PROCEEDINGS OF THE 13th SYMPOSIUM ON THE GEOLOGY OF THE BAHAMAS AND OTHER CARBONATE REGIONS

Edited By
Lisa E. Park and Deborah Freile

Production Editor
Lisa E. Park

Gerace Research Centre
San Salvador, Bahamas
2008

Front Cover: Rice Bay Formation, looking southwest along Grotto Beach. Photograph by Sandy Voegeli.

Back Cover: Dr. John Milliman, The College of William and Mary. Keynote Speaker for the 13th Symposium. Photograph by Sandy Voegeli.

WATER CHEMISTRY ON SAN SALVADOR ISLAND, BAHAMAS

Paul J. Moore and Jonathan B. Martin
Department of Geological Sciences
University of Florida
Gainesville, FL 32611
pjmoore@geology.ufl.edu

ABSTRACT

Surface and groundwater on San Salvador Island originates from two sources: rain water, which is undersaturated with respect to carbonate minerals, and seawater, which is supersaturated with respect to carbonate minerals. Analyses of 63 water samples from surface and groundwater show how San Salvador water evolves from these two sources through mixing and water-rock interactions. Chemical modeling of these analyses show that increases in Ca^{2+} concentrations are controlled primarily by the dissolution of metastable aragonite and that most water samples are supersaturated with respect to calcite. Dissolution of carbonate minerals on San Salvador Island results from two main processes: mixing of fresh water and seawater, and the increase in the partial pressure of carbon dioxide in solution (PCO_2), which is the primary cause for mineral dissolution.

INTRODUCTION

Chemical analysis of surface and ground water can lead to a better understanding of geological processes that occur on carbonate platforms, such as San Salvador Island, Bahamas. Some of these processes include dissolution of the highly soluble carbonate rocks making up the island and its hydrology, as well as the linkages between dissolution and hydrology. On San Salvador Island, dissolution has led to karstification, such as surface sculpturing of exposed rock (e.g., karren) and cave development, including pit caves on the surface, and flank margin caves and banana holes in the subsurface. These dissolution fea-

tures and caves have been widely described in the literature (e.g. Mylroie and Carew, 1990; Mylroie et al., 1991; Mylroie and Carew, 1995a, b; Mylroie et al., 1995), but direct comparisons on San Salvador Island between modern water chemistry and these features are less common (e.g. Moore et al., 2004). In addition to karstification, understanding island hydrology is critical for wise use and conservation of water resources.

The work of Davis and Johnson (1989) used ground water chemistry to help conceptualize the regional hydrology of San Salvador Island. Their work has led to a better understanding of the hydrodynamics of freshwater lenses and the effects of carbonate dissolution as applied to San Salvador Island. Similar chemical analyses could also be used to identify which water-rock interactions influence water compositions and may lead to a better understanding of the mechanisms and rates of formation of the dissolution features commonly seen across the island. For this reason, we present chemical analyses of 63 water samples collected on San Salvador Island from two flank margin caves, one freshwater spring, three lakes, two blue holes, five groundwater wells, and a catchment pond on four separate occasions from January 2004 to June 2006 (see Appendices) and include a limited discussion of these data.

LOCATION AND GEOLOGIC BACKGROUND

San Salvador Island, Bahamas, is a small, isolated carbonate platform located approximately 650 km southeast of Miami, Florida (Figure 1). The island is tectonically stable and assumed to have an isostatic subsidence of 1-2 m per 100,000 years (Mullins and Lynts, 1977; Carew and Myl-

roie, 1995). The exposed rocks are Holocene and Pleistocene carbonate sediments of subtidal, reef and beach facies at low elevations, and dune facies at elevation above 6 m (Carew and Mylroie, 1985). Eolian dunes dominate the landscape, rising to a maximum of 40 meters above present sea level (masl) with most dunes ranging from 10 to 20 masl. Lying between the dunes are low elevation plains, wetlands and interior, saline-to-hypersaline lakes. Surface streams are absent due to the high porosity (≤ 30%) of the limestone (e.g. Vacher and Mylroie, 2002).

Figure 1. Map of Bahamas showing location of San Salvador Island. Insert of San Salvador Island shows water sampling locations - gray represents land area and white represents water bodies.

San Salvador Island has a subtropical marine climate dominated by northeast trade winds. The island experiences a warm rainy season from May to October, and a cool dry season from November to April (Whitaker and Smart, 1997). Recharge to the freshwater lenses that form below the dune ridges occurs through diffuse infiltration through the vadose zone. Precipitation is delivered by cold fronts during the winter, convective thunderstorms during summer, and transitional stationary fronts. Annual rainfall on San Salvador Island

ranges from 1000 to 1250 mm/yr, with potential evapotranspiration (PET) estimated between 1250 and 1375 mm/yr (Sealey, 1994). The negative water budget restricts ground water recharge to rain events that exceed PET.

