CHARACTERIZATION OF SALINITY SOURCES IN SOUTHWESTERN BANGLADESH EVALUATED THROUGH SURFACE WATER AND GROUNDWATER GEOCHEMICAL ANALYSES

By

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TABLE OF CONTENTS

Page

Chapter

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

This water resource investigation was designed to identify the source of surface water and groundwater salinity in a polder in southwestern Bangladesh through geochemical analyses. A polder is a tidal island located close to or below sea level surrounded by brackish water. Inhabitants of southwest Bangladesh have constructed earthen embankments along perimeters of polders to protect life, livestock, and agriculture resources from tidal and monsoonal inundation. In the following I discuss drinking water resources in this setting.

Drinking Water

Surface Water Ponds

Inhabitants of southwest Bangladesh collect meteoric water during the wet season into ponds (reservoirs) excavated by hand into surface soils. The stored water is rationed until the beginning of the next wet season for domestic purposes, including; drinking, cooking, and cleaning. In direct response to the domestic function that these fresh water ponds serve, they are universally contaminated with microbial pathogens and anthropogenic pollutants (Michael and Voss, 2009). Non-government organizations have intermittently provided pond sand filters (PSFs) to rural communities in southwest Bangladesh to filter microbial agents from freshwater ponds. Unfortunately, most PSFs are poorly maintained and tend to become non-operational shortly after construction.

Tube Wells

The presence of biological pathogens in fresh water ponds drives inhabitants of southwest Bangladesh to bacteria-free groundwater resources. Groundwater is the primary source of drinking water for more than 97% of the population in Bangladesh (Michael and Voss, 2009). The groundwater resource within the shallow aquifer in southwest Bangladesh is harvested through tube wells. Tube wells are constructed using 2-inch diameter well pipe and screened within the shallow aquifer. Tube wells are completed at the surface with a hand-pumped well cap. Unfortunately, groundwater in southwest Bangladesh has higher salinity and arsenic levels than surface water ponds. Previous hydrochemical analysis reveals that drinking water salinity in southwest Bangladesh, as measured by electrical conductivity, ranges from 962 to 9,370 microsiemens per centimeter (µS/cm) (Bahar and Reza, 2010), equivalent to salinities of 0.47 to 5.24 ppt (for reference, seawater is 35 ppt).

When consumed, salinities higher than 3.25 ppt (Davis and DeWiest, 1966) can cause undesirable effects like renal failure, kidney disease, and gastrointestinal irritation (Plunkett, 1976). Arsenic is a carcinogen to humans (World Health Organization, 2008) and exposure in drinking water can increase the risk of skin cancer and lead to skin lesions (keratosis, hyperpigmentation, hypopigmentation) (Tondel et al., 1999).

Effects of Land Use

Historically, land use has been dominated by rice cultivation on the polders in southwest Bangladesh. Beginning in 1985, land cover has experienced a strong shift from smallholder subsistence rice farming to extensive brine shrimp farming (Ali, 2006). The change in land use is driven by economics (Ali, 2006): shrimp farming can yield a landowner 12 times the amount of money per hectare as rice farming (Shang et al., 1998).

Brine shrimp ponds are constructed into surface soils and are generally located adjacent to tidal channels containing brackish water to facilitate the diversion of saline water into and out of the ponds. It is common practice in southwest Bangladesh to rotate land use between rice farming and shrimp farming (Azad et al., 2009). Rice is harvested within the wet season while shrimp are produced during the dry season. Discharge of saltwater during seasonal change-out can cause salination of adjoining rice and other agricultural lands (Azad et al., 2009).

In this study I attempted to measure concentrations of dissolved salts and arsenic in drinking water sources (freshwater ponds and tube wells), irrigation water from rice paddies, and potential salt sources (tidal channels and brine shrimp ponds). A companion study will characterize the composition of meteoric water and water in inland stream channels. The objective was to evaluate the extent of salt and arsenic contamination in drinking and agricultural water and to identify the source(s) of these contaminants. Companion studies focus on water composition baselines (from the adjacent undeveloped Sunderbans mangrove forest), groundwater flow models, water security, environmental migration, land use, sediment budgets and the effects of sea level rise.

CHAPTER II

SITE DESCRIPTION

Site Location

The investigated site is located within the Bengal Basin of India and Bangladesh on the Ganges Delta about 30 km south of Khulna, Bangladesh and about 60 km north of the Bay of Bengal (**Figure 1**).

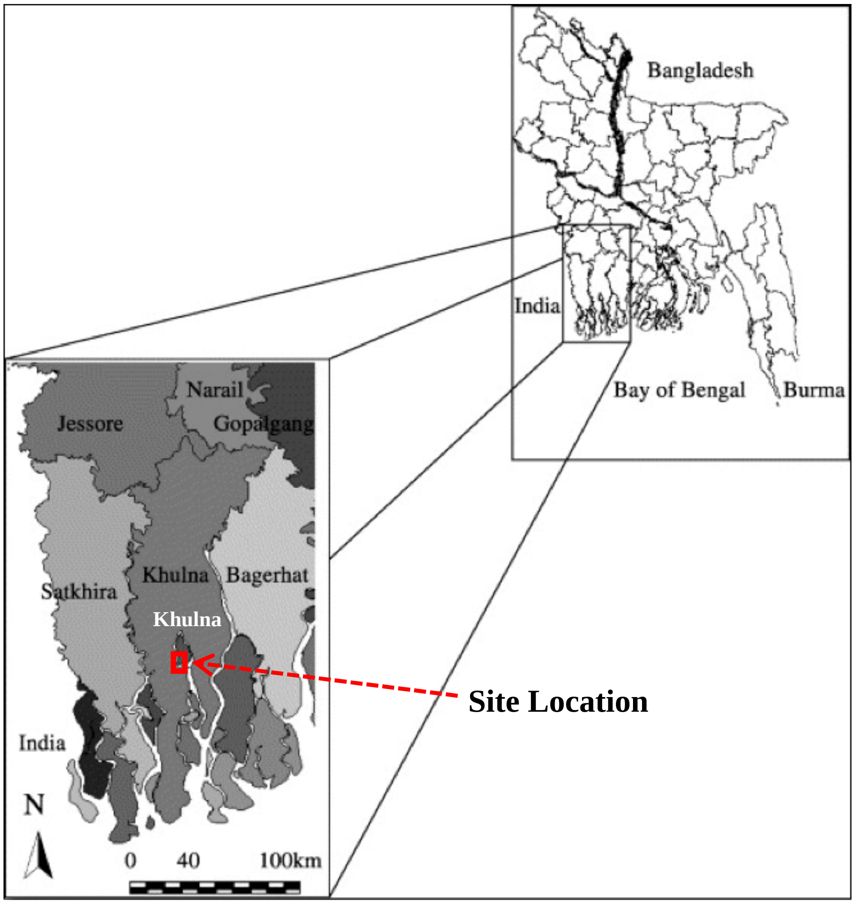

Figure 1. Site location map (Salam et al., 2003). Provincial names in black. City names in white.

The site is approximately 17 km long and 7 km wide with approximately 120 km^2 of surface area and is identified as Polder 32 (**Figure 2**). Four main tidal channels containing brackish water surround Polder 32. A review of **Figure 2** shows that three of the four surrounding tidal channels encroach onto Polder 32's land surface in multiple locations; the Dhaki River in the north and northwest, the Nalian River in the southeast, and the Sibsar River in the west and southwest. Examination of **Figure 2** also reveals that surface plots of land appear to be filled with water and are concentrated in areas adjacent to tidal channels at the perimeter and in the interior of Polder 32. These plots of land may be used for agriculture and/or aquaculture.

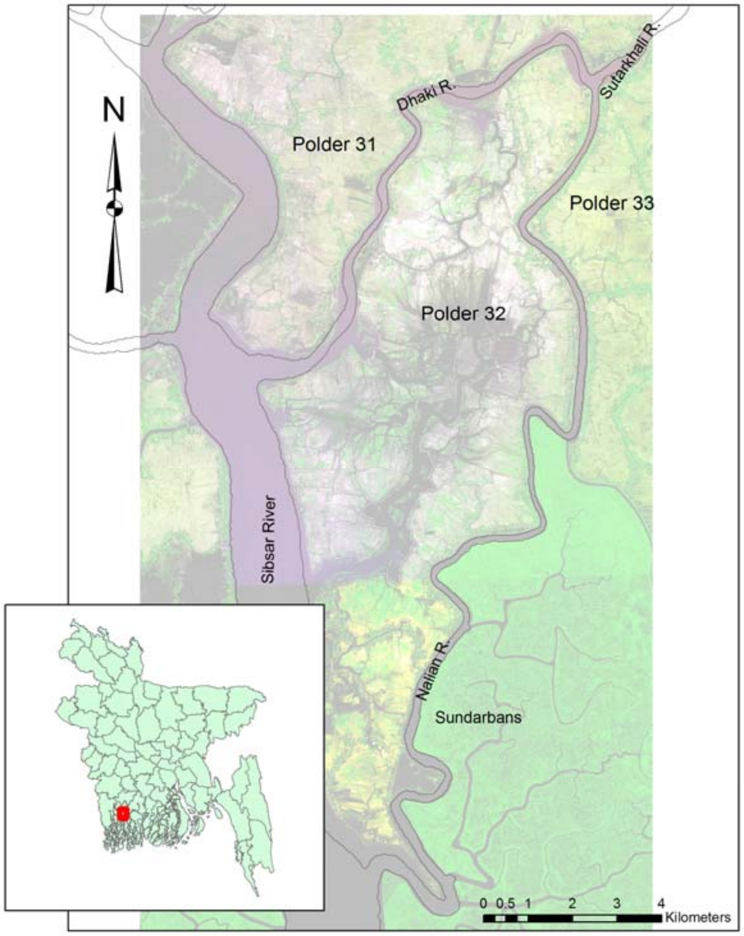

Figure 2. Site-specific map of Polder 32 (GeoEye satellite imagery, February 9, 2012).

Climate

Southwest Bangladesh experiences a humid, biseasonal climate (Nobi and Gupta, 1997) with a dry season from November to May and wet season from June to October. The South Asian Monsoon is active during the wet season (Michael and Voss, 2009), when about 90% of the annual rainfall in southwest Bangladesh occurs (Nobi and Gupta, 1997). Annual rainfall ranges from 1,500 mm to 2,100 mm (Nobi and Gupta, 1997). Tropical cyclones typically form over the Bay of Bengal during the transitional monsoon months of May and November (Singh et al., 2000). The tropical cyclone frequency in the Bay of Bengal has a prominent El Niño-Southern Oscillation cycle of 2 to 5 years during the wet season and transitional monsoon months (Singh et al., 2000).

Cyclone Aila

Cyclone Aila formed within the northern Indian Ocean and made landfall over southwest Bangladesh on May 25, 2009 (Dasgupta et al., 2011). Aila hit the north coast along the Bay of Bengal during high tide and maintained cyclonic intensity for approximately 15 hours after making landfall (Dasgupta et al., 2011). Tidal surges from Cyclone Aila reached 6.5 m in height and breached more than 1,742 km of embankments over 11 southwest Bangladesh coastal districts (Dasgupta et al., 2011), including Polder 32. Google Earth satellite imagery shows that portions of Polder 32 remained inundated with water post Cyclone Aila through February, 2011. One objective of this study was to evaluate whether inundation leads to later salination of soil and water in rice paddies.

Geology

The Bengal Basin is bounded by the Himalayas to the distant north, the Shillong Plateau to the immediate north, the Indo-Burman ranges to the east, the Indian Craton to the west, and the Bay of Bengal to the south (Shamsudduha and Uddin, 2007) (**Figure 3**). The basin is a major depositional center of sediments from the Himalayan and Indo-Burman ranges drained by the Ganges, Brahmaputra, and Meghna rivers (Shamsudduha and Uddin, 2007) and is filled with approximately 5 x 10^5 km^3 of sediments (Johnson, 1994). Types of deposits within the Bengal Basin include alluvial, deltaic, and marine as well as river avulsion and overbank flood deposits. Sediments occur in a continuous vertical sequence from land surface extending to depths of several kilometers in the south, or to tens of meters or less near the margins of the basin and in areas with shallow basement bedrock (Michael and Voss, 2009). Deposition resulted in a highly stratified fabric consisting of laterally extensive layers of sand, silt, and clay (Michael and Voss, 2009; Shamsudduha et al., 2011). Due to the high annual frequency of overbank flooding within the Bengal Basin, the predominant surficial feature is a silt and clay cap that extends from the surface down to a depth of 10 m to 25 m (Shamsudduha et al., 2011) and is known as the Madhupur Clay (Shamsudduha et al., 2007). Polder 32 is mainly composed of floodplain and delta plain sequences (**Figure 3**).

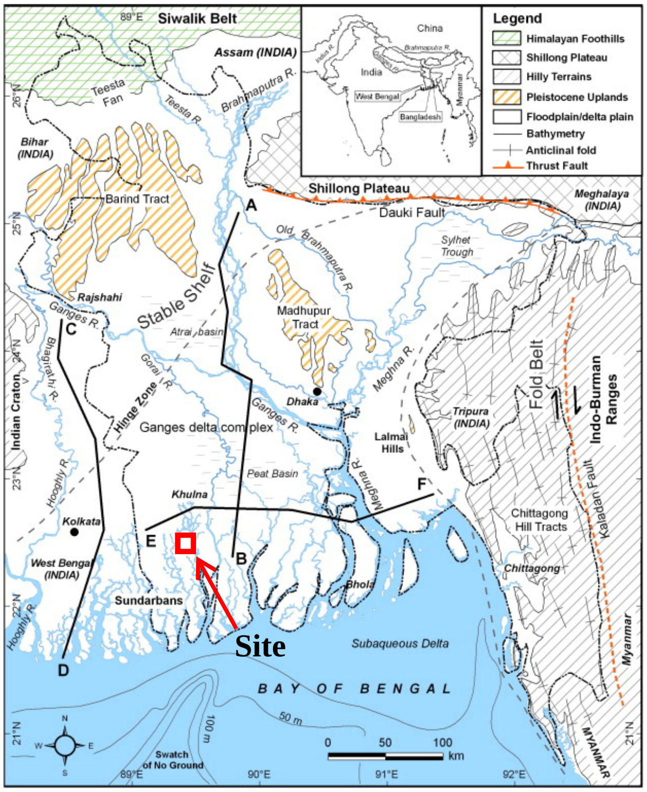

Figure 3. Quaternary geomorphic map (Shamsudduha and Uddin, 2007).

Polder 32 is located to the south of the E-F profile in **Figure 3**, between Satkhira and Khulna. Assuming the stratigraphy does not change significantly between Polder 32 and the E-F profile, we infer from **Figure 4** that with increasing depth beneath the surface Polder 32 sediments transition from the Madhupur Clay cap at the surface, to very fine to fine sand layers from depths of ~10 to 100 m below ground level (bgl), to medium to coarse sand / gravel layers from depths of ~100 to 140 m bgl, confined by clay and silt layers from depths of ~140 to 150 m bgl.

