.011	0.4	0.602	0.672	0.193	0.08	0.09	9.4	1.4	
		6	150	21.8	34.6	1.6	7.6	27.5	1810	12.7		0.01	0.92	1.38	1.462	0.379	0.22	0.25	9.5	1.3	0.70875
		7	190	19.6	31.4	2.3	7.8	28.5	1514	11.5	8.63	0.0085	0.94	0.447	14.166	0.035	0.12	1.18	5.7		0.70881
	BRL2	1	10	19.2	30.9	1.3	7.6	26.7	1428	11.2	8.36	0.001	0.19	0.57	0.295	0.003	N/A	0.02	2.5	2.0	0.70883
		2	30	18.1	30.1	1.4	7.7	26.9	1455	10.9	8.28	0.002	0.56	0.887	0.861	0.011	N/A	0.05	3.4	1.6	0.70882
		3	50	18.1	29.2	0.5	7.7	26.5	1381	10.6		0.003	0.52	1.037	0.861	0.095	N/A	0.06	4.5	1.6	0.70877
		5	110	22	34.9	0.5	7.6	25.7	1808	12.9		0.004	0.41	1.06	0.293	0.243	0.06	0.11	7.8	1.8	0.70878
		6	150	24.7	38.8	0.6	7.6	25.8	2106	14.3		0.005	0.59	1.04	1.072	0.213	0.05	0.08	6.6	2.0	0.7088
		7	190	25.3	39.9	0.6	7.4	25.5	2238	15.2		0.007	0.59	1.15	1.001	0.249	0.09	0.12	6.5	2.0	0.70879
		8	230	27.1	42.3	0.7	7.5	24.8	2229	15.7	8.44	0.005	0.75	1.165	1.302	0.307	0.15	0.15	6.8	1.9	0.70881
	BRL5	5	20	19.1	30.6	0.7	7.6	27	1431	11.1		0.004	1.12	1.314	0.707	0.178	0.06	0.02	5.7	1.7	
		8	130	31.2	47.9	1.2	7.5	25.9	2521	14.3		0.006	1.2	2.333	3.025	0.149	0.03	N/A	17.5	1.1	
Transect 2	BRL6	4	18	20.9	34.3	1.3	7.5	26.5	1486	11.2	8.5	0.005	0.54	0.849	0.865	0.082	N/A	0.07	3.3	1.9	0.70882
		5	48	20.1	33.4	1.6	7.9	27.2	1387	10.7	8.25	0.003	0.61	0.976	1.039	0.074	N/A	0.08	3.6	1.7	0.70879
		6	88	19.5	32.9	3.5	7.9	28	1326	10.2	8.65	0.004	0.89	1.347	0.898	0.033	N/A	0.05	5.4	1.8	0.70881
		8	168	20.6	32.9	1.2	7.7	27	1644	11.8	8.55	0.005	0.85	1.026	1.078	0.085	N/A	0.09	10.3	1.8	0.70881
	BRL7	3	14	21.6	36.3	3.1	7.7	28.5	1507	11.3	8.62	0.007	0.94	1.018	0.926	0.116	0.12	0.17	3.9	1.9	0.70881
		4	44	20.7	34.6	4.6	7.9	27.5	1439	10.9		0.018	1.19	0.189	0.227	0.096	0.1	0.17	6.6	1.8	
		5	74	19.8	32.4	1.8	7.8	26.3	1331	10.2	7.8	0.007	1.14	N/A	1.451	0.256	0.11	0.18	9	1.5	0.70883
		6	114	21.4	34.7	2.1	7.8	25.7	1447	11.2	7.96	0.014	1.44	1.515	1.479	0.58	0.37	0.46	8.3	1.6	0.70893
		7	154	25	39.9	0.6	7.8	26.1	1875	12.9	8.15	0.005	1.55	1.396	1.452	1.064	0.79	0.9	5.9	1.6	0.70888

Appendix D.7. Multi-sampler water chemistry data, May 2000

* Port number of multi-sampler.** Depth below the sediment-water interface.

Station	Salinitv	Cond.	Oxvaen	Нα	Temp.	SO4	CI	Sr	NO3+NO2	NH4	TSN	TN	PO4	TSP	TP	SiO2	¹⁸ O ⁸⁷ Sr/ ⁸⁶ Sr
	(ppt)	(mS/cm)	(mg/L)		(oC)	(mg/L)	(g/L)	(ppm)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L)	(mg/L)	
BHSpring	2	3.8	0.6	7.8	24.8	196	1.21	14.29	0.006	0.43	0.559	0.536	0.03	N/A	0	15	0.707824
GW331	1.4	2.7	0.2	7.5	25.2	110	0.85	14.46	0.001	0.53	0.602	0.582	0.002	N/A	0	15.9	0.707829
GW921	1.9	3.5	0.3	7.9	26	159	1.10	13.09	0	0.55	0.619	0.586	0.001	N/A	0	15.7	0.707857
GW1472	0.1	0.2	0.4	4.3	24.5	30	0.18		0.006	0.41	N/A	2.25	0.081	0.04	N/A	16.5	
GW1580	1.1	2.1	2.3	7.6	25.6	138	0.67		0.009	0.38	0.49	0.404	0.759	N/A	0	16.3	
GW1647	1.1	2.2	0.1	7.6	31.5	115	0.71	14.85	0.008	0.44	0.607	0.502	0.001	N/A	0	17.7	0.707821
GW1473	0.3	0.6	0.7	6.9	24.7		0.14	8.17	0.002	0.63	0.176	0.141	0.001	0.56	0.56	12.1	0.709040
SEBINL	36	56.3	7.3	8.3	26.6	2988	13.61		0.051	0.02	0.281	0.061	0.001	N/A	0.02	0.4	
STSEBR	27.8	48.1	6.1	8.3	29.8	2579	18.83		0.003	0.02	0.122	0.222	0.027	0.02	0.04	1.5	
EAUGALL	18	32.6	7.3	8.4	28.8	1389	10.46		0.003	0.04	0.346	0.404	0.041	0.05	0.1	3.9	
TURKEYCR	23.7	40.6	5.5	8.1	29.2	1066	8.08		0.017	0.05	0.244	0.324	0.031	0.02	0.04	8.5	
CRANECR	20.6	36.5	6	8.2	30.4	1688	12.69		0.013	0.04	0.3485	0.277	0.102	N/A	0.16	2.9	