METHODS

Sixty-three surface and groundwater samples were collected across San Salvador Island during four trips--January through June 2004, April 2005, and June 2006. Samples collected in January 2004 and April 2005 represent water from the dry season, while samples collected in June 2004 and 2006 represent water from the wet season. In the field, we measured pH and temperature using an Orion #250A portable pH/ temperature meter, and conductivity and salinity using an Orion model #130 portable conductivity meter. For samples collected in April 2005 and June 2006, alkalinity was titrated with 0.1N hydrochloric acid (HCl) using the Gran technique within 24 hours of collection (e.g. Drever, 1997). Alkalinity was not measured for the samples collected in January and June 2004. Surface grab samples were collected from inland lakes, tidal pools within Majors Cave (a flank margin cave located on Hog Cay), from a submarine spring at Grotto Beach, and several hand dug wells around the island (Figure 1). One sample was also collected from the catchment pond behind the Gerace Research Centre (GRC) following a torrential rainstorm that occurred the previous day.

In Majors Cave, vertical profiles of water samples were collected with tubing attached to an extendable rod taking care not to mix the water and pumping water to the surface with either a hand-held vacuum pump or a 12 volt GeoTech II peristaltic pump. At the Grotto Beach spring, a horizontal profile of water samples was collected into the spring throat with tubing attached to an extendable rod and pumping water with the peristaltic pump. Samples from most wells were also collected using the peristaltic pump, with exception of two wells located behind the GRC that were pumped using an electric motor-driven pump at a rate of about 23 L/min. At one of the
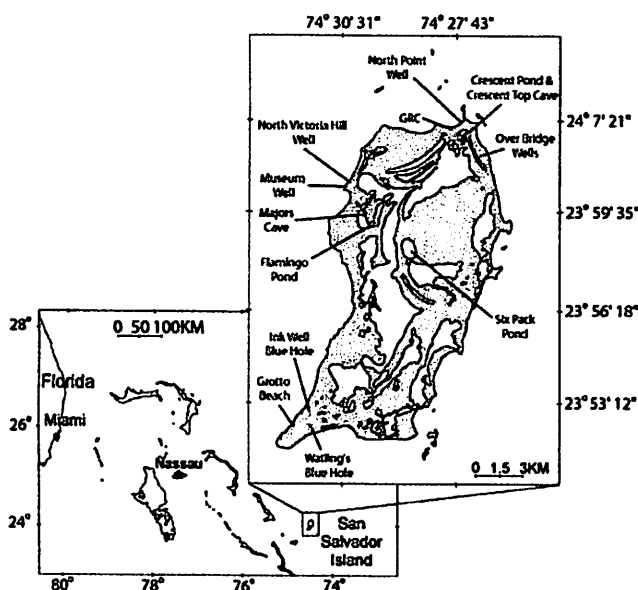
wells behind the GRC, we collected samples both prior to pumping (GRC1-2006) and following purging the wells of about 1000 L (GRC1PT-2006), or several well volumes, that we assume represents pristine sampling of fresh ground water. These two samples were collected to determine how much water composition changes by remaining stagnant in the numerous hand-dug wells that occur across the island. In the other well behind the GRC, we collected all samples only after purging was completed (GRC2PT-2006).

Samples were pumped into clean dry HDPE bottles for major ions analyses and glass bottles for dissolved inorganic carbon (DIC) analyses, capped and returned to the laboratory. Dissolved inorganic carbon was only collected in June 2006. Major ion and DIC concentrations were measured at Department of Geological Sciences at the University of Florida. Major ion concentrations were measured using an automated Dionex 500 ion chromatograph, and DIC concentrations were measured with a Coulometrics CO_2 coulometer using a 3% silver nitrate scrubber solution, nitrogen as the carrier gas, and 2N HCL to evolve the CO_2 from the water. Precision of the measurements was assessed by replicate measurements of internal standards and was found to be < 5% (1 σ) for major ions and < 3.5% (1 σ) for DIC. Charge balance for samples collected in April 2005 and June 2006 is < 3%. Samples with higher charge balance errors have low salinity, with concentrations close to the detection limit of the instrument.