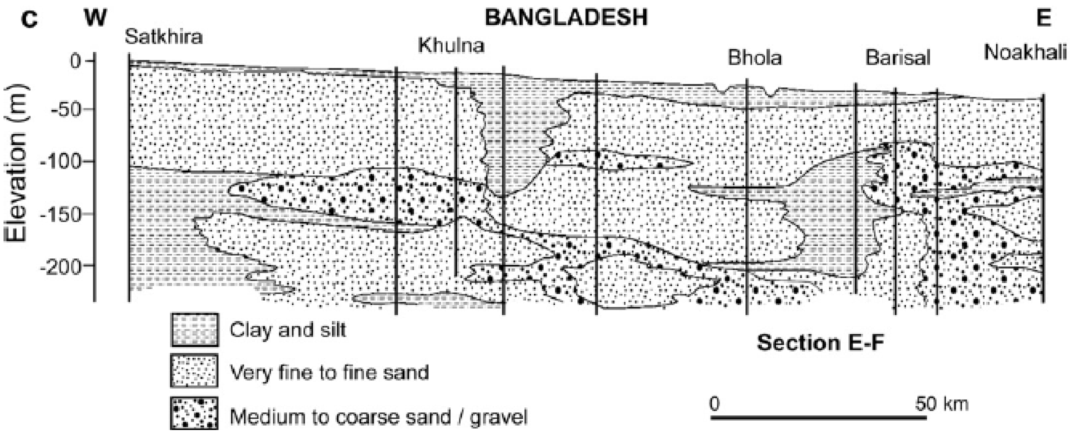

Figure 4. Geologic cross section E-F (Shamsudduha and Uddin, 2007). In sectional view, Polder 32 is roughly projected equidistant between Satkhira and Khulna landmarks.

Hydrogeology

Surface Water

The floodplain and delta plain in southwest Bangladesh are composed of a series of polders (islands) separated by a network of distributary tidal channels (Allison et al., 2003). Tidally forced seawater from the Bay of Bengal encroaches towards land twice daily. The saline front generated by the Bay of Bengal extends 100 km or more inland from the Bay of Bengal along the distributary tidal channels (Allison et al., 2003).

Groundwater

Groundwater occurs in unconsolidated alluvial, deltaic, and marine sediments of the Bengal Basin (Michael and Voss, 2009). Groundwater is available at depths less than 10 m bgl within unconsolidated deposits (MPO, 1987), with the water table mimicking surface topography (Ravenscroft, 2003). Groundwater and surface water gradients are to the south, toward the Bay of Bengal (Nobi and Gupta, 1997). Groundwater in the shallow aquifer occurs under confined conditions with the low permeability Madhupur Clay cap acting as a surficial aquitard (**Figure 4**). Groundwater aquifers at the Site are separated into two categories: (a) shallow within the upper 80 to 100 m bgl, and (b) deep at depths greater than 100 m bgl (Shamsudduha et al., 2011). This investigation focuses on the shallow aquifer, which is the primary source of drinking water on Polder 32.

Recharge

During the wet season in southwest Bangladesh, the potential for recharge from meteoric rainfall that could infiltrate through subsoil to the shallow aquifer is high. Potential groundwater recharge at Polder 32 is estimated from 201 to 300 mm per year (Shamsudduha et al., 2011). However, in southwest Bangladesh, the majority of potential recharge is rejected at the surface by the low permeability Madhupur Clay cap. Rejected recharge on the polders is distributed by overland flow toward surrounding tidal channels in the form of surface runoff. Actual recharge to the shallow aquifer through discontinuities within the Madhupur Clay cap is estimated from 10 to 50 mm per year (Shamsudduha et al., 2011).

CHAPTER III

METHODS

The source of salinity was identified through chemical analyses of water samples from the land surface and shallow aquifer at representative sampling sites on Polder 32. Sample and data collection took place at the end of the dry season from May 15 to 24, 2012 and at the end of the wet season from October 16 to 20, 2012.

Sampling Plan

Sampling and data collection occurred throughout the study area in the vicinity of the site locations identified in **Figure 2**. Sample locations were measured with an accuracy of 50 cm using a Trimble GeoXT 6000. Collected water samples were quantitatively analyzed for hydrochemistry. Five different water sources were sampled and characterized, including freshwater ponds (FP), shrimp ponds (SP), rice paddies (RP), and tidal channels (TC) from surface water sources and tube wells (TW) sourced from groundwater.

Surface Water

In total, 27 freshwater pond samples, 11 shrimp pond samples, 13 rice paddy water samples, and 12 tidal channel samples were collected (**Figure 5**). To record potential seasonal variability in composition of water from freshwater ponds, 11 of the October 2012 freshwater pond samples were sampled from May 2012 freshwater pond sample sites. Indicative of seasonal land use, shrimp pond samples were exclusively available during the dry season and rice paddy samples were only present during the wet season; 11 shrimp pond samples were collected in May 2012 and 13 rice paddy samples were collected in October 2012. Of the 13 rice paddy wet-season samples collected, 7 rice paddy sample sites were shrimp pond sample sites during the previous dry season of May 2012. Five tidal channel samples were collected in May 2012 and 7 tidal channel samples were collected in October 2012.

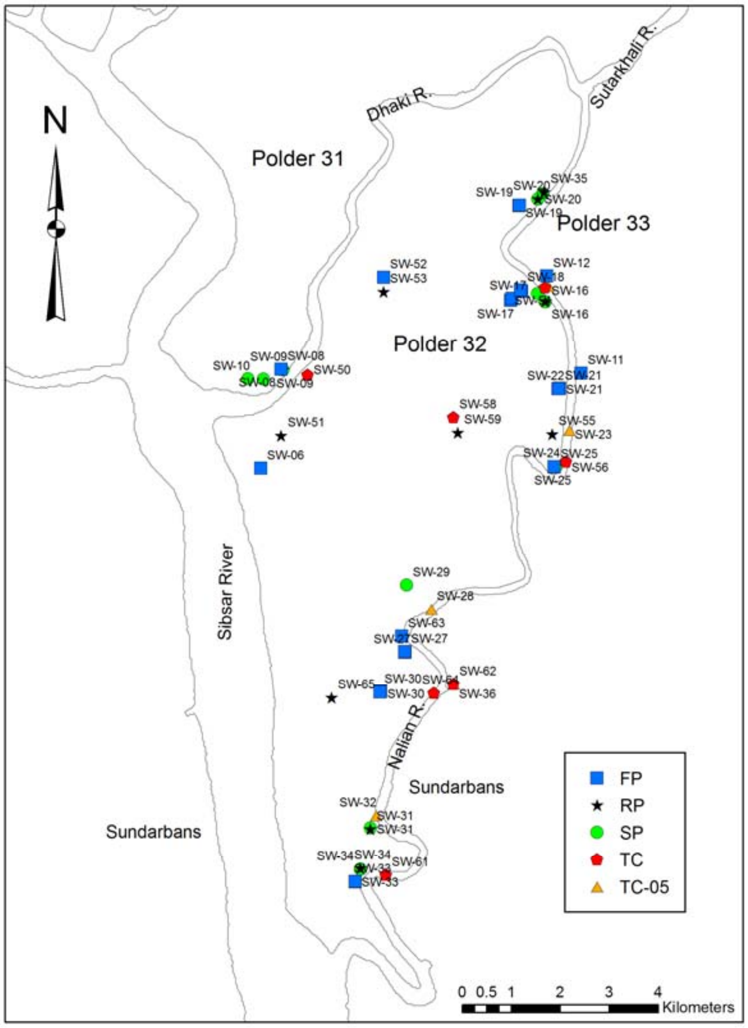

Figure 5. Surface water (SW) sample locations. FP = freshwater ponds, RP = rice paddies, SP = shrimp ponds, TC = October 2012 tidal channels, and TC-05 = May 2012 tidal channels.

Groundwater

In total, 54 tube well samples were collected over the dry and wet seasons (**Figure 6**); 33 tube well samples during May 2012 and 21 tube well samples during October 2012. To record potential seasonal variability in composition, 17 tube well samples from the October 2012 sampling event were also collected from May 2012 tube well sampling sites. Due to access constraints, not all tube wells sampled in May 2012 were re-sampled in October 2012. Tube well samples were collected from screened well depths ranging from 15 m to 52 m below ground level (bgl).

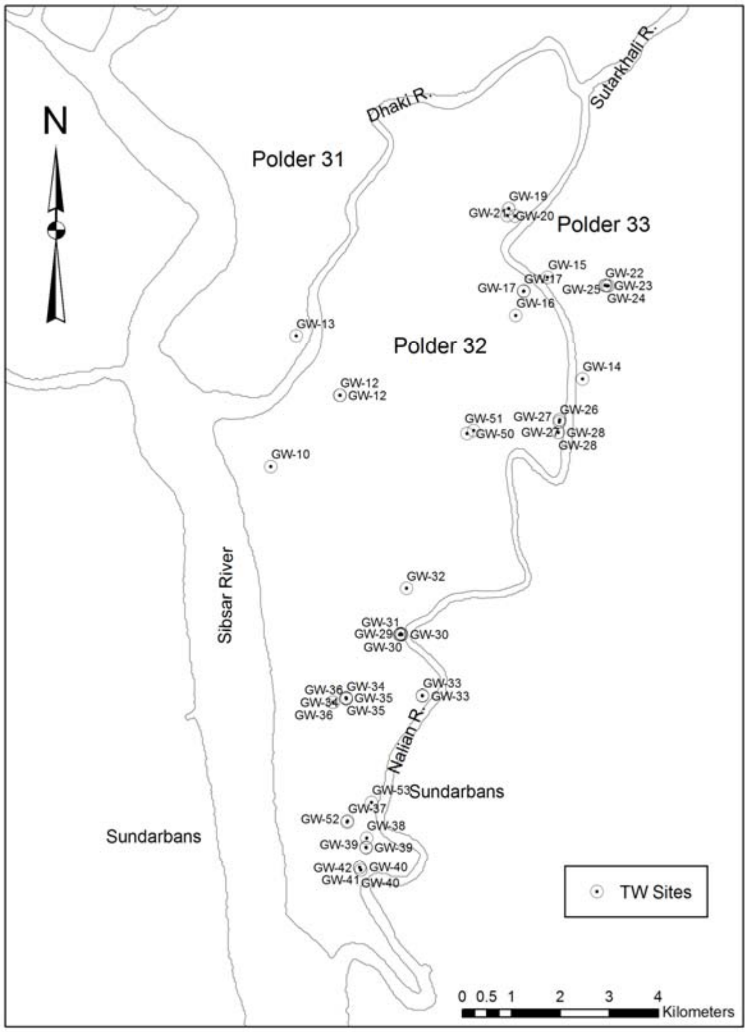

Figure 6. Groundwater (GW) sample locations. TW = tube wells.

Geochemical Analyses

Water samples were collected in the field in 1 liter (L) plastic bottles. A portable water-laboratory Hydrolab MiniSonde 4a (Hydrolab) was used to measure physical parameters of water samples including Eh oxidation-reduction potential in millivolts (mV), pH, temperature in degrees Celsius (˚C), and specific conductivity (SpC) in microsiemens per centimeter (µS/cm).

Prior to the May 2012 sampling event, the Hydrolab was calibrated on April 26, 2012 by the manufacturer for Eh, pH, temperature, and SpC. During the May 2012 sampling event, the Hydrolab was field-calibrated daily for pH and SpC using wet standards of pH = 4.01, pH = 7.01, pH = 10.01, and SpC = 1,000 µS/cm.

Similarly, prior to the October 2012 sampling event, the Hydrolab was calibrated on September 28, 2012 for pH and SpC employing standards set forth in the Hydrolab User Manual. Again, during the October 2012 sampling event, the Hydrolab was field-calibrated daily for pH and SpC using wet standards of pH = 4.01, pH = 7.01, pH = 10.01, and SpC = 1,000 µS/cm.

An Eh linear drift correction was applied to October 2012 Eh data. The Hydrolab was calibrated for Eh on December 11, 2012. The change in Eh (ΔEh), as compared to wet standards, was measured between April 2012 and December 2012 calibration events. An Eh drift correction value of -36 mV was applied to October 2012 data utilizing the following equation:

$$Eh\ drift\ correction = (\Delta Eh / d_1) * d_2$$

where; d_1 = days between April 2012 and December 2012 calibration events and d_2 = days between April 2012 calibration event and October 2012 sampling event.

All field values of SpC were normalized / corrected to 25˚C utilizing theory on specific conductance from Miller et al. 1988:

$$k_{25} = k_T / [1+0.0191(T-25)]$$

where; k_{25} = specific conductivity in µS/cm normalized to 25˚C, k_T = in-field measured SpC in µS/cm, and T = in-field measured temperature in ˚C.

Dry Season

Sixty milliliters (mL) of each water sample was withdrawn through a filtered syringe and placed in a sample bottle. One drop of concentrated nitric acid (HNO_3^-) was added as a preservative. Samples were analyzed for metal cation concentrations using inductively coupled plasma optical emission spectrometry (ICP-OES), anion concentrations using ion chromatography (IC), and organic carbon concentrations using a total organic carbon (TOC) analyzer.

Wet Season

Thirty mL of each water sample was withdrawn through a filtered syringe and placed in a sample bottle. One drop of HNO_3^- was added as a preservative. Samples were analyzed for metal cation concentrations using ICP-OES.

Additionally, 60 mL of each water sample was withdrawn through a filtered syringe and placed in a sample bottle. These unpreserved samples were analyzed for anion concentrations using IC, and organic and inorganic carbon concentrations using a TOC analyzer.

Analytical Methods

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Aqueous samples were analyzed using a Varian ICP Model 720-ES ICP-OES utilizing Environmental Protection Agency (EPA) Method 6010B. Instrument settings included plasma gas flow at 15 liters per minute (L/min), radio frequency power at 1.2 kilowatts (kW), and nebulizer flow of 0.75 L/min. Five-point standard curves were used for an analytical range between approximately 0.1 milligrams per liter (mg/L) and 25 mg/L for trace metals and approximately 0.1 mg/L and 500 mg/L for minerals. Analytical blanks and analytical check standards at approximately 0.5 mg/L were run every 20 samples and required to be within 15% of the specified value. Samples for analysis were diluted gravimetrically to within the targeted analytical range using 1% volume-volume (v/v) Optima grade nitric acid (Fisher Scientific) if the maximum calibration was exceeded. Yttrium at 10 mg/L was used as the internal standard.