Appendix D.8. Well and surface water chemistry data, May 2000.

Transect	Station	Salinity	Cond.	Oxygen	pН	Temp.	SO4	CI	Sr	NO3+NO2	NH4	TSN	TN	PO4	TSP	ТР	SiO2	δ ¹⁸ Ο	⁸⁷ Sr/ ⁸⁶ Sr
		(ppt)	(mS/cm)	(mg/L)		(oC)	(mg/L)	(g/L)	(ppm)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L)	(mg/L)		
Transect 1	IRL29	N/A	N/A	N/A	7.1	N/A	2334	16.8		0.004	1	1.01	0.95	0.256	0.25	0.22	6.7		
	IRL30	N/A	N/A	N/A	7.5	N/A	2248	16.3		0.006	1.9	2.29	2.62	0.631	0.56	0.55	11.8		
	IRL31	N/A	N/A	N/A	N/A	N/A	2257	16.1		0.012	0.45	1.93	2.45	1.272	1.03	1.2	16.6		
Transect 2	IRL32	N/A	N/A	N/A	7	N/A	2344	16.9		0.002	1.33	1.18	1.16	0.606	0.52	0.52	6.6		
	IRL33	N/A	N/A	N/A	8	N/A	2430	17.1		0.009	0.07	0.58	0.52	0.055	0.05	0.03	2.3		
Transect 3	IRL35	27.8	47.1	4	7.2	30.8	2305	16.3		0.005	0.43	1.29	1.39	0.157	0.15	0.16	4.4		
	IRL36	28.3	47.7	3.1	7	30.6	2200	16.2		0.002	1.55	3.17	2.92	1.913	1.61	2.02	20		
	IRL37	38.5	47.7	1.1	7.2	30.1	2238	16.0		0.003	0.59	1.52	1.73	0.169	0.15	0.18	4		
	IRL38	27.9	46.8	0.4	7.2	30	2257	16.2		0.001	0.11	2.09	1.97	0.729	0.65	0.75	13		
Transect 4	IRL39	26	44.6	1	7.1	31.5	2094	15.0		0.002	0.37	1.56	1.4	0.265	0.22	0.25	5.1		
	IRL41	26.8	45.1	1.9	7.1	30	2190	15.5		0.006	0.4	1.73	1.52	0.437	0.36	0.4	12.2		
	IRL42	25.8	43.8	1.8	7.2	30.4	2094	15.0		0.001	1.03	1.46	0.99	0.312	0.25	0.31	6.5		
Transect 1	BRL1	29.2	45.5	2	8.2	30.4	2209	15.6	10.58	0.001	0.08	0.76	0.82	0.07	0.03	0.03	3.4	10.6	0.70891
	BRL3	28.2	44.4	0.3	7.9	30	2075	15.0		0.006	0.38	2.64	1.8	0.816	0.74	0.78	20.4		
	BRL4	28.8	44.8	0.9	7.7	29.8	2104	15.3		0.002	0.53	1.11	1.27	0.14	0.13	0.15	5.2		
	BRL5	28.7	44.6	0.4	7.4	29.9	2113	15.2		0.001	N/A	1.14	1.04	0.296	0.24	0.25	7.2		
Transect 2	BRL6	29.1	45.3	0.2	8	30.6	2161	15.4	9.88	0.001	0.62	1.32	1.59	0.022	0.02	0.05	5.4	9.88	0.7089
	BRL7	29.2	45.3	0.5	7.3	30.1	2104	16.2	8.45	0.001	0.05	1.93	1.25	0.335	0.32	0.35	7.3	8.45	0.70882
	BRL8	29.6	46.1	0.5	7.7	29.6	2229	16.1		0.001	0.52	1.5	1.51	0.253	0.23	0.22	8		

Appendix D.9. Seep water chemistry data, August 2000.