The geochemical code EQ3NR, Version 8 (Wolery, 1992, 1994), was used to determine the carbonate mineral saturation states of water sampled in April 2005 and June 2006. Saturation states for samples collected in January and June 2004 cannot be determined since these samples lack alkalinity measurements. Activity coefficients of aqueous species were calculated using the extended Debye-Hückle equation of Helgeson (1969). Since all samples were collected at depths $\leq$ 5 m, fugacity of oxygen was assumed to be in equilibrium with atmosphere at the time of collection. The state of mineral saturation in solution is reported here as the saturation index (SI) defined by:

$$SI = \log\left(\frac{Q}{K}\right) \qquad (1)$$

where, Q is the ion activity product and K is the equilibrium constant for the reaction.

RESULTS

Surface and groundwater on San Salvador Island ranges from fresh to hypersaline; specific conductance measured in all of the water samples varied from 0.78 to 196.1 mS/cm, while salinity varied from 0.10 to 156 psu (Appendix 1-4). Temperature of the water samples range from 22.1°C to 32.4°C. Bulk chemical analysis of water samples collected from April 2005 and June 2006 show that San Salvador water evolves through a binary mixing between calcium bicarbonate fresh water and sodium chloride seawater (Figure 2). Samples collected in January and June 2004 are not displayed on Figure 2 due the lack of alkalinity measurements. Regardless, concentrations of these samples correlate with those displayed on Figure 2 by comparison of bulk chemistry, which suggest they also result from binary mixing between the two end-members. The samples collected from the GRC well (i.e., GRC1-2006 and GRC1PT-2006) prior to and following purging show little change in bulk chemistry, PCO_2 and saturation with respect to carbonate minerals. The minimal change in water chemistry, especially PCO_2 and carbonate mineral saturation, suggests there is little exchange of CO_2 between the well water and the atmosphere. Such exchange would be expected to cause CO_2 evasion, thereby increasing saturation with respect to carbonate minerals for the well water compared with formation water pumped into the well. This observation suggests that water from hand-dug wells may represent the chemical composition, including the gasses of unaltered groundwater within freshwater lenses, even if the wells are not purged prior to sampling. This conclusion is also

supported by the high PCO_2 values present in the samples from wells that were not purged (e.g., MW-2006).

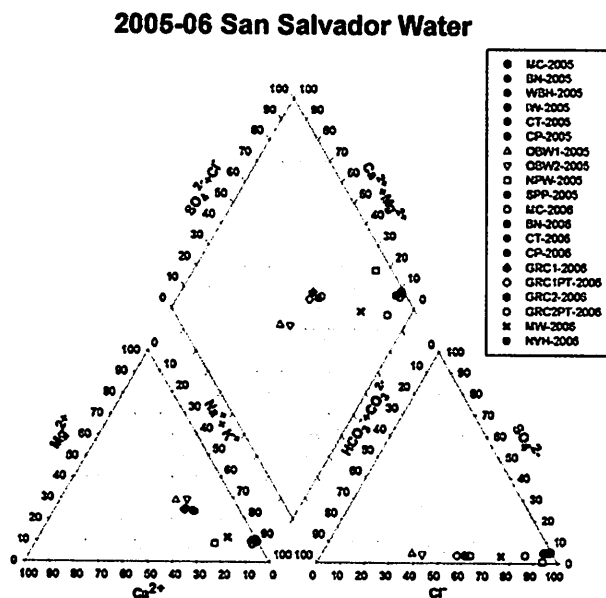**2005-06 San Salvador Water**

Figure 2. Piper diagram showing San Salvador water chemistry. Projection of water samples suggest water on San Salvador Island evolves from two end-members, calcium bicarbonate fresh water and sodium chloride seawater. Waters with the same symbol (black dot) are of similar water chemistry, i.e., sodium chloride end-member.

Saturation states of carbonate minerals in San Salvador waters were calculated for samples collected in April 2005 and June 2006. Most samples are in equilibrium with respect to aragonite, including those samples with high salinities. In addition to aragonite equilibrium over a broad range of salinity, these samples also vary by about two orders of magnitude in log PCO_2 ranging from -1.83 (GRC2-2006) to -3.73 (WBH-2005) (Appendix 3-4). One possible source of CO_2 is the soil zone, where root respiration and microbially-generated CO_2 can increase vadose water by orders of magnitude above atmospheric values (e.g. Brook et al., 1983; Schwabe et al., 2006).