Ion Chromatography (IC)

Analyses of anions were performed on a Metrohm 881 Compact IC pro employing American Society for Testing and Materials (ASTM) Method D-4327-03. Seven-point calibration curves were generated by dilution of a multi-anion standard at 500x, 200x, 100x, 50x, 10x, 2x, and 1x and were accepted with a correlation coefficient of at least 0.995. An analytical blank and check standard at approximately 10 times the dilution of the standard was run every 20 samples. The standard was required to be within 15% of the specified value. A volume of approximately 10 milliliters (mL) of undiluted sample was loaded for analysis. Samples for analysis were run at 0.7 milliliters per minute (mL/min) using an eluent of 3.2 millimoles (mmol) sodium carbonate per 1.0 mmol sodium bicarbonate. Samples were diluted automatically to within the targeted analytical range using Milli-Q water if the maximum calibration was exceeded.

Total Organic Carbon (TOC) Analyzer

Analyses of organic and inorganic carbon were performed on a Shimadzu model TOC-V CPH/CPN using ASTM Method D-7573-09. The TOC furnace run at 680 °C and zero air, at 150 mL/min, was used as the carrier gas. Five-point calibration curves, for both dissolved inorganic carbon (DIC) and non-purgeable dissolved organic carbon (DOC) analyses, were generated for an analytical range between 5 parts per million (ppm) and 100 ppm and were accepted with a correlation coefficient of at least 0.995. An analytical blank and check standard at approximately 10 ppm was run every 20 samples. The standard was required to be within 15% of the specified value. A volume of approximately 20 mL of undiluted sample was loaded for analysis. DIC analysis was performed first for the analytical blank and standard and then the samples. DOC analysis was carried out separately after completion of DIC analysis. DOC analysis started with addition of 2 Molar (M) hydrochloric acid to achieve a pH of 2 along with a sparge gas flow rate of 50 mL/min to purge inorganic carbon prior to analysis. Samples for analysis were diluted automatically to within the targeted analytical range using Milli-Q water if the maximum calibration was exceeded.

Quality Assurance / Quality Control

The neutrality of surface water and groundwater samples from October 2012 was evaluated through charge-balance error of cations and anions (**Tables 4** and **8**). Charge-balance errors for surface water samples average 3.15% (**Table 4**). Similarly, charge-balance errors for groundwater samples average 4.18% (**Table 8**). Analysis of May 2012 NO_3^- and HCO_3^- concentrations for surface water and groundwater samples was compromised due to addition of HNO_3^- as a preservative (i.e., unpreserved samples were not collected in May 2012). Therefore, results for May 2012 NO_3^- and HCO_3^- concentrations are not used in the project's data analysis nor can charge-balance errors be determined for the dry season samples.

To verify quality of geochemical analyses, duplicate sample sites were randomly selected from dry and wet season sampling events. A total of four duplicate samples were collected in the field and analyzed, as described above, using ICP-OES, IC, and TOC analyzer. The average standard deviation of duplicate samples from original samples across all analyses is 5.2%. Furthermore, sample blanks, consisting of deionized water were collected in-field from dry and wet season sampling events employing the above sampling procedures. A total of four blank samples were analyzed, as described above, using ICP-OES, IC, and TOC analyzer. Analytical results of blank sample concentrations were consistently below detection limits, indicative of deionized water.

CHAPTER IV

RESULTS

Field Observations

Sample and data collection took place at the end of the dry season and at the end of the wet season in 2012. Field analysis during southwest Bangladesh's two distinct seasons was critical to understand the relationship between Polder 32's land use and biseasonal climate. Moreover, in-field examination of the connection between tidal channels and land use practices was necessary to characterize the source of salinity in surface water and groundwater.

Surface Water

Figures 7 and **8** validate the seasonal shift in land use practice from brine shrimp farming to rice farming. Shrimp ponds dominate the landscape during the dry season (**Figure 7**) while rice paddies occupy land surface plots during the wet season (**Figure 8**).

Figure 7. Photo (5/16/12). Shrimp ponds during dry season.

Figure 8. Photo (10/16/12). Rice paddies during wet season. Note irrigation canal in foreground.

Field reconnaissance on Polder 32 confirmed two important pre-field observations; the tidal channels that surround Polder 32 encroach onto the land's surface through smaller distributary channels (**Figure 9**) and plots of land adjacent to tidal channels are developed for brine shrimp and rice farming (**Figure 10**). Field analysis also confirmed the direct relationship between the Polder's perimeter tidal channels and land use practices. Sluice gates are constructed through multiple locations of the embankment that separates Polder 32's land surface from the surrounding tidal channels (**Figure 11**); gates are opened in high tide to allow tidal channel water to fill irrigation canals that support shrimp and rice farming and later opened again during low tide to flush spent aquaculture and agriculture water from the land's surface. Field work also provided an opportunity to evaluate the stability of the earthen embankments that surround Polder 32. Even outside monsoon season, failures within the embankment are common, allowing direct communication between tidal channels and agricultural land until the compromised section can be repaired (**Figure 12**).

Figure 9. Photo (10/15/12). Tidal channel encroaching onto Polder 32's land surface from Sibsar River in background.

Figure 10. Photo (5/14/12). Shrimp pond developed inside earthen berm (right side of photo) and adjacent to Dhaki River in background.

Figure 11. Photo (5/19/12). A sluice gate constructed through Polder 32 embankment. Photo taken from inside of Polder 32 looking towards Nalian River beyond embankment.

Figure 12. Photo (Laura Benneyworth, 10/19/12). Embankment breach between a rice paddy and tidal channel (Nalian River). Photo taken from boat on Nalian River during low tide looking towards Polder 32.

An additional in-field observation made was the lack of control provided to freshwater ponds against biological pathogens and anthropogenic pollutants. In many instances, there were no measures to protect against direct contact to freshwater ponds from humans and animals (**Figure 13**).

Figure 13. Photo (10/19/12). Freshwater ponds (foreground and background) exposed to human and animal pollutant sources.

Groundwater

Pollution of freshwater resources drives inhabitants of Polder 32 to bacteria-free groundwater resources. An exhaustive well search was conducted over dry and wet season field endeavors; 37 different tube wells were located over the 120 km^2 of Polder 32's land surface. This field study was not able to identify any maintenance oversight for the tube wells. Furthermore, it was determined that some of the tube wells are privately owned. Based on field observations, some of Polder 32's inhabitants travel great lengths (more than 5 km in some instances) to access groundwater for drinking and other potable uses from tube wells (**Figure 14**).

Figure 14. Photo (5/15/12). A Polder 32 inhabitant accesses the shallow groundwater resource through a hand-pumped tube well.

Geochemical Analyses

Surface Water

Analytical results include physical parameters (**Table 1**), metal cation concentrations (**Table 2**), anion and DOC concentrations (**Table 3**), and charge imbalance and water types (**Table 4**). Labels for rice paddies and shrimp ponds are seasonally dependent, as shrimp pond samples were exclusively available during the dry season and rice paddy samples were only present during the wet season. To seasonally differentiate dry season and wet season tidal channel samples, tidal channel samples collected in May 2012 during the dry season are labeled TC-05.

Table 1. Physical parameters of surface water samples.

Table 1. Physical parameters of surface water samples (*1 of 2*)

Location	Date	Type	Temp (°C)	Eh (mV)	pH	Corr SpC (uS/cm)	Salinity (ppt)
SW-06	5/15/2012	FP	34.62	436	8.06	1,554	0.78
SW-08	5/17/2012	FP	31.13	395	7.69	1,579	0.79
SW-11	5/18/2012	FP	32.73	397	7.39	1,124	0.56
SW-12	5/18/2012	FP	35.85	396	8.45	844	0.41
SW-17	5/19/2012	FP	33.45	365	7.37	1,916	0.97
SW-18	5/19/2012	FP	34.32	350	7.10	1,942	0.99
SW-19	5/20/2012	FP	31.79	411	8.14	1,661	0.84
SW-21	5/21/2012	FP	33.10	414	7.45	1,432	0.72
SW-22	5/21/2012	FP	33.01	415	7.55	1,432	0.72
SW-25	5/21/2012	FP	37.96	415	7.88	3,484	1.83
SW-27	5/22/2012	FP	33.45	433	7.28	2,517	1.29
SW-30	5/23/2012	FP	31.79	410	8.73	1,770	0.89
SW-33	5/24/2012	FP	31.00	444	7.94	7,299	4.01
SW-06	10/16/2012	FP	31.78	360	8.66	1,121	0.81
SW-07	10/16/2012	FP	29.60	363	8.64	4,725	3.28
SW-08	10/16/2012	FP	30.16	348	8.60	1,284	0.90
SW-12	10/17/2012	FP	31.43	372	8.83	1,592	1.14
SW-17	10/17/2012	FP	32.86	305	8.61	1,939	1.43
SW-18	10/17/2012	FP	32.62	261	8.95	1,518	1.11
SW-19	10/17/2012	FP	29.82	378	8.62	1,407	0.98
SW-21	10/18/2012	FP	29.94	379	8.07	1,119	0.78
SW-25	10/18/2012	FP	30.08	286	8.97	1,705	1.20
SW-27	10/20/2012	FP	30.40	266	8.20	1,701	1.19
SW-30	10/20/2012	FP	32.26	336	8.64	1,289	0.94
SW-33	10/19/2012	FP	32.78	275	9.21	2,159	1.59
SW-52	10/16/2012	FP	32.01	349	8.97	1,239	0.90
SW-63	10/20/2012	FP	29.10	218	8.53	1,756	1.21
SW-09	10/16/2012	RP	28.55	356	8.17	3,665	2.51
SW-16	10/17/2012	RP	37.75	322	9.45	537	0.43
SW-20	10/17/2012	RP	29.22	391	8.01	1,605	1.11
SW-24	10/18/2012	RP	30.39	295	8.61	1,318	0.93
SW-31	10/19/2012	RP	30.68	244	8.24	1,800	1.28
SW-34	10/19/2012	RP	33.44	261	9.25	2,095	1.56
SW-35	10/17/2012	RP	28.49	393	8.31	773	0.50
SW-51	10/16/2012	RP	33.62	309	8.72	1,345	0.99
SW-53	10/16/2012	RP	30.49	349	8.19	600	0.49
SW-55	10/18/2012	RP	29.27	228	8.06	1,823	1.26
SW-59	10/18/2012	RP	32.49	333	8.89	3,788	2.77
SW-60	10/18/2012	RP	32.49	333	8.89	3,788	2.77
SW-65	10/20/2012	RP	32.50	259	8.58	1,173	0.86
SW-07	5/17/2012	SP	30.24	419	8.35	28,485	17.54
SW-09	5/17/2012	SP	30.63	434	8.23	25,312	15.41
SW-10	5/17/2012	SP	32.23	445	7.68	22,246	13.38
SW-14	5/19/2012	SP	31.65	430	8.58	18,786	11.13
SW-16	5/19/2012	SP	33.43	449	8.03	27,560	16.91
SW-20	5/20/2012	SP	34.02	459	7.94	26,081	15.92
SW-24	5/21/2012	SP	39.24	451	8.02	21,822	13.10
SW-29	5/22/2012	SP	34.81	473	8.33	18,741	11.10
SW-31	5/23/2012	SP	35.86	426	8.11	29,598	18.29
SW-34	5/24/2012	SP	31.44	474	7.33	31,453	19.56
SW-35	5/20/2012	SP	31.37	468	7.60	27,536	16.90
SW-13	5/18/2012	TC-05	32.62	457	6.36	27,661	16.98
SW-23	5/21/2012	TC-05	32.45	461	7.31	28,613	17.62
SW-28	5/22/2012	TC-05	32.64	496	7.24	29,302	18.09
SW-32	5/23/2012	TC-05	32.25	415	7.37	27,135	16.63
SW-36	5/24/2012	TC-05	32.30	448	7.20	29,504	18.23

Table 1. Physical parameters of surface water samples (***2 of 2***)

Location	Date	Type	Temp (°C)	Eh (mV)	pH	Corr SpC (uS/cm)	Salinity (ppt)
SW-50	10/16/2012	TC	30.46	348	8.03	468	0.33
SW-54	10/17/2012	TC	31.76	333	8.34	400	0.29
SW-56	10/18/2012	TC	30.24	284	8.29	386	0.27
SW-58	10/18/2012	TC	33.15	282	8.89	710	0.53
SW-61	10/19/2012	TC	30.48	286	8.26	751	0.53
SW-62	10/19/2012	TC	29.96	329	8.30	722	0.51
SW-64	10/20/2012	TC	30.57	289	8.20	642	0.45

Table 2. Metal cation concentrations of surface water samples.

Table 2. Metal cation concentrations of surface water samples (*__1 of 2__*)

Location	Al (ug/L)	As (ug/L)	B (ug/L)	Ba (ug/L)	Ca (ug/L)	Fe (ug/L)	K (ug/L)	Mg (ug/L)	Mn (ug/L)	Na (ug/L)	P (ug/L)	S (ug/L)	Si (ug/L)	Sr (ug/L)
SW-06	63.7	7.1	86	68.0	56324	116.1	18107	39752	25	265368	12.6	50972	3581	313.6
SW-08	13.2	3.1	102	47.3	73132	7.1	20742	40682	8	247945	20.8	82632	4171	336.1
SW-11	36.6	13.1	45	96.2	58835	24.8	23505	34141	142	163440	162.6	30270	4202	267.9
SW-12	12.6	19.8	20	33.2	69527	18.4	27436	32806	21	92937	82.7	58570	6483	210.8
SW-17	7.4	8.9	146	99.2	44553	17.9	27622	43415	168	380085	96.7	66964	5496	304.4
SW-18	3.1	18.9	113	75.7	59682	19.0	20140	42497	73	369441	44.2	45577	5382	341.9
SW-19	12.9	49.1	59	93.0	88381	7.0	30291	35909	835	284452	1470.9	19508	18264	320.6
SW-21	11.2	9.2	74	57.7	51443	1.6	22217	36922	44	230233	59.2	57567	4454	280.4
SW-22	10.9	14.6	68	54.3	49333	2.6	21846	36932	112	228798	10.6	57279	4178	279.0
SW-25	16.2	11.9	208	82.1	90662	---	39135	88758	25	876163	23.9	75195	4125	643.2
SW-27	4.4	5.5	165	55.4	42071	1.9	29904	52912	2	552101	34.6	34265	2347	335.8
SW-30	0.3	16.6	94	74.6	39340	4.6	21509	32288	5	355820	20.4	38549	3065	244.6
SW-33	22.6	38.2	577	113.0	120319	10.7	92298	167702	452	2090340	124.1	173145	5552	1112.0
SW-06	18.8	5.7	102	44.6	45782	---	11097	25215	11	190139	10.2	37774	3264	216.6
SW-07	---	6.0	447	43.4	50149	---	42852	92891	35	892282	188.0	55762	---	560.1
SW-08	24.7	6.2	133	32.9	66701	---	13229	32545	1	195189	---	66169	3609	269.8
SW-12	35.2	3.9	100	40.9	105153	2.6	26031	50214	50	290312	19.3	93545	5480	312.5
SW-17	---	36.6	218	36.1	53959	3.3	16222	46819	2	344446	267.6	63874	2569	304.4
SW-18	26.4	9.5	112	46.5	63123	8.7	11929	33431	8	290939	11.8	33076	2900	290.5
SW-19	23.7	27.3	92	53.7	72564	---	19780	28586	120	251342	922.4	14596	16692	242.0
SW-21	15.8	7.8	112	37.3	42074	2.1	14072	28140	38	173437	21.9	46128	3298	211.1
SW-25	14.7	6.1	92	22.4	41689	4.6	10792	30164	3	316340	8.7	23927	2901	238.6
SW-27	14.1	11.4	169	33.3	30345	3.8	15922	32643	19	317017	20.3	22980	1859	207.6
SW-30	16.4	7.3	138	57.4	45354	2.3	13939	29458	17	219011	12.7	44007	3159	222.2
SW-33	13.3	8.4	280	51.2	59267	12.6	28217	48996	6	399610	73.0	71584	---	363.1
SW-52	22.2	12.2	115	49.2	57637	---	14371	32147	1	194550	78.8	53283	5298	234.4
SW-63	49.7	7.5	163	71.8	34841	2.8	23466	28164	8	367767	220.1	25466	3557	210.1
SW-09	---	14.9	510	40.0	49792	---	33271	68119	249	658717	---	39765	---	487.4
SW-16	63.8	5.1	80	22.0	31354	74.0	9548	16550	5	83575	12.6	11512	3884	185.6
SW-20	21.5	7.3	167	48.0	57115	3.0	16667	39178	138	258889	22.5	21909	2538	367.3
SW-24	16.5	3.4	142	40.2	35779	4.6	15282	28507	24	229266	18.9	14613	2645	242.9
SW-31	15.0	10.6	194	36.8	41928	2.5	19655	41395	9	324979	13.5	33895	2451	323.9
SW-34	44.3	39.4	235	56.7	49114	10.6	18553	48363	22	387091	5.8	26916	339	363.8
SW-35	11.5	2.2	128	43.9	30922	2.9	14500	25612	45	207658	5.3	13608	1474	204.8
SW-51	27.7	2.7	154	43.4	50702	8.5	13344	37580	3	255340	8.4	66230	678	296.2