Transect	Station	Salinity	Cond.	Oxygen	рΗ	Temp.	SO4	CI	Sr	NO3+NO2	NH4	TSN	TN	PO4	TSP	ТР	SiO2	δ ¹⁸ Ο	⁸⁷ Sr/ ⁸⁶ Sr
		(ppt)	(mS/cm)	(mg/L)		(oC)	(mg/L)	(g/L)	(ppm)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L)	(mg/L)		
Transect 1	IRL29	29.5	45.3	8.2	8.4	28.6	2344	16.9		0.004	0.01	0.44	0.47	0.03	0.05	0.06	2.2		
	IRL30	29.2	45	7.4	8.2	29	2363	17.2		0.001	0.02	0.44	0.5	0.02	0.04	0.05	2.2		
	IRL31	28.9	44.5	7.1	8.2	29	2305	16.8		0.001	0.02	0.46	0.49	0.02	0.03	0.04	2.6		
Transect 2	IRL32	29.6	45.5	8.3	8.3	28.6	2421	17.4		0.001	0.01	0.41	0.44	0.03	0.05	0.07	2		
	IRL33	29.8	45.8	6.2	8.1	29.1	2430	17.3		0.001	0.05	0.48	0.49	0.05	0.07	0.08	2.2		
	IRL34	29.8	45.8	7.9	8.2	29.1	2421	17.5		0.002	0.02	0.42	0.42	0.05	0.07	0.08	1.7		
Transect 3	IRL35	28.6	44	7.5	8.1	29.3	2296	16.6		0.002	0.02	0.32	0.35	0.06	0.07	0.08	2		
	IRL36	28.5	44	6	8	29.3	2305	16.8		0.002	0.05	0.31	0.35	0.06	0.08	0.08	2.2		
	IRL37	28.7	44.1	6.2	8	29.3	2344	16.8		0.002	0.05	0.35	0.36	0.07	0.08	0.08	2.3		
	IRL38	28.2	43.6	29.1	8.1	6.6	2248	16.3		0.003	0.05	0.34	0.33	0.06	0.08	0.08	2.3		
Transect 4	IRL39	26.6	41.4	6.3	8.1	28.5	2132	15.6		0.001	0.01	0.3	0.35	0.06	0.07	0.08	2		
	IRL40	26.5	41.3	5.7	8.1	29	2104	15.3		0.001	0.04	0.33	0.35	0.05	0.06	0.07	2.4		
	IRL41	26.2	40.9	5.8	8	28.1	2046	15.0		0.044	0.01	0.42	0.33	0.04	0.06	0.07	2.4		
	IRL42	25.8	40.3	6.5	8.1	27.2	2056	15.0		0.002	0.01	0.31	0.36	0.03	0.05	0.06	2		
Transect 1	BRL1	28.6	44.5	4.2	8.5	27.3	2171	15.7		0.001	0.02	0.64	0.72	0.01	0.03	0.04	3		
	BRL2	29	45.1	6.7	8.6	29	2190	16.0		0.001	0.03	0.54	0.59	0.01	0.03	0.04	2.7		
	BRL3	28.4	44.2	5.4	8.4	28.5	2075	15.2		0.002	0.04	0.61	0.69	0.01	0.02	0.04	3.5		
	BRL4	28.5	44.2	6.8	8.6	28.9	2142	15.6		0.002	0.03	0.58	0.61	0.01	0.03	0.04	2.7		
	BRL5	28.6	44.5	6.9	8.6	29.1	2104	15.3		0.001	0.02	0.54	0.62	0.01	0.03	0.05	3.3		
Transect 2	BRL6	29.8	46.2	5.9	8.6	27.9	2219	16.1		0	0.02	0.5	0.52	0	0.02	0.03	2.2		
	BRL7	29.5	45.7	5.3	8.6	28.5	2219	16.1		0.001	0.02	0.51	0.58	0.01	0.03	0.05	2.7		
	BRL8	29.5	45.6	4.4	8.4	27.3	2219	16.2		0.001	0.01	0.47	0.55	0.01	0.03	0.06	2.7		

Appendix D.10. Lagoon water chemistry data, August 2000.