The PCO_2 in water sampled from the Gerace Research Centre catchment is calculated at log -4.74, which is one order of magnitude lower than atmospheric value. The pH for this sample is 9.13, which suggests rapid equilibration with the carbonate. Total alkalinity for this sample was measured to be 4.99 meq/L, and DIC was measured to be 0.44 meq/L. The difference between total alkalinity and DIC values suggests that dissolved species in addition to carbonate species may contribute to the alkalinity, which could include borate, phosphate and organic anions. Only borate has been measured in the sample, and was found to be a minimal contributor to the total alkalinity. The large charge imbalance of 43% is likely due to its dilute nature, which leads to difficulties associated with accurately measuring low concentration of major ions and the possibility of ions present in solution with concentrations below instrument detection limits.

CONCLUSIONS

Rainwater and seawater are the two sources of water found on San Salvador Island and these two sources have distinct chemical compositions that can be traced through mixing. Rainwater is undersaturated with respect to carbonate minerals, and seawater is supersaturated. The chemistry of water from these sources change from multiple processes, including freshwater—seawater mixing, influx of CO_2 from the soil and the dissolution of limestone, releasing Ca^{2+} and HCO_3^- into solution.

ACKNOWLEDGMENTS

REFERENCES

Brook, G.A., Folkoff, M.E., and Box, E.O., 1983, A world model of soil carbon dioxide: Earth Surface Processes and Landforms, v. 8, p. 79-88.

Carew, J.L., and Mylroie, J.E., 1985, The Pleistocene and Holocene stratigraphy of San Salvador Island, Bahamas, with reference to marine and terrestrial lithofacies at French Bay, *in* Curran, H.A., ed., Pleistocene and Holocene Carbonate Environments on San Salvador Island, Bahamas, GSA Annual Meeting (Orlando, FL) Guidebook for Field Trip #2: Ft. Lauderdale, CCFL Bahamian Field Station, p. 11-61.

Carew, J.L., and Mylroie, J.E., 1995, Quaternary tectonic stability of the Bahamian Archipelago; evidence from fossil coral reefs and flank margin caves: Quaternary Science Reviews, v. 14, p. 145-153.

Davis, R.L., and Johnson, J., C.R., 1989, Karst hydrology of San Salvador, *in* Mylroie, J.E., ed., Proceedings, Fourth Symposium on the Geology of the Bahamas: San Salvador, Bahamian Field Station, p. 118-135.

Drever, J.I., 1997, The Geochemistry of Natural Waters: Englewood Cliffs, NJ, Prentice Hall, 437 p.

Helgeson, H.C., 1969, Thermodynamics of hydrothermal systems at elevated temperatures and pressures: American Journal of Science, v. 267, p. 729-804.

Moore, P.J., Martin, J.B., and Gamble, D.W., 2004, Carbonate Water Mixing in a Flank Margin Cave, *in* Gamble. D.W., and Davis, R.L., eds., Proceedings of the Twelfth Symposium on the Geology of the Bahamas: San Salvador Island, Bahamas, p. 123-129.

Mullins, H.T., and Lynts, G.W., 1977, Origin of the northwestern Bahama Platform; review and reinterpretation: Geological Society of America Bulletin, v. 88, p. 1447-1461.

Mylroie, J.E., and Carew, J.L., 1990, The flank margin model for dissolution cave development in carbonate platforms: Earth Surface Processes and Landforms, v. 15, p. 413-424.

Mylroie, J.E., and Carew, J.L., 1995a, Geology and karst geomorphology of San Salvador Island, Bahamas: Carbonates and Evaporites, v. 10, p. 193-206.

Mylroie, J.E., and Carew, J.L., 1995b, Karst development on carbonate islands, *in* Budd, D.A., ed., Unconformities and porosity in carbonate strata: Memoir 63, AAPG, p. 55-76.

Mylroie, J.E., Carew, J.L., Sealey, N.E., and Mylroie, J.R., 1991, Cave development on New Providence Island and Long Island, Bahamas: Cave Science, v. 18, p. 139-151.

Mylroie, J.E., Carew, J.L., and Vacher, H.L., 1995, Karst development in the Bahamas and Bermuda, *in* Curran, H.A., and White, W.B., eds., Terrestrial and Shallow marine Geology of the Bahamas and Bermuda: Boulder, Colorado, Geological Society of America Special Paper 300, p. 251-267.

Schwabe, S.J., Herbert, R.A., and Carew, J.L., 2006, A hypothesis for biogenic cave formation (A study conducted in the Bahamas), *in* Voegeli, V., ed., Abstracts and Program of the 13th Symposium on the Geology of the Bahamas and other Carbonate Regions: San Salvador Island, Bahamas, Gerace Research Center, p. 22-23.

Sealey, N.E., 1994, Bahamian landscapes; an introduction to the physical geography of the Bahamas: Nassau, Bahamas, Media Publishing, 128 p.