Table 2. Metal cation concentrations of surface water samples (*2 of 2*)

Location	Al (ug/L)	As (ug/L)	B (ug/L)	Ba (ug/L)	Ca (ug/L)	Fe (ug/L)	K (ug/L)	Mg (ug/L)	Mn (ug/L)	Na (ug/L)	P (ug/L)	S (ug/L)	Si (ug/L)	Sr (ug/L)
SW-53	12.2	2.4	64	43.3	34493	---	7043	16586	15	110023	27.6	11893	4211	164.4
SW-55	18.6	10.7	197	47.0	56479	3.8	17037	45397	260	298538	36.4	55199	482	350.5
SW-59	18.8	4.7	301	74.9	106672	6.2	31296	91681	5	699854	41.4	143970	---	668.7
SW-60	6.9	2.5	295	75.1	105548	13.9	30916	89793	6	710657	28.9	142382	---	659.4
SW-65	17.4	3.0	110	37.5	42515	8.6	10897	29464	72	204025	32.9	22305	3471	244.1
SW-07	45.0	1.9	2226	240.4	299363	5.8	368612	771268	2	9917400	18.4	729319	1161	4358.9
SW-09	47.8	12.4	2076	295.2	229942	4.7	324791	662293	2	8642170	31.5	565102	394	3266.5
SW-10	49.4	15.3	1776	258.8	240377	16.9	296141	607049	607	7558980	150.0	557529	4522	3609.1
SW-14	65.2	33.1	902	456.9	407987	15.0	166282	478307	775	6395330	27.0	507006	2401	3448.0
SW-16	54.0	10.5	2488	280.1	259079	7.1	385052	765090	6	10137200	35.2	664982	2114	4129.1
SW-20	53.0	4.1	2220	448.9	260832	19.6	347912	724042	44	9723930	64.7	607374	1680	3741.9
SW-24	48.0	20.6	1906	403.4	235232	6.6	308220	633763	38	8565240	22.4	522127	2226	3465.6
SW-29	55.0	9.8	1263	267.5	390697	4.6	225937	520569	44	6705250	46.2	668279	702	3358.6
SW-31	60.5	14.0	2763	213.3	286541	7.1	432693	847126	22	11760400	10.2	749847	867	4918.0
SW-34	52.0	24.8	2699	218.2	287009	8.8	416318	829095	297	10886300	25.8	731071	1376	4815.0
SW-35	55.5	16.3	2216	352.2	296647	26.6	350381	721275	734	9736380	73.0	626907	2134	4293.5
SW-13	48.3	25.2	2455	184.5	248934	3.5	387516	736622	2	9964510	70.2	666403	1722	4297.0
SW-23	50.2	18.0	2567	176.5	255360	1.5	398744	763841	2	10346900	47.2	684427	1655	4489.7
SW-28	51.0	8.3	2625	159.5	259020	2.8	409917	781644	1	10384400	47.2	703019	1643	4568.6
SW-32	54.4	18.5	2634	166.8	259819	7.2	412208	782831	5	10357800	42.6	705143	1653	4570.3
SW-36	51.2	16.3	2662	169.4	261837	0.4	413449	790219	1	10669800	62.5	711203	1682	4613.9
SW-50	11.2	2.1	52	38.5	30605	---	5524	11244	1	57028	83.6	7334	4268	127.3
SW-54	10.6	2.0	33	27.8	24447	7.6	3851	7839	2	44204	36.5	4929	3914	96.1
SW-56	8.5	4.6	31	34.1	30935	---	4712	10292	1	41060	26.8	6253	4474	121.7
SW-58	16.5	2.6	65	36.9	34179	4.6	8221	17143	2	122779	46.8	12706	3967	168.3
SW-61	13.4	3.1	68	40.4	34008	2.9	7835	17195	1	119551	35.7	11844	4315	169.0
SW-62	12.3	7.3	64	41.0	34388	4.3	7514	16956	1	111727	45.7	11409	4398	167.1
SW-64	15.7	5.1	60	38.8	33521	2.6	6923	15398	0	107869	59.5	10373	4328	156.8

Table 3. Anion and DOC concentrations of surface water samples.

Table 3. Anion and DOC concentrations of surface water samples (*1 of 2*)

Location	F (ug/L)	Cl (ug/L)	Br (ug/L)	NO3 (ug/L)	PO4 (ug/L)	SO4 (ug/L)	HCO3 (ug/L)	DOC (ug/L)
SW-06	2823	391514	663	---	---	92275	---	13120
SW-08	2880	331567	---	---	3024	152947	---	12460
SW-11	2193	220255	---	---	---	55205	---	13040
SW-12	3031	122566	---	---	1272	106214	---	22650
SW-17	2634	506383	1381	---	---	122179	---	12640
SW-18	3481	551482	---	---	---	82190	---	14440
SW-19	3343	385114	---	---	1994	31651	---	24600
SW-21	2306	305376	---	---	---	109922	---	10100
SW-22	1841	301872	---	---	168	103973	---	12870
SW-25	4305	1279169	3787	---	---	130819	---	12510
SW-27	3829	809695	---	---	780	61973	---	9301
SW-30	3920	483607	---	---	1879	68621	---	19960
SW-33	9537	2840222	---	---	1858	309185	---	34190
SW-06	117	283135	1500	---	---	143845	19970	3162
SW-07	---	1374986	---	---	518	194964	30590	12180
SW-08	59	295720	1413	172	---	260911	24200	10570
SW-12	94	376996	1606	---	---	326616	24990	5680
SW-17	---	448774	---	---	788	238993	29180	10860
SW-18	40	434827	1894	---	---	128751	31810	12180
SW-19	---	370900	1660	---	2560	55257	44500	8870
SW-21	66	256492	1365	176	---	172364	29680	6710
SW-25	61	484830	1999	---	---	91661	20170	7820
SW-27	166	497956	2034	---	---	85715	22150	8990
SW-30	137	329508	1605	---	---	168398	28060	6370
SW-33	---	602182	---	---	---	256335	27880	7220
SW-52	100	298489	1434	---	227	211263	22070	3880
SW-63	176	500460	2048	367	561	92997	20770	6180
SW-09	---	922043		---	---	142892	53770	12450
SW-16	112	118678	1034	---	---	38957	23170	4573
SW-20	87	400102	1817	176	---	83497	20430	5580
SW-24	118	353361	1656	178	---	51636	24750	5080
SW-31	122	504274	2110	183	---	128284	24690	7120
SW-34	---	523351	---	---	---	98263	30270	8000
SW-35	94	312519	1558	298	---	50405	19350	4676
SW-51	83	357648	1554	173	---	260750	24710	5660
SW-53	99	163142	1125	347	---	44906	21480	3770
SW-55	97	431958	1788	---	---	218580	21890	4672
SW-59	---	904791	---	---	---	530632	21410	6950
SW-60	---	1086652	---	---	---	534528	22760	6510
SW-65	102	312824	1496	---	---	85834	27570	6390
SW-07	27609	13678068	14638	---	1553	1383000	---	19240
SW-09	23278	12104683	13835	---	---	1030034	---	20580
SW-10	22526	10685506	21077	---	---	1019383	---	23550
SW-14	19979	8718384	15703	---	---	900480	---	45890
SW-16	29429	14084621	15696	---	---	1233470	---	21120
SW-20	27509	13247148	25317	---	---	1106882	---	33990
SW-24	24971	11925588	21136	---	---	957470.4	---	19210
SW-29	20410	9027403.2	20197	---	---	1295148	---	43110
SW-31	32999	16031678	32866	---	---	1440494	---	18070
SW-34	30260	15676824	32635	---	---	1418592	---	14040
SW-35	27459	13526338	23838	---	---	1181006	---	33940
SW-13	26580	13879282	25269	---	---	1262436	---	9619
SW-23	28608	14309323	15461	---	---	1302912	---	8207
SW-28	28778	14765081	29033	---	458	1348464	---	11630
SW-32	30799	14903657	27003	---	---	1363898	---	10900
SW-36	29898	14810518	29947	---	---	1352726	---	9341
SW-50	91	85979	925	531	231	24577	27120	7970

Table 3. Anion and DOC concentrations of surface water samples (*2 of 2*)

Location	F (ug/L)	Cl (ug/L)	Br (ug/L)	NO3 (ug/L)	PO4 (ug/L)	SO4 (ug/L)	HCO3 (ug/L)	DOC (ug/L)
SW-54	102	68731	883	556	---	16764	43450	10630
SW-56	102	64784	868	277	---	22262	407	3864
SW-58	97	182279	1164	---	---	46141	21150	7920
SW-61	102	179040	1172	544	---	43233	22280	3148
SW-62	105	165888	1137	557	125	38734	22460	4536
SW-64	99	143485	1063	---	---	36248	22690	4944

Table 4. Charge imbalance error and water type of surface water samples.

Table 4. Charge imbalance error and water types of surface water samples

Location	Date	Charge imbalance error	Water type	SI>0*
SW-06	10/15/2012	0.56%	Na-Cl	Dol, Calcite
SW-07	10/15/2012	4.80%	Na-Cl	Hap, Dol, Calcite
SW-08	10/15/2012	-3.83%	Na-Cl	Dol, Calcite
SW-09	10/15/2012	5.88%	Na-Cl	Dol, Calcite
SW-12	10/16/2012	7.37%	Na-Cl	Hm, Goethite, Dol, Cacite, Qtz
SW-16	10/16/2012	0.42%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-17	10/16/2012	4.23%	Na-Cl	Hap, Hm, Goethite, Dol, Calcite
SW-18	10/16/2012	2.53%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-19	10/16/2012	5.47%	Na-Cl	Hap, Dol, Calcite, Qtz
SW-20	10/16/2012	9.51%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-21	10/17/2012	-4.06%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-24	10/17/2012	4.65%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-25	10/17/2012	3.09%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-27	10/19/2012	1.90%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-30	10/19/2012	-2.58%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-31	10/18/2012	2.98%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-33	10/18/2012	-0.19%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-34	10/18/2012	9.14%	Na-Cl	Hm, Dol, Goethite, Calcite
SW-35	10/16/2012	6.35%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-50	10/15/2012	-1.25%	Na-Cl	Hap, Dol, Calcite, Qtz
SW-51	10/15/2012	-2.10%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-52	10/15/2012	-2.22%	Na-Cl	Hap, Dol, Calcite, Qtz
SW-53	10/15/2012	4.63%	Na-Cl	Dol, Calcite, Qtz
SW-54	10/16/2012	-21.77%	Na-HCO3	Hm, Goethite, Dol, Calcite, Qtz
SW-55	10/17/2012	3.80%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-56	10/17/2012	29.95%	Na-Cl	Qtz
SW-58	10/17/2012	3.71%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-59	10/17/2012	7.11%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-60	10/17/2012	0.47%	Na-Cl	Hm, Goethite, Dol, Calcite
SW-61	10/18/2012	4.16%	Na-Cl	Hm, Goethite, Dol, Calcite, Qtz
SW-62	10/18/2012	4.98%	Na-Cl	Hap, Hm, Goethite, Dol, Calcite, Qtz
SW-63	10/19/2012	7.30%	Na-Cl	Hap, Hm, Goethite, Dol, Calcite, Qtz
SW-64	10/19/2012	7.65%	Na-Cl	Hm, Goethite, Dol, Calcite, Qtz
SW-65	10/19/2012	2.51%	Na-Cl	Hm, Goethite, Dol, Calcite

*SI = Saturation Index, calculated using the program Spec8 in the Geochemist's Workbench v. 9.

Freshwater pond and rice paddy samples are all Na-Cl water type and are oversaturated in dolomite and calcite ± hydroxyapatite and goethite. Shrimp pond samples are Na-Cl water type and are oversaturated in dolomite and calcite ± goethite. One tidal channel sample is Na-HCO3 water type while all others are Na-Cl water type. Tidal channel samples are saturated in goethite, calcite, and dolomite ± quartz and hydroxyapatite.

Groundwater

Geochemical analyses for physical parameters, metal cation concentrations, anion and DOC concentrations, and charge imbalance error and water types of tube well samples are included in **Tables 5** through **8**, respectively.

Table 5. Physical parameters of groundwater samples.