Transect	Station	Port	Depth*	Salinity	Cond.	Oxygen	рΗ	Temp.	SO4	CI	Sr	NO ₃	NH4	TSN	TN	PO4	TSP	ТР	SiO2	δ ¹⁸ Ο	⁸⁷ Sr/ ⁸⁶ Sr
			(cm)	(ppt)	(mS/cm)	(mg/L)		(oC)	(mg/L)	(g/L)	(ppm)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L)	(mg/L)		
Transect 1	IRL29	4	80	20.6	35.5	1.1	7.4	30.1	1537	12.3	8.46	0.002	1.44	1.16	1.44	0.198	0.13	0.17	17.8	1.44	0.70889
		5	110	20.7	35.6	1.9	7.6	29.8	1662	16.9	8.84	0	0.59	1.44	1.19	0.095	0.1	0.09	11.5	1.62	0.70889
		6	150	N/A	N/A	N/A	N/A	N/A	2353	15.9	10.67	0	0.03	0.47	0.48	0.014	0.04	0.04	2.3	2.77	0.70897
Transect 1	BRL1	1	10	26.7	34.9	1	7.6	29.9	2152	12.4	10.8	0	0.05	0.63	0.62	0.036	0.07	0.08	5.6	2.86	0.70889
		5	110	20.6	35.1	0.8	7.4	29.1	1700	12.9	9.39	0	1.36	1.71	1.32	0.24	0.22	0.25	13.3	1.76	0.70884
		6	150	22.1	37.7	0.7	7.2	29.7	1950	15.9		0.002	1.73	0.99	1.74	0.509	0.45	0.54	11.5		
	BRL2	1	10	26.7	44.5	0.6	7.9	29.4	2190	15.1	10.62	0	0.13	0.67	0.66	0.02	0.05	0.04	3.9	2.7	0.70894
		2	30	25.1	42.2	0.8	7.8	29.3	2046	13.6	10.55	0	0.34	0.89	0.79	0.065	0.08	0.07	3.8	2.61	0.7089
		3	50	23.1	39	0.2	7.6	29.4	1844	11.7	9.91	0	0.62	1.31	1.09	0.094	0.11	0.11	4.8	2.45	0.70885
		4	80	19.9	34	0.2	7.6	29.1	1566	13.1		0.002	0.82	1.1	1.15	0.125	0.11	0.1	7.8		
		5	110	27.5	36.3	0.2	7.4	28.9		14.0		0.001	0.25	1.01	1.12	0.35	0.3	0.34	10.3		
		6	150	23.9	40	0.4	7.3	28.8	2017	15.2		0.001	0.46	1.25	0.97	0.4	0.36	0.38	10.6	1.9	
		7	190	26	42.6	0.3	7.2	28.2	2209	15.6	11.58	0.001	0.57	1.4	1.35	0.364	0.31	0.31	9.9	2.17	0.70883
		8	230	26.5	44	N/A	7.5	28.9	2277	15.5	11.76	0.002	0.75	1.34	1.24	0.495	0.39	0.33	7.4	2.07	0.70887
	BRL5	2	20	26.4	43.8	0.4	8	29.1	2094	14.9		0.001	0.25	0.86	0.82	0.124	0.11	0.11	7.2	2.67	
		3	40	24.9	41.7	0.3	7.5	29.1	2075	14.5		0.001	0.54	1.45	1.34	0.118	0.12	0.13	6	2.41	
		4	70	24.2	40.8	0.3	7.5	29.3	2008	16.2		0.001	0.1	2.01	1.56	0.075	0.08	0.08	6.9	1.6	
		5	100	27.5	45.7	0.6	7.4	29.3		16.0		0.002	0.67	1.33	1.81	0.116	0.11	0.1	10	1.95	
Transect 2	BRL6	1	10	26.9	45.8	2.1	8.1	31.1	2209	15.2	10.71	0.002	0.26	0.78	0.83	0.023	0.05	0.05	4.5	2.69	0.70891
		2	30	26	43.9	0.3	7.7	29.9	2056	12.9	10.48	0.002	0.42	1.26	1.17	0.111	0.1	0.09	4.5	2.41	0.7089
		3	50	21.6	37.6	0.5	7.6	31	1662	12.6	9.52	0.002	0.75	1.19	1.21	0.084	0.08	0.09	4.9	2.04	0.70884
		4	80	20.9	36.5	1.4	7.6	31.1	1623	12.4	9.41	0	0.75	1.29	1.11	0.076	0.06	0.07	5.7	2.04	0.70887
		6	150	21.3	36.7	0.4	7.6	30.1	1681	15.8	8.93	0.001	0.62	1.02	1.1	0.088	0.08	0.08	9.6	1.84	0.70882
	BRL7	3	14.5	26.9	37.3	1.1	7.8	30.2	2209	15.8		0.002	0.27	0.81	0.83	0.115	0.11	0.13	4.2	2.47	
		4	44.5	27.6	44.8	2.2	7.7	29.4													
		7	154.5	27.2	45.4	3.9	8.6	29.7													

Appendix D.11. Multi-sampler water chemistry data, August 2000.

	Station	Salinity	Cond.	Oxygen	рΗ	Temp.	SO4	CI	Sr	NO3+NO2	NH4	TSN	TN	PO4	TSP	TP	SiO2	δ ¹⁸ Ο	⁸⁷ Sr/ ⁸⁶ Sr
		(ppt)	(mS/cm)	(mg/L)		(oC)	(mg/L)	(g/L)	(µg/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L)	(mg/L)		
E	3HSpring	1.8	3.5	1.8	7.6	26.6	202	1.1		0	0.18	0.43	0.44	0.002	0	0	15.3		
(GW 1647	0.9	2.1	2.1	7.7	32.4	106	0.7	14.56	0.02	0.4	0.55	0.54	0.003	0	0	18.2		0.707804
	GW331	1.2	2.5	0.5	7.5	27.1	106	0.8	14.38	0	0.4	0.6	0.61	0.003	0	0	16.2		0.707809
(GW 1580	0.9	2.1	1.6	7.6	25.7	144	0.7		0	0.35	0.57	0.63	0.003	0	0	16.3		
(GW 1473	0	0.6	0.3	6.7	25.7		0.2		0	0.59	1.33	1.34	0.742	0.62	0.71	11.8		
	GW921	1.6	3.3	2.1	7.8	27.6	154	1.1		0	N/A	0.67	0.69	0.003	0.01	0	15.9		
с	RANECR	23	36.3	6.5	7.9	30.3	1835	13.5		0	0.03	0.46	0.54	0.089	0.09	0.11	2.3		
Н	ORSECR	26.9	41.7	3.9	7.5	32.4	1633	12.0		0.02	0.04	0.39	0.52	0.063	0.08	0.11	3		
E	AUGALL	26.1	40.5	8.3	8.1	30.8	2094	15.4		0	0.03	0.36	0.51	0.054	0.07	0.09	2		
	SEBINL	33.7	51	8.6	8.2	29.5	2843	20.2		0.01	0.01	0.07	0.12	0.011	0.02	0.02	0.4		
	TURCR	0.2	0.9	8.2	7.7	30.2	58	0.4		0.07	0.06	1	0.99	0.02	0.03	0.04	12.8		
SI	EBRIVER	21.6	34.1	7.7	8.1	31.1	1681	12.6		0	0.02	0.28	0.38	0.052	0.06	0.09	4.6		