Vacher, H.L., and Mylroie, J.E., 2002, Eogenetic karst from the perspective of an equivalent porous medium: Carbonates and Evaporates, v. 17, p. 182-196.

Whitaker, F.F., and Smart, P.L., 1997, Climatic control of hydraulic conductivity of Bahamian limestones: Ground Water, v. 35, p. 859-868.

Wolery, T.J., 1992, EQ3NR, A computer program for geochemical aqueous speciation solubility calculations: Theoretical manual, user's guide, and related documentation (Version 7.0), UCRL-MA-110662-PT-III, Lawrence Livermore National Laboratory, Livermore, California.

Wolery, T.J., 1994, Letter Report: EQ3/6 Version 8: Differences from Version 7, UCRL-ID-129749, Lawrence Livermore National Laboratory, Livermore, California.

APPENDIX
Appendix 1. Water chemistry of samples collected in January 2004.

Samples	Depth (m)	pH	Cond. (mS/cm)	Temp. (C)	Salinity (psu)	Na$^+$ (mM)	K$^+$ (mM)	Mg^{2+} (mM)	Ca^{2+} (mM)	Cl$^-$ (mM)	Br$^-$ (mM)
Majors Cave											
MC-A-2004	0.1	7.95	33.80	22.10	23.70	327.51	6.45	37.67	7.81	383.45	0.563
MC-B-2004	0.5	7.89	34.70	22.20	24.60	331.26	6.78	38.31	7.84	393.54	0.573
MC-C-2004	1.0	7.80	35.70	22.40	25.20	350.52	7.17	40.66	8.25	406.41	0.588
MC-D-2004	1.5	7.70	36.80	22.50	26.40	360.42	7.35	41.51	8.36	417.65	0.620
MC-E-2004	2.0	7.68	36.60	22.50	26.00	362.01	7.40	42.03	8.55	418.92	0.611

Samples	SO$_4^{2-}$ (mM)	SiO$_{2(aq)}$ (uM)	B(OH)$_{3(aq)}$ (mM)	Alk. (meq/L)	DIC (meq/L)	Log PCO$_2$	SI$_{cal}$ (log Q/K)	SI$_{arag}$ (log Q/K)	SI$_{dol}$ (log Q/K)	% Charge Error
Majors Cave										
MC-A-2004	19.74									
MC-B-2004	20.32									
MC-C-2004	21.12									
MC-D-2004	21.77									
MC-E-2004	21.82									

Appendix 2. Water chemistry of samples collected in June 2004

Samples	Depth* (m)	pH	Cond. (mS/cm)	Temp. (C)	Salinity (psu)	Na$^+$ (mM)	K$^+$ (mM)	Mg^{2+} (mM)	Ca^{2+} (mM)	Cl$^-$ (mM)	Br$^-$ (mM)
Majors Cave											
MC-1-2004	0.1	7.64	44.30	23.9	29.0	361.16	7.59	42.29	9.08	416.21	0.615
MC-2-2004	1.0	7.59	44.70	24.1	29.3	363.76	7.54	42.54	8.85	419.42	0.643
MC-3-2004	2.0	7.59	45.10	24.1	29.5	367.00	7.87	43.08	9.02	427.01	0.646
MC-4-2004	3.0	7.30	45.70	24.4	29.7	372.77	7.92	43.40	8.93	431.03	0.647
MC-5-2004	4.0	7.41	46.10	24.1	30.2	373.76	7.81	43.62	9.15	437.77	0.653
MC-6-2004	5.0	7.18	46.10	24.1	30.2	369.57	7.61	43.07	9.13	441.53	0.673
BN-1-2004	0.1	7.63	41.50	23.8	27.1	325.69	6.74	37.97	7.94	406.93	0.595
BN-2-2004	0.4	7.60	42.40	23.9	27.6	340.04	6.86	39.44	8.31	395.82	0.571
BN-3-2004	0.8	7.48	43.40	23.9	28.4	354.62	7.11	41.40	8.59	415.58	0.628
BN-4-2004	1.2	7.60	44.00	23.9	28.7	362.35	7.55	42.21	8.88	419.85	0.609
BN-5-2004	1.6	7.53	44.30	23.9	29.0	356.80	7.39	41.70	8.77	421.97	0.631
BN-6-2004	2.0	7.45	44.70	24.1	29.2	358.69	7.45	41.87	8.80	425.43	0.627
Flamingo Pond											
FP-2004	0.1	8.41	109.00	31.6	69.40	841.58	16.56	97.62	17.50	969.44	1.42
OF-2004	0.1	8.25	196.10	28.3	~120	1905.65	38.02	227.91	35.62	2198.32	3.26
Grotto Beach Spring											
GB-1-2004	-1.5	7.52	45.80	27	27.90	350.87	7.16	40.63	7.88	411.49	0.589
GB-2-2004	-1.5	7.39	42.00	27	25.30	320.03	6.43	37.18	7.55	372.09	0.541
GB-3-2004	-2.0	7.37	41.00	26.9	24.90	313.25	6.45	36.47	7.39	364.72	0.532
GB-4-2004	0.0	7.9	54.50	27.8	33.30	419.59	8.71	49.05	9.24	491.43	0.710
GB-5-2004	+3	8.28	64.30	28.4	40.00	502.35	10.64	58.93	11.04	589.86	0.866
North Point Well											
NP-2-2004	0.4	7.63	1.14	27	0.30	4.62	0.26	0.85	0.72	3.55	0.005
NP-1-2004	0.1	7.67	0.78	27.3	0.10	2.79	0.16	0.52	0.58	1.48	0.004