Table 5. Physical parameters of groundwater samples

Location	Date	Type	Temp (°C)	Eh (mV)	pH	Corr SpC (uS/cm)	Salinity (ppt)
GW-10	5/15/2012	TW	31.92	181	6.60	4913	2.63
GW-11	5/15/2012	TW	28.80	165	6.89	4283	2.27
GW-12	5/16/2012	TW	33.93	179	6.59	4232	2.24
GW-13	5/17/2012	TW	31.07	135	6.47	13650	7.87
GW-14	5/18/2012	TW	29.15	103	6.48	3058	1.59
GW-15	5/18/2012	TW	30.03	141	6.60	5046	2.70
GW-16	5/19/2012	TW	33.41	95	6.69	5954	3.23
GW-17	5/19/2012	TW	30.46	124	6.45	7938	4.39
GW-19	5/20/2012	TW	28.41	141	6.56	7522	4.14
GW-20	5/20/2012	TW	30.06	117	6.67	7199	3.95
GW-21	5/20/2012	TW	30.16	129	6.54	6647	3.63
GW-22	5/20/2012	TW	29.71	183	6.62	5114	2.74
GW-23	5/20/2012	TW	28.69	161	6.71	4803	2.57
GW-24	5/20/2012	TW	27.98	147	6.66	6501	3.54
GW-25	5/20/2012	TW	28.15	164	6.72	4961	2.66
GW-26	5/21/2012	TW	32.48	324	6.86	7775	4.29
GW-27	5/21/2012	TW	29.63	114	6.35	10608	5.99
GW-28	5/21/2012	TW	31.92	125	6.41	7761	4.28
GW-29	5/22/2012	TW	31.45	132	6.80	5621	3.03
GW-30	5/22/2012	TW	30.83	246	6.98	3916	2.07
GW-31	5/22/2012	TW	28.63	134	6.92	3676	1.93
GW-32	5/22/2012	TW	28.20	143	6.52	11067	6.27
GW-33	5/23/2012	TW	28.23	143	6.37	10113	5.69
GW-34	5/23/2012	TW	29.08	153	6.59	5131	2.75
GW-35	5/23/2012	TW	29.34	128	6.59	7079	3.88
GW-36	5/23/2012	TW	29.30	149	6.73	5235	2.81
GW-37	5/23/2012	TW	31.64	170	6.51	4263	2.26
GW-38	5/23/2012	TW	28.05	128	6.80	5386	2.90
GW-39	5/23/2012	TW	28.74	118	6.63	6301	3.43
GW-40	5/24/2012	TW	29.74	149	6.55	6457	3.52
GW-41	5/24/2012	TW	29.31	134	6.56	7335	4.03
GW-42	5/24/2012	TW	29.31	134	6.56	7335	4.03
GW-44	5/15/2012	TW	28.80	165	6.89	4283	2.27
GW-10	10/16/2012	TW	29.59	135	7.39	5198	3.63
GW-12	10/16/2012	TW	28.90	122	7.29	4607	3.15
GW-15	10/17/2012	TW	28.17	102	7.43	5302	3.60
GW-17	10/17/2012	TW	28.43	117	7.26	8148	5.56
GW-19	10/17/2012	TW	28.53	130	7.29	7488	5.11
GW-27	10/18/2012	TW	27.91	88	7.17	10851	7.37
GW-28	10/18/2012	TW	28.28	88	7.27	8685	5.91
GW-29	10/20/2012	TW	27.27	94	7.70	6271	4.19
GW-30	10/20/2012	TW	27.29	90	7.91	4368	2.91
GW-31	10/20/2012	TW	27.56	81	7.82	3857	2.59
GW-33	10/20/2012	TW	28.47	105	7.14	10181	6.97
GW-34	10/20/2012	TW	27.74	92	7.40	5297	3.56
GW-35	10/20/2012	TW	27.90	88	7.42	7005	4.72
GW-36	10/20/2012	TW	28.50	94	7.52	5303	3.61
GW-39	10/19/2012	TW	28.63	99	7.46	6303	4.32
GW-40	10/19/2012	TW	29.12	107	7.34	6330	4.37
GW-41	10/19/2012	TW	29.19	110	7.36	7355	5.10
GW-50	10/18/2012	TW	29.11	111	7.79	3306	2.28
GW-51	10/18/2012	TW	28.28	99	7.69	3761	2.56
GW-52	10/19/2012	TW	27.56	121	7.39	5537	3.71
GW-53	10/18/2012	TW	27.83	122	7.24	8544	5.77

Table 6. Metal cation concentrations of groundwater samples.

Table 6. Metal cation concentrations of groundwater samples (*<u>1 of 2</u>*)

Location	Al (ug/L)	As (ug/L)	B (ug/L)	Ba (ug/L)	Ca (ug/L)	Fe (ug/L)	K (ug/L)	Mg (ug/L)	Mn (ug/L)	Na (ug/L)	P (ug/L)	S (ug/L)	Si (ug/L)	Sr (ug/L)
GW-10	13.1	176	748	559.8	80625	1764	41372	78353	79	1143700	4010.2	1478	23823	735.3
GW-11	3.9	62	761	114.2	51942	661	37055	67117	64	656799	5801.9	1127	26646	505.3
GW-12	22.2	196	515	571.1	116991	1025	35156	88582	70	724025	1742.2	1761	23219	968.1
GW-13	49.0	20	564	2555.7	388162	750	107334	412844	299	4260970	160.6	4986	15319	3043.5
GW-14	16.8	62	440	85.4	106546	122	20023	70493	149	392126	1540.7	1748	31703	646.6
GW-15	31.3	13	330	765.4	163134	6975	49762	152845	289	1251370	1469.9	2354	20759	1224.6
GW-16	21.8	84	539	528.8	138912	166	15789	46108	59	1387780	969.6	13041	23493	522.5
GW-17	42.8	16	352	346.5	311578	174	59837	222032	916	2134450	84.2	124906	16020	1523.0
GW-19	21.7	21	872	152.5	124150	238	16294	89206	167	1702030	6777.8	3084	32294	528.1
GW-20	24.4	13	640	144.2	150257	647	20678	78635	102	1752950	8693.2	2611	31516	741.6
GW-21	31.8	26	461	131.7	202894	546	34341	117283	565	1692950	3321.1	65213	28185	856.2
GW-22	21.1	80	611	763.5	108712	1108	54588	119810	84	1057360	1857.7	1657	27012	1032.1
GW-23	14.1	67	661	486.1	92954	252	54284	108371	78	860849	1923.0	1557	29365	927.4
GW-24	28.4	94	625	861.0	146737	914	61559	151241	79	1318280	1506.5	2052	26056	1306.4
GW-25	11.2	53	686	298.0	90088	345	55768	107930	59	885963	2230.3	1509	28018	902.4
GW-26	34.2	30	567	575.5	189717	1346	33919	149438	160	2137540	63.9	3253	21915	1072.9
GW-27	39.3	32	553	1131.6	283398	2932	43853	213285	266	3008670	602.7	4324	22017	1486.2
GW-28	36.8	24	551	569.1	216000	885	55197	202833	712	2237190	175.1	3000	22460	1462.8
GW-29	14.0	4	567	161.1	89486	707	53417	111695	68	1341920	1181.3	1235	24904	847.2
GW-30	0.0	20	626	61.8	38919	461	36617	50275	36	692525	3044.1	719	25027	387.9
GW-31	0.0	21	474	63.5	43645	1091	39037	56085	76	642293	2283.7	661	25263	392.4
GW-32	39.7	115	620	1442.6	242452	4797	60223	232476	678	3084970	1216.5	6502	20872	2042.8
GW-33	51.5	27	579	398.7	337062	2666	97414	416032	891	2834600	578.4	4303	33081	2823.2
GW-34	15.3	154	518	544.5	107763	230	32602	85498	85	1005140	1878.1	1473	25110	779.7
GW-35	31.7	254	487	939.8	176676	630	36416	136414	77	1708880	668.6	2356	20001	1323.6
GW-36	21.9	114	489	564.6	107234	717	32265	87519	65	1039640	2256.5	1577	21459	759.7
GW-37	23.3	158	286	370.0	125927	173	34457	97894	84	855470	1349.5	1988	30469	967.2
GW-38	6.6	78	613	103.1	65561	615	40538	77890	44	1199680	2436.2	1289	28959	680.0
GW-39	33.8	104	300	617.1	195157	442	37969	131579	132	1490140	573.6	2734	21671	1399.7
GW-40	40.7	48	392	724.3	248469	913	46164	159986	238	1688580	573.4	5458	31352	1808.1
GW-41	46.4	30	251	1395.6	352743	1387	42972	186710	267	1960600	609.3	14028	28686	2144.4
GW-42	47.8	43	256	1432.3	352436	2204	43681	186924	269	1909600	743.4	14003	28963	2166.4
GW-44	4.4	65	712	106.2	52506	456	37303	66287	63	633273	6058.0	1073	26943	504.4
GW-10	---	183	836	452.2	86135	559	28176	78914	74	999580	3232.8	540	21796	734.3
GW-12	28.1	158	615	553.6	127368	821	24855	93476	72	909688	1681.9	520	22664	998.5

Table 6. Metal cation concentrations of groundwater samples (*2 of 2*)

Location	Al (ug/L)	As (ug/L)	B (ug/L)	Ba (ug/L)	Ca (ug/L)	Fe (ug/L)	K (ug/L)	Mg (ug/L)	Mn (ug/L)	Na (ug/L)	P (ug/L)	S (ug/L)	Si (ug/L)	Sr (ug/L)
GW-15	48.0	4	407	840.6	184062	6149	37633	158736	322	856395	1288.2	524	19709	1298.5
GW-17	119.4	43	414	390.3	326052	12204	41807	212847	960	1240510	810.5	122017	14302	1534.2
GW-19	30.4	27	898	266.5	140670	3870	11415	102399	228	1418490	7287.0	8947	30184	616.1
GW-27	95.0	58	613	1445.7	290967	17482	27474	204861	281	1833070	2355.2	1106	19992	1447.8
GW-28	93.8	15	639	776.6	232246	13334	38165	203134	637	1462220	2267.4	2381	20411	1494.7
GW-29	26.6	31	636	202.9	103470	2076	39172	123578	83	1139460	1466.0	153	24247	937.5
GW-30	---	6	730	60.2	44512	390	26394	54433	37	908338	2875.2	360	25009	411.6
GW-31	---	21	587	66.4	52784	1007	29315	65060	97	839499	2235.7	196	25933	435.7
GW-33	117.9	10	605	417.3	355088	9161	68585	384659	1057	1363370	1652.3	320	30841	2796.5
GW-34	18.6	96	624	729.0	113070	3316	21900	86716	93	958310	3008.6	405	23345	778.1
GW-35	41.5	209	576	1159.3	177838	3541	24137	130054	82	1234020	1748.3	399	19426	1256.5
GW-36	24.4	109	564	607.4	114480	1356	22098	90140	71	1001350	2300.9	430	19566	763.5
GW-39	56.2	87	350	682.3	215359	1467	25486	136566	158	1010000	851.4	345	20197	1468.2
GW-40	81.8	41	439	956.2	271887	4044	32962	162497	214	942932	1470.0	273	30234	1889.3
GW-41	129.5	56	325	1375.4	364414	7368	29630	181045	243	1024180	1510.4	7916	27539	2119.2
GW-50	---	15	620	105.1	45710	58	26132	52008	37	738903	1537.2	377	24264	398.4
GW-51	---	26	778	68.1	47214	654	24056	50494	47	902396	3735.5	491	31795	366.1
GW-52	51.6	198	351	605.0	183675	2657	29262	132891	91	868919	1189.6	413	27614	1404.7
GW-53	108.0	20	416	558.4	280167	6955	25990	237580	290	1283060	898.3	666	27278	1371.3

Table 7. Anion and DOC concentrations of groundwater samples.

Table 7. Anion and DOC concentrations of groundwater samples

Location	F (ug/L)	Cl (ug/L)	Br (ug/L)	NO3 (ug/L)	PO4 (ug/L)	SO4 (ug/L)	HCO3 (ug/L)	DOC (ug/L)
GW-10	4515.8	1527902	---	---	6504	571	---	28870
GW-11	4762.4	897660	---	---	91367	835	---	39410
GW-12	5109.6	1035674	1216	---	---	---	---	49900
GW-13	12577.6	5966090	11104	---	1834	312	---	38220
GW-14	3914.8	532128	---	---	---	---	---	43030
GW-15	4968.3	1741402	---	---	---	---	---	13060
GW-16	6112.8	2085163	5056	---	---	19296	---	46850
GW-17	7338.7	3057674	6382	---	---	223270	---	21950
GW-19	6201.4	2567076	5312	---	9461	---	---	46260
GW-20	7020.3	2591563	5625	---	13781	---	---	57440
GW-21	5981.1	2427322	5438	---	---	111799	---	23200
GW-22	5011.4	1435999	---	---	7008	401	---	32920
GW-23	5669.9	1150207	---	---	1212	---	---	44320
GW-24	5911.7	1918961	---	---	9271	1800	---	35440
GW-25	5061.7	1185850	3077	---	2407	235	---	49680
GW-26	7322.0	3008146	---	---	1555	962	---	35290
GW-27	9412.3	4223544	9515	---	---	---	---	45850
GW-28	7439.3	3183991	5378	---	---	454	---	28130
GW-29	6455.2	1919803	---	---	1666	958	---	22930
GW-30	4384.1	986863	---	---	5234	---	---	27350
GW-31	4285.9	899383	1221	---	1730	---	---	28940
GW-32	10176.1	4343873	8795	---	---	4106	---	33550
GW-33	9886.3	4034069	8773	---	---	---	---	26000
GW-34	5878.2	1423426	2763	---	---	370	---	38750
GW-35	7855.9	2419152	6528	---	---	---	---	39130
GW-36	5727.3	1403222	775	---	---	694	---	45270
GW-37	5107.2	1201896	1102	---	511	---	---	46050
GW-38	6048.2	1617355	2466	---	3130	---	---	38300
GW-39	6246.9	2115943	3657	---	262	2282	---	29600
GW-40	6316.3	2249436	4487	---	1070	2580	---	27170
GW-41	7492.0	2757322	4949	---	---	15979	---	26640
GW-42	6558.2	2727936	---	---	2952	14645	---	21430
GW-44	5054.5	884993	2297	---	9576	583	---	44880
GW-10	---	1520695	4926	178	9151	1776	189400	47030
GW-12	---	1145481	4177	174	4863	1809	237000	49390
GW-15	---	1321431	5417	174	3373	1898	125000	17520
GW-17	---	2002596	8987	176	2314	426900	110000	13920
GW-19	---	2185749	8051	174	19532	30590	139500	32890
GW-27	---	2721687	12246	186	6320	3737	204300	41230
GW-28	---	2365573	9642	182	6398	7913	171200	28960
GW-29	---	1956317	5701	176	3849	593	151300	21270
GW-30	---	1503386	3540	179	7889	1314	185900	32170
GW-31	---	1077852	3127	179	6469	859	167700	25680
GW-33	---	1918713	10885	186		1192	168100	24740
GW-34	---	1552987	4729	176	8603	1324	210000	40740
GW-35	---	2118905	6896	178	4779	1390	205600	31440
GW-36	---	1435414	4871	175	6462	1513	225800	44910
GW-39	---	1709229	5762	180	2121	1161	154000	22800
GW-40	---	1508586	5980	194	3611	928	153100	22040
GW-41	---	1506038	7283	229	4269	26334	157000	22370
GW-50	---	1105576	2975	178	4594	1357	165500	35430
GW-51	---	1339137	2924	178	9745	1776	216500	43260
GW-52	---	1280784	5786	178	3221	1396	190000	41260
GW-53	---	2100586	8514	182	2288	2198	181500	29190

Table 8. Charge imbalance error and water type of groundwater samples.