Appendix D.12. Well and surface water chemistry data, August 2000.

Transect	Station	Salinity	Cond.	Oxygen	рН	SO4	CI	Sr	NO3	NH4	TSN	TN	PO4	TSP	ТР	SiO2	δ ¹⁸ Ο	⁸⁷ Sr/ ⁸⁶ Sr
		(ppt)	(mS/cm)	(mg/L)		(mg/L)	(g/L)	(mg/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L)	(mg/L)		
Transect 1	IRL29	29	45.9	8.17	8	2334	17.2	10.32	0.01	0.18	1.72	1.66	0.146	0.15	0.15	4.13	10.3	0.70886
	IRL30	30.8	49	7.26	8.75	2488	18.1		0.01	0.78	1.99	1.97	0.017	0.08	0.1	4.4		
Transect 2	IRL32	29.6	31.99	4.5	7.87	2094	15.8		0	0.4	2.34	2.85	0.354	0.34	0.36	4.06		
	IRL33	29.8	47.4	7.88	7.85	2392	17.4		0.02	0.27	1.24	1.14	0.058	0.08	0.09	4.56		
	IRL34	29.8	48.2	-	8.34	2459	17.7		0.01	0.04	0.88	0.85	0.007	0.02	0.03	2.12		
Transect 3	IRL35	26.4	42.8	5.18	7.74	2084	15.5		0	0.67	2.08	2.05	0.288	0.28	0.13	4.94		
	IRL36	26.8	43.8	7.3	8.14	2161	15.7		0	0.33	1.31	1.43	0.083	0.09	0.12	4.23		
	IRL37	27.3	44.6	7.38	8.37	2171	16.0		0.01	0.46	1.38	1.51	0.065	0.08	0.16	3.55		
	IRL38	26.8	43.5	5.4	8.12	2104	15.6		0	0.67	1.56	1.74	0.072	0.09	0.1	4.86		
Transect 4	IRL39	24.5	40.3	4.48	8.03	1921	14.3		0	0.84	2.37	2.31	0.3135	0.32	0.28	4.95		
	IRL40	25.1	41.1	6.33	8.38	1988	14.7		0	0.68	1.56	1.68	0.233	0.19	0.21	6.27		
	IRL41	24.9	40.8	5.47	8.51	1960	14.5		0.01	0.2	1.08	1.14	0.043	0.06	0.08	2.52		
Transect 1	BRL1	24.1	38.9	7.43	8.77	1921	14.2	10.15	0	0.04	0.89	0.96	0.005	0.02	0.05	1.95	10.2	0.70889
	BRL2	24.4	39.4	4.98	8.19	1921	14.2	9.93	0	0.05	0.79	0.93	0.005	0.01	0.04	1.32	9.93	0.70885
	BRL3	24.3	39.3	7.31	8.73	1931	14.2		0	0.2	1.05	1.74	0.058	0.07	0.26	4.68		
	BRL5	24.5	39.5	5.15	8.28	1931	14.4		0	0.06	0.93	1.15	0.004	0.02	0.06	2.47		
Transect 2	BRL6	24.3	39.6	5.34	8.48	1931	14.2	10.56	0	0.03	0.94	0.98	0.017	0.04	0.06	2.6	10.6	0.70897
	BRL7	24.1	39.1	4.88	8.3	1931	14.3		0	0.1	0.89	1	0.02	0.04	0.07	2.47		
	BRL8	24.5	39.5	4.45	8.18	1940	14.3		0	0.02	0.94	1.02	0.038	0.06	0.09	4.02		

Appendix D.13. Seep water chemistry data, December 2000.