Appendix 2. cont.

Samples	SO₄²⁻ (mM)	SiO₂(aq) (uM)	B(OH)₃(aq) (mM)	Alk. (meq/L)	DIC (meq/L)	Log PCO₂	SIcal (log Q/K)	SIarag (log Q/K)	SIdol (log Q/K)	% Charge Error
Majors Cave										
MC-1-2004	20.91	6.37	0.280							
MC-2-2004	21.16	0.00	0.264							
MC-3-2004	21.56	18.73	0.305							
MC-4-2004	21.81	7.50	0.265							
MC-5-2004	22.17	0.00	0.271							
MC-6-2004	22.43	0.00	0.292							
BN-1-2004	21.17	20.69	0.232							
BN-2-2004	20.55	20.41	0.249							
BN-3-2004	21.70	19.57	0.256							
BN-4-2004	21.86	19.85	0.256							
BN-5-2004	22.01	19.29	0.271							
BN-6-2004	22.20	19.29	0.262							
Flamingo Pond										
FP-2004	47.32	0.00	0.762							
OF-2004	107.05	0.00	1.346							
Grotto Beach Spring										
GB-1-2004	21.31	0.00	0.273							
GB-2-2004	18.97	29.40	0.231							
GB-3-2004	18.54	26.31	0.221							
GB-4-2004	25.98	7.22	0.338							
GB-5-2004	32.06	0.00	0.443							
North Point Well										
NP-2-2004	0.29	79.37	0.062							
NP-1-2004	0.29	59.15	0.051							

* Depth at Grotto Beach Spring represents sampling interval at the fissure, where negative values represent distance into the fissure. Sample GB-4-2004, at 0.0 m, was collected at the rock wall, and GB-5-2004 represents seawater collected 3 m away from the fissure.

Appendix 3. Water chemistry of samples collected in April 2005.

Samples	Depth (m)	pH	Cond. (mS/cm)	Temp. (C)	Salinity (psu)	Na⁺ (mM)	K⁺ (mM)	Mg²⁺ (mM)	Ca²⁺ (mM)	Cl⁻ (mM)	Br⁻ (mM)
Majors Cave											
MC-0-2005	0.1	7.68	38.70	23.8	27.80	358.26	7.33	41.94	8.82	423.97	0.593
MC-1-2005	1.0	7.68	38.80	23.7	27.80	361.71	7.39	42.19	8.86	423.49	0.606
MC-2-2005	2.0	7.67	38.80	23.7	27.80	361.82	7.38	42.41	9.04	424.60	0.595
MC-3-2005	3.0	7.67	38.80	23.7	27.80	366.59	7.57	42.58	8.79	424.57	0.610
MC-4-2005	4.0	7.59	39.00	23.8	28.00	370.09	7.74	43.13	9.23	429.33	0.609
MC-5-2005	4.5	7.55	39.40	23.9	28.30	379.29	7.59	44.70	9.45	435.89	0.613
BN-0-2005	0.1	7.63	35.70	23.3	25.30	328.49	6.68	38.36	8.21	384.54	0.534
BN-1-2005	0.5	7.55	37.90	23.8	27.10	362.62	7.30	41.96	8.48	412.60	0.660
BN-2-2005	1.0	7.59	38.30	23.8	27.50	363.36	7.25	42.21	8.59	422.19	0.604
Watling's Blue Hole											
WBH-2005	0.1	8.51	43.20	30.6	27.80	368.69	7.39	43.23	9.26	422.23	0.596
Ink Well Blue Hole											
IW-2005	0.1	7.7	9.32	24.2	5.20	66.52	1.29	7.15	3.32	77.82	0.108
Crescent Top Cave											
CT-2005	0.1	7.44	55.80	26.5	35.50	483.06	19.07	51.79	9.80	544.79	0.772
Crescent Pond											
CP-2005	0.1	8.44	61.00	28.4	37.80	491.91	10.31	57.56	11.16	581.47	0.845
Over Bridge Wells											
OBW-1-2005	0.1	7.87	0.99	26.1	0.30	3.08	0.00	1.79	1.56	2.89	0.004
OBW-2-2005	0.1	7.87	1.27	27.8	0.50	4.37	0.00	2.38	1.66	4.32	0.003
North Point Well											
NP-2005	0.1	7.6	3.79	26.1	1.90	18.82	0.19	2.15	4.89	30.15	0.048
Six Pack Pond											
SPP-2005	0.1	8.37	74.60	25.3	51.70	679.01	13.73	78.29	15.28	780.68	1.091