Table 8. Charge imbalance error and water types of groundwater samples

Location	Date	Charge imbalance error	Water type	SI>0*
GW-10	10/15/2012	-2.67%	Na-Cl	Hm, Hap, Goethite, Dolom, Calcite, Qtz
GW-12	10/15/2012	3.56%	Na-Cl	Hap, Dolom, Qtz, Calcite
GW-15	10/16/2012	12.72%	Na-Cl	Hm, Hap, Goethite, Dolom, Calcite, Qtz
GW-17	10/16/2012	9.92%	Na-Cl	Hm, Hap, Goethite, Dolom, Calcite, Qtz
GW-19	10/16/2012	2.76%	Na-Cl	Hm, Hap, Goethite, Dolom, Qtz, Calcite
GW-27	10/17/2012	10.02%	Na-Cl	Hm, Hap, Goethite, Dol, Calcite, Qtz
GW-28	10/17/2012	7.74%	Na-Cl	Hm, Hap, Goethite, Dol, Calcite, Qtz
GW-29	10/19/2012	-1.31%	Na-Cl	Hm, Hap, Goethite, Dol, Calcite, Qtz
GW-30	10/19/2012	-10.80%	Na-Cl	Hm, Hap, Goethite, Dol, Calcite, Qtz
GW-31	10/19/2012	1.09%	Na-Cl	Hm, Hap, Goethite, Dol, Qtz, Calcite
GW-33	10/19/2012	25.56%	Na-Cl	Hm, Goethite, Dol, Qtz, Calcite
GW-34	10/19/2012	-4.74%	Na-Cl	Hm, Hap, Goethite, Dol, Qtz, Calcite
GW-35	10/19/2012	-1.49%	Na-Cl	Hm, Hap, Goethite, Dol, Calcite, Qtz
GW-36	10/19/2012	-1.23%	Na-Cl	Hm, Hap, Goethite, Dol, Calcite, Qtz
GW-39	10/18/2012	4.90%	Na-Cl	Hm, Hap, Goethite, Dol, Calcite, Qtz
GW-40	10/18/2012	11.95%	Na-Cl	Hm, Hap, Goethite, Dol, Calcite, Qtz
GW-41	10/18/2012	17.93%	Na-Cl	Hm, Hap, Goethite, Dol, Calcite, Qtz
GW-50	10/17/2012	-6.65%	Na-Cl	Hap, Hm, Goethite, Dol, Qtz, Calcite
GW-51	10/17/2012	-9.20%	Na-Cl	Hm, Hap, Goethite, Dol, Qtz, Calcite
GW-52	10/18/2012	7.12%	Na-Cl	Hm, Hap, Goethite, Dol, Calcite, Qtz
GW-53	10/17/2012	10.69%	Na-Cl	Hm, Hap, Goethite, Dol, Qtz, Calcite

*SI = Saturation Index, calculated using the program Spec8 in the Geochemist's Workbench v. 9.

All tube well samples are Na-Cl water type. Tube well samples are oversaturated in hydroxyapatite, goethite, dolomite, calcite and quartz.

CHAPTER V

DISCUSSION

Geochemical Analyses

As observed in concentrations of major ions and differential in Eh oxidation reduction potential (Eh), surface water and groundwater have separate and distinct chemical signatures. Average concentrations of major ions in surface water occur in the order $Cl^- > Na^+ > SO_4^{2-} > Mg^{2+} > K^+ > NO_3^-$. Conversely, average concentrations of major ions in groundwater occur in the order $Cl^- > Na^+ > Mg^{2+} > K^+ > SO_4^{2-} > NO_3^-$. Eh values range from a maximum of 496 mV in surface water to a minimum of 81 mV in groundwater (**Tables 1** and **5**). Surface water samples tend to have higher Eh values, indicating a more oxidizing environment consistent with their being in contact with oxygen in the atmosphere.

For groundwater samples no systematic trends with depth were observed for salinity, temperature, Eh, As, Fe, Mn, Mo or S in May and October 2012 samples. Furthermore, no correlations were observed between measures of Eh, concentrations of reducing agents (DOC), and concentrations of metals with variable oxidation states (As, Fe, Mn, M, and S). Dry and wet season samples appear to exhibit redox disequilibrium.

Water Types

Box plots were evaluated to establish sources of all water samples. Freshwater pond samples demonstrate little seasonal compositional variation (**Tables 1, 2,** and **3**) and are grouped together for the purpose of comparing sample types. Although tube well samples show small seasonal variations in composition (**Table 10**), as a group they pass normality tests for many compositional variables, suggesting they can be treated as a single group. Conversely, tidal channel samples exhibit considerable seasonal variation in composition (**Tables 1, 2,** and **3**) and are un-grouped for the purpose of comparing sample types; TC-05 = samples collected in May 2012 and TC = samples collected in October 2012.

Figure 15 box plot presents specific conductivity (SpC) measurements across dry and wet season surface water and groundwater samples. **Figure 15** shows that tidal channel water contains higher concentrations of SpC during the dry season. SpC measurements also demonstrate the high seasonal variability in tidal channel samples (TC and TC-05). Additionally, rice paddy samples have higher SpC values than tidal channel samples. Furthermore, **Figure 15** demonstrates two groups of surface water with no overlap; saline (SP and TC-05) and fresh (FP, RP, and TC). Similar values of SpC within saline and fresh surface water groups support seasonal sourcing of tidal channel water to freshwater ponds and rice paddies, and of dry season tidal channel water to shrimp ponds. SpC of groundwater appears to fall somewhere in the middle of the saline and fresh surface water groups.

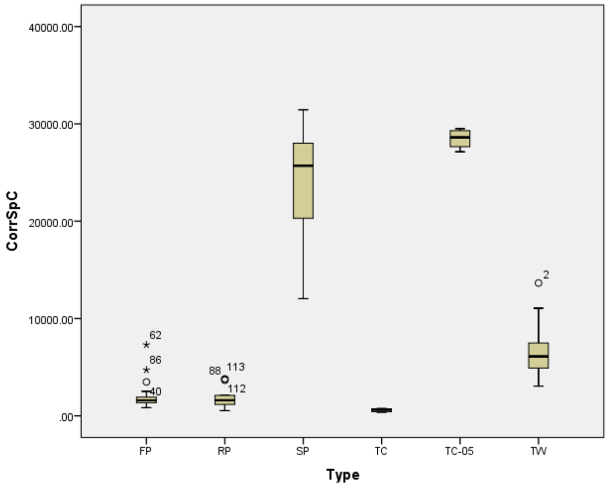

Figure 15. Box plot for specific conductivity (SpC) in µS/cm for six water types: FP = freshwater ponds, RP = rice paddies, SP = shrimp ponds, TC = October 2012 tidal channels, TC-05 = May 2012 tidal channels, and TW = tube wells.

Figure 16 presents concentrations of sulfur across dry and wet season surface water and groundwater samples. **Figure 16** demonstrates that tidal channel water contains higher concentrations of sulfur during the dry season. The high seasonal variability of sulfur concentration in tidal channel samples (TC and TC-05) further supports that freshwater ponds and rice paddies are seasonally sourced from wet season tidal channels, while shrimp ponds are seasonally sourced from dry season tidal channels. **Figure 16** also demonstrates two groups of surface water with no overlap; higher sulfur concentrations (SP and TC-05) and lower sulfur concentrations (FP, RP, and TC). In addition, it appears that sulfur exists in greater concentrations in surface water samples than groundwater samples. Sulfur was likely removed from groundwater by sulphate reduction, with organic carbon acting as the reducing agent.

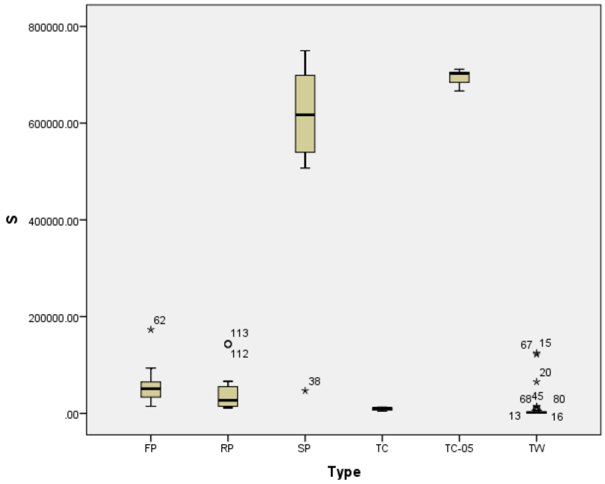

Figure 16. Box plot for Sulfur in µg/L for six water types: FP = freshwater ponds, RP = rice paddies, SP = shrimp ponds, TC = October 2012 tidal channels, TC-05 = May 2012 tidal channels, and TW = tube wells.

Figure 17 presents concentrations of DOC across dry and wet season surface water and groundwater samples. High concentrations of DOC exist in shrimp pond and tube well samples. High DOC in shrimp pond samples is expected from organic fertilizers introduced and animal fecal matter produced from shrimp aquaculture activities. High DOC in tube well samples may indicate that the shallow aquifer is contaminated with sewage from surface latrines. This indicates that communication between the surface and shallow aquifer may exist. Alternatively, tube well DOC may be sourced from shrimp ponds. However, mixing calculations show that shrimp pond water cannot be combined with any other water source to produce observed tube well compositions because shrimp pond and tube well samples have very different salt contents but similar DOC contents. As suggested by Mailloux et al. (2013), a high concentration of DOC in groundwater facilitates iron oxyhydroxide reduction, which mobilizes arsenic from sediments and causes sulfide precipitation.

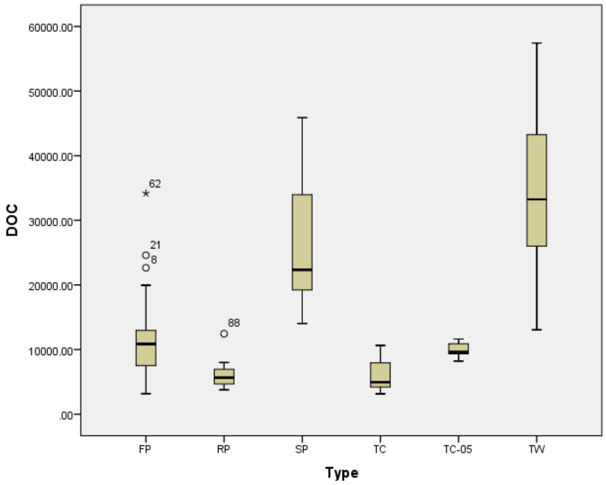

Figure 17. Box plot for Dissolved Organic Carbon (DOC) in µg/L for six water types: FP = freshwater ponds, RP = rice paddies, SP = shrimp ponds, TC = October 2012 tidal channels, TC-05 = May 2012 tidal channels, and TW = tube wells.

Figures 15 through **17** reveals two pairs of surface water samples; wet season tidal channel water paired with freshwater ponds and rice paddies and dry season tidal channel water paired with shrimp ponds. The lack of overlap observed between tube wells and any of the surface water pairs may indicate that high concentrations of salt observed in surface water samples are not introduced by groundwater during irrigation practices, but by tidal channel water during dry season aquaculture and wet season agriculture practices. This is consistent with field observations: seasonal land use shifts from brine shrimp farming to rice farming, shrimp ponds and rice paddies developed adjacent to tidal channels, and sluice gates constructed through Polder 32 embankments to allow tidal channels to supply irrigation canals with water. Shrimp ponds are sourced from TC-05 water, but have higher concentrations of DOC as a result of shrimp aquaculture activities.

Mixing Trends

Linear correlations between element concentrations in surface water and groundwater samples identify elements that behave conservatively. Conservative elements occur at the same ratio to one another regardless of total salinity. **Figure 18** shows that these elements occur in constant proportions throughout freshwater pond, rice paddy, shrimp pond, and tidal channel samples, suggesting that they behave conservatively in surface waters. Data in the bivariate plots fall on a linear trend that point towards the origin, suggesting dilution by meteoric water. As tidal channels are the source of all surface waters with the exception of freshwater ponds, which are filled with meteoric water, the observed scatter is interpreted as the dilution of tidal channel water with meteoric water.

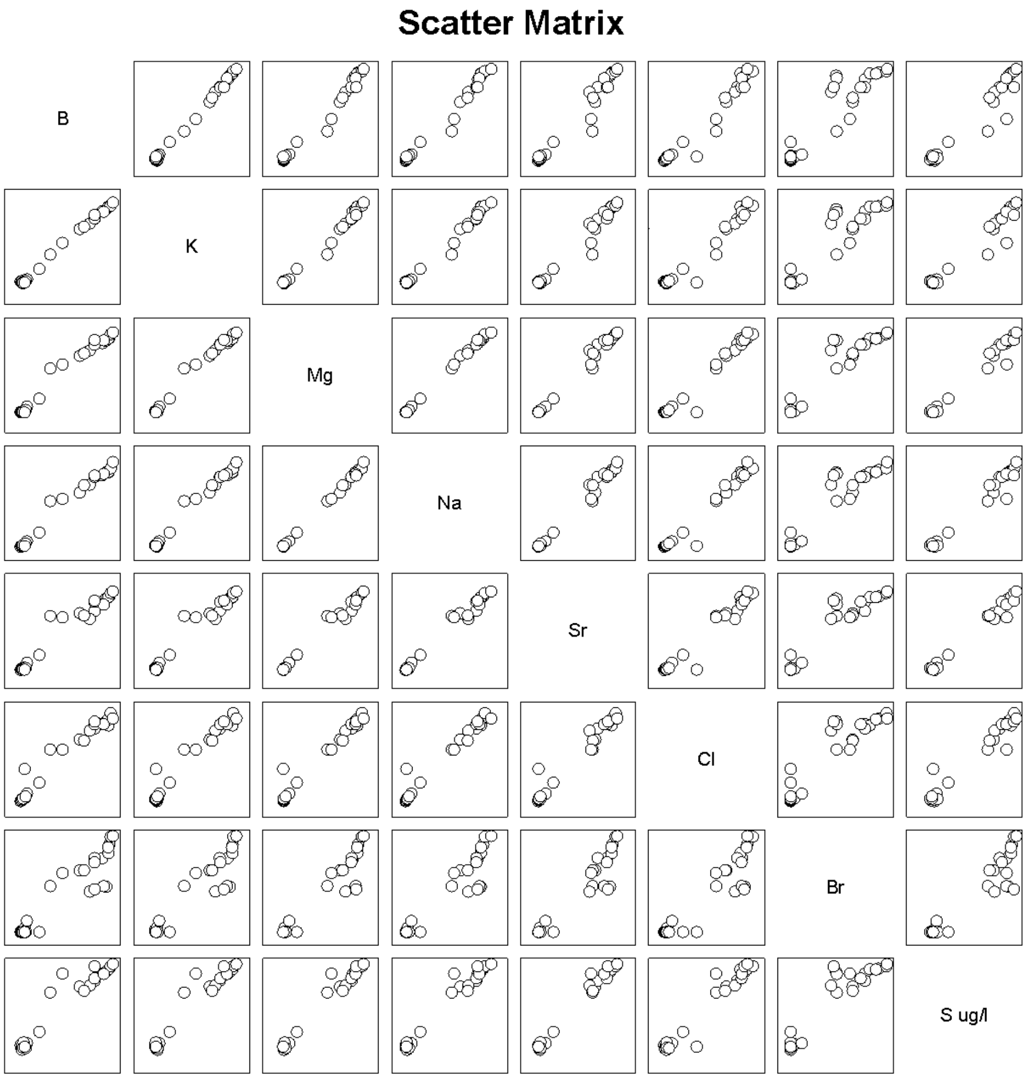

Figure 18. Element correlation matrices for May 2012 surface water samples. Linear trends between elemental pairs are indicative of conservative elements. Scatter in concentration trends suggests dilution with meteoric water.