Transect	Station	Salinity	Cond.	Oxygen	рΗ	Temp.	SO4	CI	Sr	NO3	NH4	TSN	TN	PO4	TSP	ТР	SiO2	δ ¹⁸ Ο	⁸⁷ Sr/ ⁸⁶ Sr
		(ppt)	(mS/cm)	(mg/L)		(°C)	(mg/L)	(g/L)	(mg/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L)	(mg/L)		
Transect 1	IRL29WC	30.5	47.6	7.87	8.45	16.4	2507	18.0		0.017	0.036	0.801	0.897	0.007	0.015	0.032	1.185		
	IRL30WC	30.7	47.7	7.34	8.39	16.4	2469	18.1		0.017	0.037	0.8185	0.911	0.008	0.0155	0.041	1.1465		
	IRL31WC	29.9	46.9	7.31	8.46	16.5	2478	17.9		0.01	0.029	0.797	0.853	0.012	0.015	0.03	1.04		
Transect 2	IRL32WC	29.5	46	7.54	8.47	16.1	2411	17.4		0.011	0.037	0.793	0.939	0.01	0.016	0.032	0.737		
	IRL33WC	29.2	45.9	7.41	8.43	16.8	2392	17.6		0.016	0.048	0.893	0.917	0.011	0.017	0.036	0.899		
	IRL34WC	29	45.6	7.32	8.38	16.5	2353	17.5		0.017	0.045	0.848	0.907	0.01	0.016	0.038	0.895		
Transect 3	IRL35WC	27.5	43.4	9.14	8.66	17	2229	15.9		0.005	0.027	0.79	0.882	0.009	0.015	0.028	0.598		
	IRL36WC	27.2	43.1	8.08	8.53	17	2171	16.4		0.016	0.043	0.818	0.963	0.01	0.015	0.031	0.851		
	IRL37WC	27.1	42.8	7.71	8.43	17	2209	16.2		0.016	0.048	0.875	0.976	0.012	0.019	0.033	0.862		
Transect 4	IRL38WC	27.2	43	7.82	8.44	17.3	2200	15.9		0.014	0.065	0.853	0.942	0.011	0.017	0.033	0.789		
	IRL39WC						2094	15.2		0.008	0.036	0.855	0.834	0.011	0.018	0.024	0.497		
	IRL40WC						2190	15.7		0.022	0.115	0.9465	0.986	0.018	0.0265	0.04	1.1965		
	IRL41WC						2008	14.8		0.005	0.032	0.787	0.869	0.021	0.016	0.041	0.05		
	IRL42WC	24.7	39.4	10.69	8.39	17.3	1979	14.7		0.003	0.021	0.762	0.876	0.008	0.014	0.041	0.049		
Transect 1	BRL1WC	23.7	37.9	10.97	8.74	16.7	1883	14.7	9.85	0.002	0.007	0.765	0.878	0.008	0.012	0.034	0.073	9.85	0.70888
	BRL2WC	23.9	38.3	11.26	8.78	16.8	1912	14.6	9.98	0.002	0.019	0.74	0.862	0.006	0.013	0.04	0.063	9.98	0.70889
	BRL3WC	23.9	38	8.26	8.63	16.8	1912	14.3		0.003	0.013	0.686	0.914	0.005	0.013	0.048	0.049		
	BRL4WC	24.1	38.4	10.53	8.7	16.4	1912	14.4		0.002	0.017	0.7	0.873	0.006	0.013	0.045	0.031		
	BRL5WC	24.3	38.7	10.27	8.77	16.6	1931	14.6		0.003	0.014	0.759	0.926	0.006	0.013	0.038	0.018		
Transect 2	BRL6WC	23.9	38.2	10.36	8.77	16.7	1940	14.4	11	0.002	0.021	0.761	0.887	0.005	0.013	0.039	0.004	11	0.70895
	BRL7WC	23.9	38.2	9.84	8.69	16.3	1931	14.4		0.002	0.022	0.761	0.892	0.005	0.013	0.041	0		
	BRL8WC	23.7	38	9.7	8.6	16.1	1902	14.4		0.002	0.026	0.772	0.93	0.005	0.014	0.041	0		

Appendix D.14. Lagoon water chemistry data, December 2000.