Appendix 3. cont.

Samples	SO₄²⁻ (mM)	SIO₂(aq) (uM)	B(OH)₃(aq) (mM)	Alk. (meq/L)	DIC (meq/L)	Log PCO₂	SI_cal (log Q/K)	SI_arag (log Q/K)	SI_dol (log Q/K)	% Charge Error
Majors Cave										
MC-0-2005	21.46	18.45	0.272	2.395		-2.801	0.163	0.019	2.216	-0.25
MC-1-2005	21.40	18.45	0.279	2.415		-2.799	0.166	0.021	2.223	0.28
MC-2-2005	21.48	18.17	0.289	2.436		-2.785	0.168	0.023	2.220	0.24
MC-3-2005	21.47	18.45	0.293	2.498		-2.775	0.165	0.021	2.230	0.78
MC-4-2005	21.76	19.37	0.298	2.482		-2.696	0.106	-0.039	2.094	0.81
MC-5-2005	22.13	19.10	0.295	2.557		-2.645	0.085	-0.059	2.061	1.37
BN-0-2005	19.31	20.13	0.220	2.433		-2.735	0.105	-0.039	2.091	0.34
BN-1-2005	20.79	19.01	0.286	2.461		-2.655	0.034	-0.111	1.976	1.63
BN-2-2005	21.35	18.73	0.261	2.4		-2.708	0.065	-0.080	2.035	0.56
Watling's Blue Hole										
WBH-2005	21.30	0.00	0.276	2.218		-3.734	0.963	0.819	3.838	1.59
Ink Well Blue Hole										
IW-2005	3.71	21.82		2.848		-2.589	0.223	0.079	1.976	0.39
Crescent Top Cave										
CT-2005	28.28		0.437	2.091		-2.687	-0.045	-0.190	1.859	1.92
Crescent Pond										
CP-2005	30.41		0.460	2.079		-3.727	0.895	0.715	3.665	-0.40
Over Bridge Wells										
OBW-1-2005	0.31	73.75	0.159	4.015		-2.514	0.442	0.297	2.259	10.73
OBW-2-2005	0.37	23.50	0.169	5.048		-2.415	0.658	0.514	2.668	10.79
North Point Well										
NP-2005	0.20	60.56	0.159	1.799		-2.633	0.293	0.149	1.439	1.08
Six Pack Pond										
SPP-2005	38.72	0.00	0.590	2.523		-3.629	0.902	0.757	3.738	1.21

Appendix 4. Water chemistry of samples collected in June 2006.