Figure 19 presents pairwise plots of concentrations of conservative elements in dry season groundwater samples. Groundwater differs from surface water in that B and S do not behave conservatively. Groundwater has lower Eh values than surface water (**Tables 1** and **5**), indicating a more reducing environment, which may cause S removal through sulfate reduction. The correlation plots in **Figure 19** also demonstrate a rough trend that points toward the origin. Like surface water samples, meteoric water is considered the origin and the observed scatter is also interpreted as the dilution of tidal channel water with meteoric water.

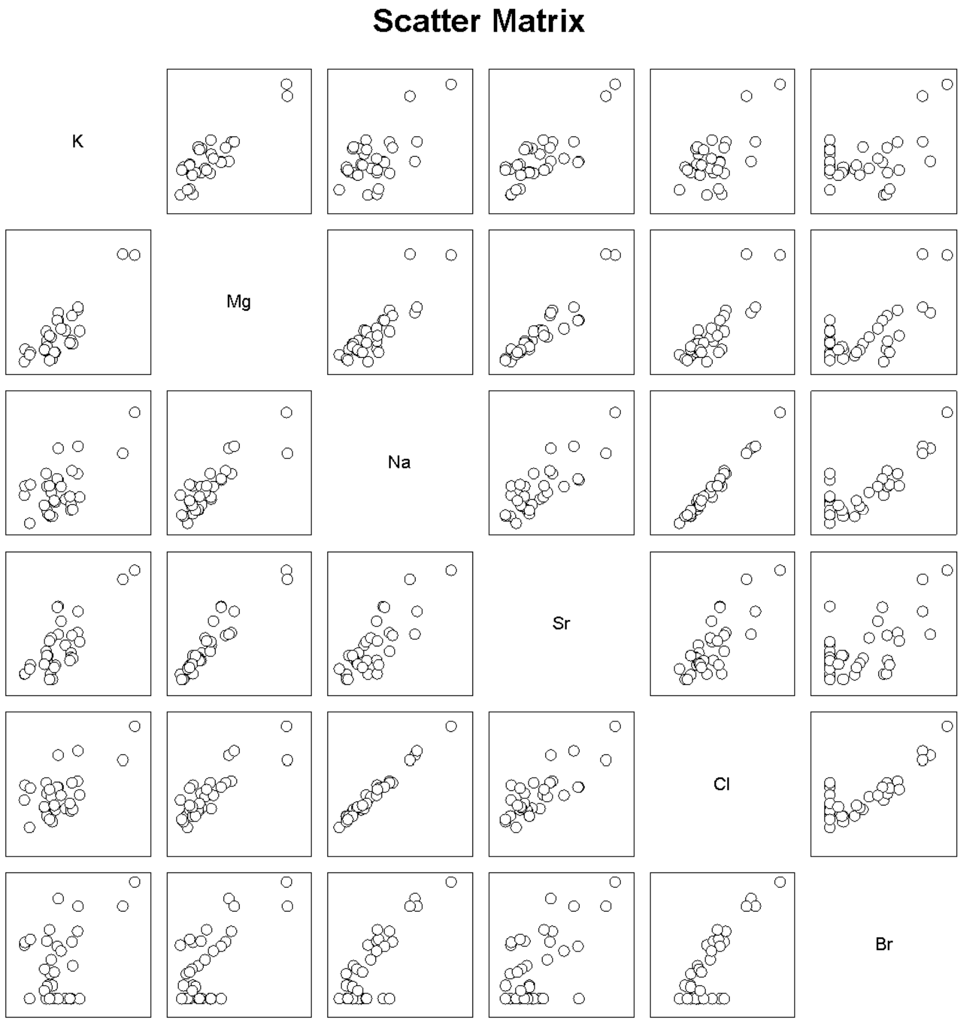

Figure 19. Element correlation matrices for May 2012 groundwater samples. Linear trends between elemental pairs are indicative of conservative elements. Scatter in concentration trends suggests dilution with meteoric water.

Figure 20 presents correlation matrices for wet season surface water. Similar to dry season surface water samples (**Figure 18**), **Figure 20** demonstrates good linear correlation and a dilution trend between element pairs. In addition, the same elements in surface water behave conservatively in the wet season as in the dry season.

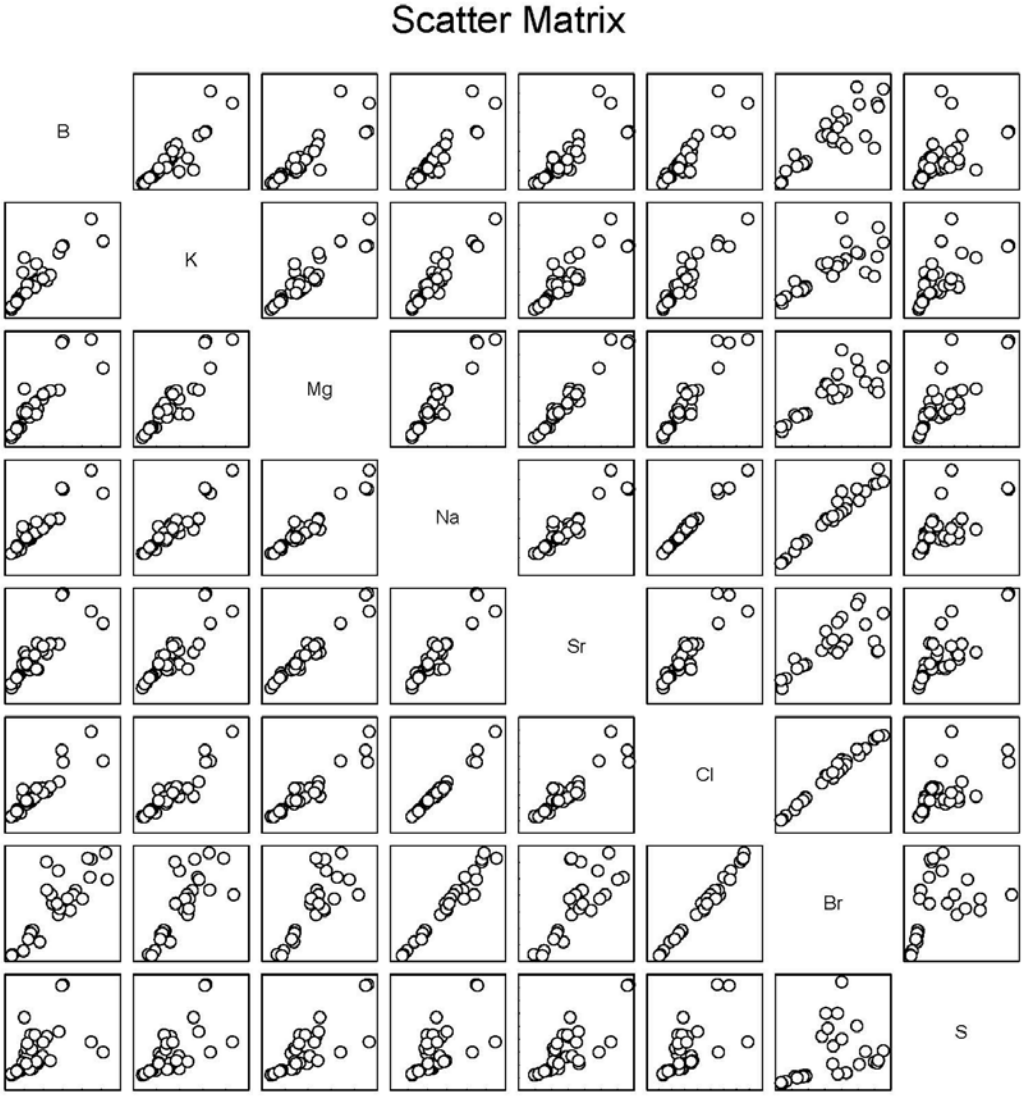

Figure 20. Element correlation matrices for October 2012 surface water samples. Linear trends between elemental pairs are indicative of conservative elements. Scatter in concentration trends suggests dilution with meteoric water.

Figure 21 presents correlation matrices for wet season groundwater. Like dry season groundwater samples (**Figure 19**), **Figure 21** exhibits a rough linear correlation and a dilution trend between element pairs. Furthermore, the same elements in groundwater behave conservatively in the wet season as in the dry season.

Figure 21. Element correlation matrices for October 2012 groundwater samples. Linear trends between elemental pairs are indicative of conservative elements. Scatter in concentration trends suggests dilution with meteoric water.

It appears that all water samples are mixtures of tidal channel water and meteoric water. Tidal channel water salinity changes dramatically from an average of 17.5 ppt in the dry season to 0.4 ppt in the wet season (**Table 1**). Rice paddies appear to be irrigated using relatively fresh tidal channel water, but rice paddy samples are higher in salinity than wet season tidal channel samples; average rice paddy salinity = 1.3 ppt and average tidal channel salinity = 0.4 ppt (**Table 1**). Greater salinity in rice paddy samples than tidal channel samples may indicate evaporation. **Table 9** tests concentration factors for conservative elements in rice paddy and tidal channel samples. For conservative elements:

Concentration Factor (CF) = (RP Concentration/TC Concentration)

Table 9. Concentration factors from average concentrations of October 2012 Tidal Channel (TC) and Rice Paddy (RP) samples.

Conservative Elements	**October 2012 TC (ug/L)**	**October 2012 RP (ug/L)**	**Concentration Factor (CF)**
K	6369	18309	2.87
Mg	13724	44479	3.24
Na	86317	340662	3.95
Cl	127169	491641	3.87

Results from **Table 9** indicate that rice paddy water is tidal channel water that has been concentrated 3-4 times by evaporation.

Drinking water sources often exceed the safe limit for human consumption established by Davis and DeWiest, 1966; 61% of tube well samples exceed 3.25 ppt. Similarly, 30% of rice paddy samples exceed the upper limit for rice crops of 1.56 ppt set by Bahar and Reza, 2010. Salinity of shrimp pond samples averages 15.38 ppt. In that 54% of the rice paddy samples were shrimp pond sample sites during the previous dry season of May 2012, shrimp ponds could be a potential source of the observed excess salinities. To test this hypothesis, a t-test was used to compare conductivities of water in rice paddies used for brine shrimp aquaculture and water in rice paddies used exclusively for rice production (**Table 10**). Results show that mean wet season Na concentration and SpC are higher for sites that were previously shrimp ponds, but the difference is not significant at the 95% level (i.e., the P value for a one-tailed t-test is not < 0.025). More data is needed before we can safely conclude that using rice paddies for shrimp ponds leads to salination of soil water.

Table 10. Parametric t-test of Shrimp Pond (SP) to Rice Paddy (RP) wet season samples.

Parameter	**Mean *SP to RP* *(n=7)***	**Mean *RP* *(n=6)***	**One-tailed P Value**	**Significantly Different (P < 0.025) (Y/N)**
Na (ug/L)	370163	225363	0.106	N
SpC (uS/cm)	1997	1309	0.145	N

Spatial Analysis

Measured values of specific conductivity in tube well samples are plotted as graduated symbols using ArcGIS software. SpC of dry season and wet season tube well samples are represented in **Figures 22** and **23**.

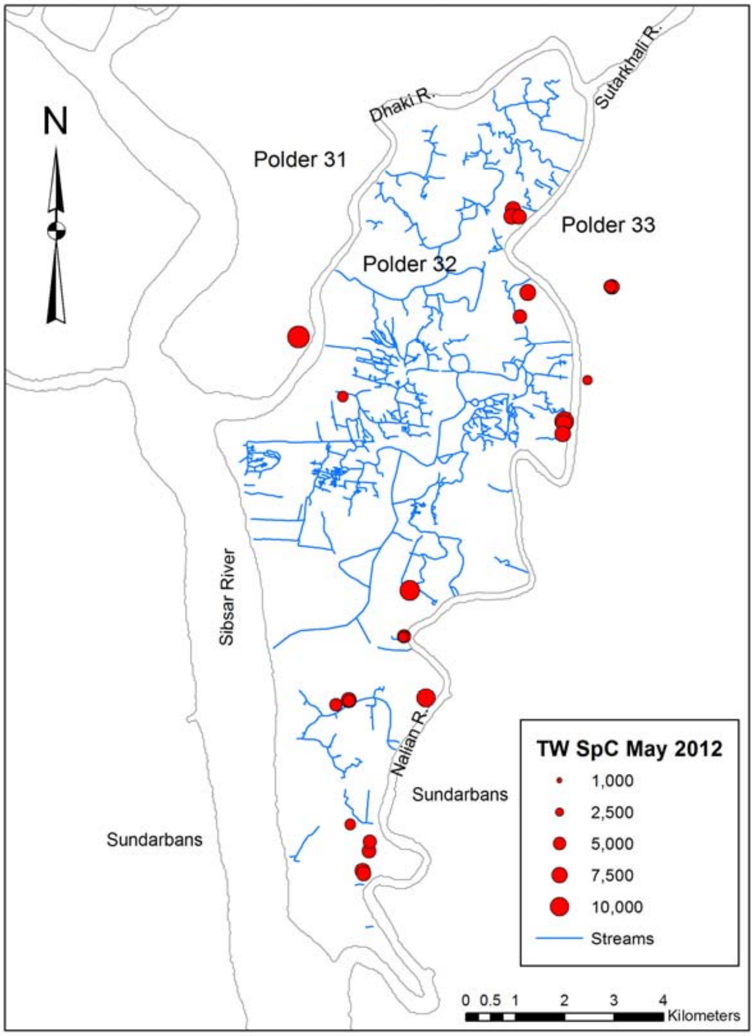

Figure 22. Specific conductivity (SpC) in uS/cm of May 2012 tube well samples. Measured specific conductivities are plotted as graduated symbols in red. TW = tube wells.