Transect	Station	Port	Depth	Salinity	Cond.	Oxygen	Нq	Temp.	SO4	CI	Sr	NO3	NH4	TSN	TN	PO4	TSP	TP	SiO2	δ ¹⁸ Ο
			(cm)	(ppt)	(mS/cm)	(mg/L)		(oC)	(mg/L)	(g/L)	(ppm)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L) (mg/L)	
Transect 1	IRL29	2	30	26.8	42.61	4.2	7.97	26.4	1950	14.4	9.4	0.02	0.38	1.6	1.75	0.173	0.16	0.16	11.06	1.79
		4	80	21.2	33.7	3.32	7.42	28.1							1.19			0.13		
		5	110	23.7	37.07	0.46	8.08	23.3	1758	12.8	11.11	0	0.29	1.72	1.93	0.083	0.1	0.05	9.84	1.5
	IRL31	1	10	32.5	39.6	2.33	8.29	20.8	2488	17.9		0.03	0	0.95	1.07	0.031	0.04	0.06	3.7	
Transect 2	IRL32	1	10	29.2	45.19	2.49	8.34	22.4	2171	15.9		0	0.01	1.04	0.97	0.095	0.1	0.08	1.67	
		2	30	25.4	39.74	0.58	8.11	21.3	1883	14.3		0	0.5	1.3	1.17	0.162	0.16	0.16	5.6	
		3	50	23.2	36.67	1.89	8.13	24.4							1.07			0.69		
		4	80	23.3	36.08	0.55	8.22	22.4	1681	12.4		0.01	0.57	1.24	1.17	0.132	0.13	0.16	6.61	
Transect 1	BRL1	1	10						1921	14.2	9.33	0	0.13	0.77	0.93	0.014	0.02	0.05	0.03	2
		2	30						1854	13.8		0	0	1.39	1.44	0.172	0.13	0.16	6.65	1.74
		5	110						1854	13.3	9.76	0.01	0.49	2.04	2.11	0.182	0.16	0.16	7.77	2.03
		6	150						1902	13.5	9.96	0	0.51	1.64	1.73	0.349	0.36	0.31	5.8	1.65
	BRL2	1	10	26.4	41.04	2.25	8.51	20.6	1921	14.6	9.82	0.01	0	0.87	0.81	0.01	0.02	0.02	2.44	2.16
		2	30	25.6	39.89	1	8.07	21.6	1815	14.1	9.46	0	0.11	1.36	1.08	0.003	0.03	0.06	4.05	1.85
		3	50	23.2	21.9	0.9	8.21	21.9	1595	12.7	9.14	0.01	0	1.62	1.57	0.037	0.06	0.08	4.9	1.73
		4	80	23.4	21.2	0.49	8.17	21.2	1691	12.8	9.27	0.01	0.09	1.94	1.7	0.0615	0.07	0.07	5.34	1.93
		5	110	24.1	21.6	0.39	8.11	21.6	3708	13.1	9.67	0.01	0.26	1.83	1.74	0.154	0.15	0.16	7.32	1.54
		6	150	26.4	21.8	0.36	8.02	21.8	2065	14.4	10.76	0	0.37	1.6	1.64	0.232	0.19	0.26	7.38	1.78
		7	190	27.7	22.3	0.5	8.06	22.3	2152	15.1	11.28	0	0.33	1.58	1.69	0.216	0.18	0.29	6.67	1.91
		8	230	28.2	22.6	0.97	8.02	22.6	2152	15.4	11.26	0	0.4	1.72	1.77	0.226	0.19	0.26	6.14	1.94
	BRL5	1	10	26.8	41.66	10.86	9.29	18.1	1950	14.6		0	0	0.8	0.89	0.014	0.02	0.04	0	2.04
		2	30	26.7	41.61	0.56	8.66	18.4	1940	14.6		0	0.17	1.23	1.31	0.081	0.09	0.09	4.47	2.13
		3	50	26.5	41.32	0.43	8.42	18.7	1931	14.6		0.01	0.39	1.54	1.41	0.078	0.09	0.12	4.18	2.04
		4	80	28.7	44.34	0.42	7.99	19.5	2181	15.7		0	0	2.32	4.15	0.034	0.09	0.07	7.79	1.37
		5	110	31.8	48.63	0.26	7.94	20.2	2488	17.5		0	0	3.45	3.74	0.119	0.12	0.11	16.58	1.2
Transect 2	BRL6	1	10	26.4	40.8	3.12	8.81	20.1	1931	14.5	9.82	0	0	1.06	0.96	0.081	0.09	0.06	3.06	2.26
		2	30	25.9	40.4	0.31	8.48	20.3	1902	14.3	9.82	0	0.35	1.24	1.23	0.045	0.06	0.07	3.59	2.21
		3	50	24.9	39.16	0.33	8.21	21.5	1777	13.8	9.32	0	0.53	1.74	1.74	0.06	0.08	0.08	4.19	1.84
		4	80	24.8	38.92	0.52	8.16	21.5	1806		9.68	0	0.53	1.51	1.45	0.046	0.06	0.08	5.21	2
		6	150	23.3	36.81	0.25	8.08	22.6	1652			0.01	0.46	1.48	1.55	0.081	0.08	0.09	9.22	1.77
	BRL7	3	50						1691			0.01	0.51	1.69	1.76	0.187	0.15	0.16	7.07	1.65
		4	80						1806			0.01	0.58	1.69	1.71	0.249	0.21	0.19	6.86	1.77
		5	110						1767	12.8		0.01	0.59	1.98	2.05	0.541	0.54	0.68	6.57	1.4
		6	150						1988	13.8		0.01	0.77	2.09	2.17	0.941	0.98	0.95	5.93	1.47

Appendix D.15. Multi-sampler water chemistry data, December 2000.

Station	Salinity	Cond.	Oxygen	рН	Temp.	SO4	CI	Sr	NO3	NH4	TSN	TN	PO4	TSP	TP	SiO2	δ ¹⁸ O ⁸⁷ Sr/ ⁸⁶ Sr
	(ppt)	(mS/cm)	(mg/L)		(oC)	(mg/L)	(g/L)	(ppm)	(mgN/L)	(mgN/L)	(mgN/L)	(mgN/L)	(mgP/L)	(mgP/L)	(mgP/L)	(mg/L)	
BHSpring						173	1.2	14.34	0.001	0.327	0.581	0.504	0.012	0.009	0.004	15.661	0.707826
GW1647	0.9	1.823	0.48	7.47	31.3	144	0.7		0	0.325	0.566	0.528	0.003	0	0	36.131	
GW331	1.5	2.837	1.05	8.08	25	96	0.9	14.68	0.002	0.38	0.607	0.61	0.003	0	0.001	17.746	0.707810
GW1473						106	0.2		0.005	0.422	1.335	1.418	0.797	0.703	0.699	12.583	
GW1561						192	0.8		0	0.296	0.546	0.502	0.002	0	0	17.193	
GW921						1767	1.1	13.32	0.005	0.39	0.6225	0.6285	0.001	0	0	16.1895	0.707843
CRANECR	2					1489	11.3		0.185	0.131	0.929	1.1	0.052	0.058	0.158	2.265	
HORSECR	R					2017	14.6		0.185	0.06	1.196	1.206	0.021	0.026	0.113	1.071	
EAUGAL	25.9	40.56	7.36	8.61	23.7	1921	14.2		0.02	0.105	0.869	0.931	0.025	0.03	0.055	0.652	
SEBINL	35.6	53.9	8.25	8.6	22.8	2738	19.4		0.004	0.011	0.183	0.154	0.013	0.013	0.023	0.179	
SEBRIVER	R 16.1	26.1	8.19	8.59	22.6	1162	8.7		0.009	0.006	0.395	0.438	0.019	0.022	0.044	5.808	

Appendix D.16. Well and surface water chemistry data, December 2000.