Samples	Depth (m)	pH	Cond. (mS/cm)	Temp. (C)	Salinity (psu)	Na⁺ (mM)	K⁺ (mM)	Mg²⁺ (mM)	Ca²⁺ (mM)	Cl⁻ (mM)	Br⁻ (mM)
Majors Cave											
MC-0-2006	0.1	8.00	3.17	24.3	1.80	22.97	0.71	2.16	1.17	23.06	0.032
MC-1-2006	0.1	7.84	11.75	24.2	7.60	93.16	2.32	9.54	2.77	104.22	0.152
MC-2-2006	0.3	7.78	29.40	24.1	20.30	242.81	4.94	27.65	6.21	269.42	0.393
MC-3-2006	0.4	7.76	38.70	24.1	27.80	330.26	6.99	38.62	8.19	390.44	0.584
MC-4-2006	0.5	7.78	41.40	24.1	30.00	347.54	7.09	40.81	8.52	420.86	0.614
MC-5-2006	1.0	7.72	42.70	24.1	31.00	355.73	7.48	41.31	8.48	424.49	0.637
MC-6-2006	1.5	7.59	43.00	24.1	31.10	356.60	7.54	41.65	8.60	414.36	0.633
BN-0-2006	0.1	7.64	38.30	24.1	27.40	323.68	6.79	37.85	7.96	366.00	0.533
BN-1-2006	0.3	7.65	40.60	24.1	29.20	336.82	7.26	39.51	8.11	387.44	0.599
BN-2-2006	0.5	7.61	42.00	24.1	30.30	354.67	7.46	41.15	8.39	402.66	0.598
BN-3-2006	1.0	7.57	43.00	24.2	31.10	362.22	7.50	41.91	8.62	411.63	0.616
BN-4-2006	2.0	7.54	43.40	24.2	31.50	367.88	7.77	42.69	8.71	415.70	0.609
Crescent Top Cave											
CT-2006	0.1	7.55	53.40	26.6	40.10	456.32	9.87	53.80	10.28	541.72	0.841
Crescent Pond											
CP-2006	0.1		50.30	32.4	37.50	437.97	9.54	51.13	9.73	499.55	0.772
GRC Wells											
GRC-1-2006	0.1	7.39	1.43	27.4	0.50	4.54	0.14	2.07	2.01	7.46	
GRC-1PT-2006	0.1	7.40	1.40	27.3	0.50	4.59	0.15	2.14	1.98	7.38	
GRC-2PT-2006	0.1	7.27	1.55	26.7	0.60	5.75	0.16	2.35	2.03	9.18	
Museum Well											
MW-2006	0.1	7.37	2.12	27.3	0.90	10.58	0.26	1.59	1.76	15.84	
North Victoria Well											
NVH-2006	0.1	7.48	15.15	26.5	10.00	112.75	1.97	13.00	3.85	128.18	0.191
GRC Catchment											
Catchment-2006	0.1	9.18	0.07	30	0.00	0.12	0.01	0.03	0.03	0.09	

Appendix 4. cont.

Samples	SO₄²⁻ (mM)	SiO₂(aq) (uM)	B(OH)₃(aq) (mM)	Alk. (meq/L)	DIC (meq/L)	Log PCO₂	SI_cal (log Q/K)	SI_arag (log Q/K)	SI_dol (log Q/K)	% Charge Error
Majors Cave										
MC-0-2006	0.91		0.060	3.030	2.31	-2.82	0.27	0.13	2.00	4.27
MC-1-2006	4.81		0.121	2.712	2.67	-2.78	0.19	0.05	2.12	1.56
MC-2-2006	12.64		0.187	2.775	2.87	-2.79	0.28	0.13	2.41	3.10
MC-3-2006	19.81		0.283	2.823	2.88	-2.80	0.30	0.16	2.49	-0.25
MC-4-2006	21.50		0.309	2.804	2.83	-2.83	0.32	0.18	2.54	-1.55
MC-5-2006	21.62		0.310	2.808	2.84	-2.77	0.26	0.11	2.42	-0.89
MC-6-2006	20.90		0.316	2.877		-2.63	0.15	0.01	2.20	0.65
BN-0-2006	18.34		0.267	2.940	3.09	-2.66	0.20	0.06	2.29	2.12
BN-1-2006	19.33		0.243	2.925		-2.67	0.21	0.06	2.31	1.26
BN-2-2006	20.17		0.263	2.809		-2.66	0.15	0.01	2.21	1.81
BN-3-2006	20.65		0.263	2.881		-2.60	0.13	-0.01	2.17	1.73
BN-4-2006	20.90		0.266	2.857	3.83	-2.58	0.10	-0.04	2.11	2.06
Crescent Top Cave										
CT-2006	28.43		0.407	2.569	2.62	-2.65	0.12	-0.03	2.18	-0.62
Crescent Pond										
CP-2006	25.59		0.373	2.351	1.84					
GRC Wells										
GRC-1-2006	0.43			4.316	4.88	-2.01	0.19	0.05	1.60	0.91
GRC-1PT-2006	0.43		0.058	4.841	5.30	-1.96	0.26	0.11	1.75	-0.41
GRC-2PT-2006	0.47		0.054	4.787	5.06	-1.84	0.11	-0.03	1.48	-0.83
Museum Well										
MW-2006	0.63		0.049	4.365	4.33	-1.98	0.10	-0.05	1.35	-10.28
North Victoria Well										
NVH-2006	6.35		0.120	3.465	4.34	-2.30	0.09	-0.06	1.92	1.45
GRC Catchment										
Catchment-2006	0.01		0.043	4.999	0.44	-4.741	-0.675	-0.819	-0.033	-43.56