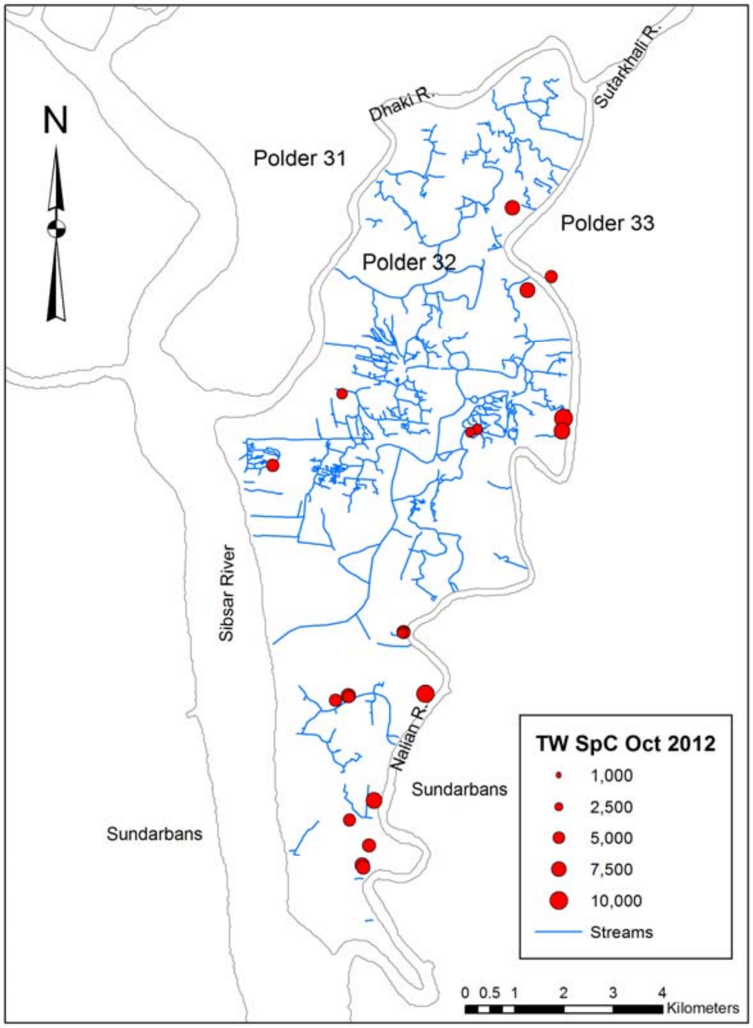

Figure 23. Specific conductivity (SpC) in uS/cm of October 2012 tube well samples. Measured specific conductivities are plotted as graduated symbols in red. TW = tube wells.

Figures 22 and **23** demonstrate high spatial variability of SpC in tube well samples with little or no seasonal variation. The high spatial variability observed across tube well samples (**Figures 22** and **23**) suggests low flow gradients and flow velocities across the shallow aquifer.

Project Data Analysis

Statistical Analysis

As stated earlier, 17 tube wells were sampled in both May and October 2012. Element concentrations were statistically analyzed for variance to test for seasonal variation. K, Na, and Cl concentrations exhibit lognormal distributions; therefore, log concentration values were compared using the parametric paired t-test to see if significant differences exist between the wet and dry season groundwater concentrations of conservative elements (**Table 11**).

Table 11. Parametric t-test of repeated dry and wet season tube well samples.

Conservative Elements	**Two-tailed P Value**	**Different at 95% level (P < 0.050)**	**Power**	**Mean Element Concentration Ratio (May/Oct)**
log K	<0.001	Y	1	1.5
log Na	0.004	Y	0.3	1.4
log Cl	0.035	Y	0.58	1.3

Results of the paired t-test (**Table 11**) indicate that concentrations of K, Na, and Cl vary significantly from dry to wet season. May concentrations of K, Na, and Cl are significantly higher than October. The lower elemental concentrations observed in October tube well samples may be caused by recharge of meteoric water to the shallow aquifer during the wet season. Recharge may occur where the clay cap is breached, most likely by human excavations or tube wells that are not properly cased.

Salinity Sources

Salts may be added to the land's surface from monsoonal inundation and/or over flooding of tidal channels. SpC was compared to identify if salinity of freshwater pond sites that were inundated after Cyclone Aila is greater than freshwater pond sites that were not (**Table 12**). Because both salinity and log salinity measurements failed the Shapiro-Wilk normality test, the nonparametric Mann-Whitney Rank Sum Test was run on salinity measurements.

Table 12. Parametric t-test of inundated and non-inundated Freshwater Pond (FP) samples.

Parameter	n	Median	Significantly Different at 95% level ($P < 0.050$) (Y/N)
SpC of FP	10	0.919	N
SpC of Inundated FP	17	0.984	N

Although median SpC is greater for inundated freshwater pond sites, results (**Table 12**) do not indicate a statistically significant difference between the two groups ($P = 1.000$). Therefore, salts in freshwater pond samples likely are not derived from soil that was salinized during inundation.

CHAPTER VI

CONCLUSION

Surface water and groundwater show significant compositional variability in both space and time in the vicinity of Polder 32 in southwest Bangladesh. Water found in freshwater ponds and rice paddies is sourced from meteoric water or tidal channel water in the wet season and concentrated by evaporation. Saline water found during the dry season in brine shrimp ponds is sourced from tidal channels, which contain water that is significantly more saline than in the wet season. The salinity of 61% of surface water samples exceeds the safe limit for human consumption while 30% of surface water samples exceed the yield limit for rice agriculture. Conservative elements B, K, Mg, Na, Sr, Cl, Br, and S occur in constant proportions throughout surface water samples regardless of total salinity, but concentrations vary due to dilution or evaporation. Groundwater is chemically unique from surface water in that B and S have precipitated out of solution.

Geochemical analyses suggest that groundwater is a mixture of tidal channel and meteoric water. Recently collected Carbon-14 ages of Polder 32 groundwater (Scott Worland, personal communication, October 4, 2013) indicate the groundwater in the shallow aquifer is connate, confined during Pleistocene depositional events. The estimated Pleistocene age of groundwater, in concert with observed low flow gradients and flow velocities across the shallow aquifer, suggests that its measured salinity originated at the time of sediment deposition through entrapment of tidal channel water as pore water. Therefore, the dilution observed in groundwater is indicative of either recharge with meteoric water on a point scale through surface discontinuities or seasonal variation in salinity of tidal channel water at the time of deposition.

Analysis of specific conductivity in groundwater shows high spatial variability with no coherent spatial trends, which implies poor mixing within the shallow aquifer and low groundwater flow gradients. Statistical tests show significant seasonal changes in groundwater composition. Most conservative elements in groundwater show a dilution trend during the wet season, which implies significant local recharge of meteoric water at tube well sites. However, conservative elements in groundwater also exhibit a dilution trend during the dry season, indicating that some of the variability in concentration may have originated at the time of deposition of tidal channel water.

Arsenic is present at elevated concentrations in groundwater. Specifically, 94% of groundwater samples exceed the World Health Organization's (2008) drinking water quality standard of 10 micrograms per liter (μg/L). Furthermore, 48% of groundwater samples surpass the Bangladesh drinking water limit (Tondel et al., 1999) of 50 μg/L, which is five times higher than World Health Organization standard.

Sulfur concentrations are lower in groundwater than in surface water. High DOC concentration in groundwater may indicate contamination of the shallow aquifer by surface sewage through uncased or poorly constructed tube wells or latrines. Elevated concentrations of DOC can cause iron oxyhydroxide reduction, which adds arsenic to groundwater and causes sulfide precipitation.

Because the number of samples is small, the higher specific conductivity of water in rice paddies that were previously shrimp ponds was not statistically significant; it is expected that continued sampling will increase the power of the statistical tests. Although the composition of water in rice paddies is similar to freshwater ponds, field observations and geochemical analyses show that it is sourced from wet season tidal channels and then concentrated by evaporation.

Most surface waters appear to be mixtures of meteoric and tidal channel water. Salt contents increase as a result of evaporation, especially in the dry season. However, field observations suggest that freshwater ponds are sourced not from wet season tidal channel water but from meteoric water. Moreover, statistical testing reveals that freshwater ponds that were inundated by Cyclone Aila are not significantly greater in salinity than freshwater ponds that were unaffected by inundation. Therefore, measured salinity in freshwater ponds may originate from meteoric water concentrated by evaporation. For all other water types tidal channels are the source of salts.

Additional geochemical analyses, including salt content in surface soil, are recommended to improve the statistical power of these conclusions and to inform the sustainability of seasonally alternating between aquaculture and agriculture.

REFERENCES

Ali, A.M.S. 2006. “Rice to shrimp: Land use/land cover changes and soil degradation in Southwestern Bangladesh.” *Land Use Policy*, 23: 421-435.

Allison, M.A., Khan. S.R., Goodbred, S.L., and S.A. Kuehl. 2003. “Stratigraphic evolution of the late Holocene Ganges-Brahmaputra lower delta plain.” *Sedimentary Geology*, 155: 317-342.

Azad, A.K., Jensen, K.R., and C.K. Lin. 2009. “Coastal Aquaculture Development in Bangladesh: Unsustainable and Sustainable Experiences.” *Environmental Management*, 44: 800-809.

Bahar, M.M. and M.S. Reza. 2010. “Hydrochemical characteristics and quality assessment of shallow groundwater in a coastal area of Southwest Bangladesh.” *Environ Earth Sci*, 61: 1065-1073.

Dasgupta, S., Huq, M., Khan, Z.H., Ahmed, M.M.Z., Mukherjee, N., Khan, M.K., and K. Pandey. 2011. “Cyclones in a Changing Climate: The Case of Bangladesh.” *Environment Department of the World Bank*, Economics of Adaptation to Climate Change Study.

Davis, S.N. and Dewiest, R.J. 1966. *Hydrogeology*. Wiley, New York.

Hydrolab. 1998. *DataSonde 4 and Mini Sonde Water Quality Multiprobes*. User’s Manual. Hydrolab Corporation, Texas.

Johnson, M.R.W. 1994. Volume balance of erosional loss and sediment deposition related to Himalayan uplifts. *Journal of the Geological Society of London*, 151: 217-220.

Mailloux, B.J., Trembath-Reichart, E., Cheung, J., Watson, M., Stute, M., Freyer, G.A., Ferguson, A.S., Ahmed, K.M., Alam, M.J., Buchholz, B.A., Thomas, J., Layton, A.C., Zheng, Y., Bostick, B.C., and A. van Geen. 2013. “Advection of surface-derived organic carbon fuels microbial reduction in Bangladesh groundwater.” *PNAS Early Edition*, 1-5.

Master Plan Organisation (MPO). 1987. “Groundwater Resources of Bangladesh.” *Technical Report No. 5*. Master Plan Organisation, Dhaka.

Michael, H.A. and C.I. Voss. 2009. “Controls on groundwater flow in the Bengal Basin of India and Bangladesh: regional modeling analysis.” *Hydrogeology Journal*, 17: 1561 1577.

Miller, R. L., Bradford, W. L., and N. E. Peters. 1988. “Specific Conductance: Theotretical Considerations and Application to Analytical Quality Control.” *U. S. Geological Survey*, Water-Supply Paper 2311.

Mondal, M.K., Tuong, T.P., and M.A. Sattar. 2008. “Quality and groundwater level dynamics at two coastal sites of Bangladesh: implications for irrigation development.” CGIAR Challenge Program on Water and Food.

Nobi, N., and A.D. Gupta. 1997. “Simulation of Regional Flow and Salinity Intrusion in an Integrated Stream-Aquifer System in Coastal Region: Southwest Region of Bangladesh.” *Ground Water*, 35: 786-796.

Plunkett, E.R. 1976. “Handbook of industrial toxicology.” *Chem Publ Coy Ltd*, New York, pp 99-101.

Ravenscroft, P. 2003. Overview of the hydrogeology of Bangladesh. In: Rahman A.A., Ravenscroft, P. (eds) Groundwater resources and development in Bangladesh: background to the arsenic crisis, agricultural potential and the environment, chap. 3. Bangladesh Centre for Advanced Studies, Univ Press, Dhaka, pp 43-86.

Salam, M.A., Ross, L.G., and C.M.M. Beveridge. “A comparison of development opportunities for crab and shrimp aquaculture in southwestern Bangladesh, using GIS modeling.” *Aquaculture*, 220: 477-494.

Shamsudduha, M. and A. Uddin. 2007. “Quaternary shoreline shifting and hydrogeologic influence on the distribution of groundwater arsenic in aquifers on the Bengal Basin.” *Journal of Asian Earth Sciences*, 31: 177-194.

Shamsudduha, M., Marzen, L.J., Uddin, A., Lee, M.-K., and J.A. Saunders. 2009. “Spatial relationship of groundwater arsenic distribution with regional topography and water table fluctuations in the shallow aquifers in Bangladesh.” *Environmental Geology*, 57: 1521-1535.

Shamsudduha, M., Taylor, R.G., Ahmed, K.M., and A. Zahid. 2011. “The impact of intensive groundwater abstraction on recharge to a shallow regional aquifer system: evidence from Bangladesh.” *Hydrogeology Journal*, 19: 901-916.

Shang, Y.C., Leung, P., and B.H. Ling. 1998. “Comparative economics of shrimp farming in Asia.” *Aquaculture*, 164 (1-4): 183-200.

Singh, O.P., Ali Khan, T.M., and M.S. Rahman. 2000. “Changes in the frequency of cyclones over the North Indian Ocean.” *Meteorology and Atmospheric Physics*, 75 (1-2): 11-20.

The World Bank. 2011. *Data. Bangladesh*. Retrieved August 15, 2012 from http://data.worldbank.org/country/bangladesh.

Todd, D.K. 1980. *Groundwater hydrology*. Wiley International Edition. Wiley, New York.

Tondel, M., Rahman, M., Magnuson, A., Chowdhury, A., Faruquee, M. H., and S. A. Ahmad. 1999. “The Relationship of Arsenic Levels in Drinking Water and the Prevalence Rate of Skin Lesions in Bangladesh.” *Environmental Health Perspectives*, 107 (9): 727-729.

World Health Organization. 2008. *Guidelines for drinking-water quality*. Third Edition, Incorporating the First and Second Addenda. Geneva.