Station	Depth*	Sal.	DO	Cond	т	CI	SO₄	NH₄	NO ₃	TSN	TN	PO₄	TSP	ТР	SiO ₂
	(cm)	(‰)	(mg/L)	(mS/cm)	(°C)	(mg/L)	(g/L)	(mg N/L)	(mgN/L)	(mgN/L)	(mgN/L)	(uM)	(mgP/L)	(mgP/L)	(mg/L)
IRL 4	39	22.3	1.0	35.6	21.8	12.9	1857	2.69	0	2.68	2.83	7.478	0.176	0.22	12.96
	64	30.2	0.7	46.4	22.5	16.5	2501	5.14	0.002	3.86	3.86	5.516	0.126	0.12	13.67
	95	33.3	1.0	51.0	22.4	18.9	2753	5.66	0.004	2.15	4.20	5.615	0.174	0.16	16.40
	124	33.4	1.1	51.0	22.6	19.1	2941	3.53	0.001	3.13	3.07	2.477	0.072	0.08	11.35
	156	33.8	0.8	51.6	22.9	19.3	2973	2.98	0.011	2.09	2.47	2.379	0.089	0.09	11.00
	185	33.3	0.8	51.0	23.3	19.1	2950	2.21	0.014	1.97	2.04	1.888	0.067	0.09	10.13
IRL 6	-69	22.4	0.7	25.8	21.5	13.5	2053	0.78	0.004	1.11	1.10	1.202	0.038	0.04	4.13
	-14	24.8	5.7	39.2	21.1	14.4	1926	0.13	0.014	0.81	0.88	0.025	0.015	0.05	2.37
	47	24.5	1.1	38.8	21.5	14.1	2049	0.59	0.001	1.02	1.02	1.104	0.036	0.04	3.64
IRL 5	-30	24.8	6.4	39.1	21.5	14.4	2113	0.10	0.006	0.63	1.01	0.025	0.006	0.06	2.18
	1	24.8	5.5	39.1	21.7	14.3	2127	0.11	0.006	0.70	0.95	0.123	0.009	0.05	2.18
	31	24.8	6.2	39.1	21.7	14.2	2130	0.12	0.021	0.66	0.99	0.025	0.009	0.06	2.18
	60	24.1	1.0	38.2	21.9	13.9	2079	1.22	0.005	1.56	1.59	3.751	0.103	0.12	5.30
	89	29.3	1.0	45.4	22.0	16.8	2534	1.44	0.004	1.80	1.73	1.986	0.056	0.06	7.73
IRL 22	-29	27.4	4.5	42.7	23.0	15.7	2248	0.41	0.018	0.82	0.95	1.202	0.042	0.07	2.29
	4	27.5	1.6	42.9	22.5	15.7	2260	0.74	0.002	0.95	0.97	1.104	0.033	0.04	2.97
	32	27.9	0.8	43.6	22.2	16.0	2317	1.07	0.036	1.29	1.33	1.986	0.058	0.05	4.01
	123	28.7	0.5	46.2	22.1	17.6	2636	1.88	0.151	2.00	1.93	4.046	0.015	1.06	9.09

Appendix D.17. Pore water chemistry from multisamplers

* Negative numbers represent ports in the water column.

Station	Port*	Depth	Salinity	Cond.	Oxygen	рН	Temp.	TN	TP
		(cm)	(ppt)	(mS/cm)	(mg/L)		(oC)	(mgN/L)	(mgN/L)
IRL4WC	WC		36	54.7	5.05	7.94	22.1		
IRL4MS1	1		36	54.8	3.51	7.6	21.8	0.979	0.099
IRL4MS2	2		35.3	53.9	0.81	7.51	21.5	0.897	0.051
IRL4MS3	3		35.2	53.8	0.95	7.79	21.3	1.251	0.027
IRL4MS4	4		33.7	51.6	0.82	7.63	21.3	1.454	0.029
IRL22WC	WC		35.3	54	6.49	8	20.6		
IRL22MS1	1		36	54.7	1.02	7.64	21.3	1.75	0.119
IRL22MS2	2		36.1	54.7	2.21	7.69	22.4	1.733	0.226
IRL22MS3	3		35.7	54.3	1.34	7.63*	22.2	1.71	0.294
IRL22MS4	4		31.9	49.1	0.63	7.43	21.1	1.999	0.47
IRL22MS6	6		31.5	48.9	0.37	7.39	21.4	1.261	0.164
IRL22MS8	8		33.7	51.7	0.74	7.34	23	1.102	0.284

Appendix D.18. Multi-sampler water chemistry from northern area data, December 2000.

*WC = water column