

EFFECT ON GROUNDWATER QUALITY FROM PROXIMAL SURFACE WATER
BODIES AND EFFECT ON ARSENIC DISTRIBUTION IN BANGLADESH:
GEOCHEMICAL CONTROLS

by

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Abstract

The province (upazila) of Matlab in SE Bangladesh is highly affected with elevated concentrations of dissolved As content and widespread fecal contamination in untreated drinking waters. The study area is sedimentologically composed of thick floodplain deposits of Holocene age overlying Plio-Pleistocene grey fine to coarse sands with considerable clays (consisting of Dupi Tila formation). The goal of the current study is to understand the possible impact of co-occurrence of dissolved organic carbon (along with As release) and fecal indicator bacteria (e.g., *E.coli*) in aquifers from shallow to deep groundwater quality in this area. Nineteen groundwater (spanning a depth range of 14 to 240 m) samples and nine surface water samples (eight ponds and one canal in proximity to the piezometer nests) were collected from four different piezometric nests within north and south Matlab Upazila in Bangladesh during the monsoonal season (Jun-Jul 2014). The analyses of dissolved organic carbon (DOC) and its fluorescence properties indicate that the chemical character of DOC from shallow to intermediate groundwaters (<150 m) and surface water is dominated by more aromatic and humic materials than deeper groundwaters. Both groundwaters and surface waters may receive humic substances leached from soil and/or from the cellular constituents and exudates of indigenous aquatic organisms. Dissolved organic carbons in groundwater and surface waters are composed of predominantly UVA and UVC-humic like along with tryptophan like components. Only 15% of total C is modern carbon at shallowest depths (<30 m) in groundwaters. The recharge source of groundwaters is from local precipitation, with or without some evaporation before infiltration as depicted by the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ variations and the water is infiltrating through mostly terrestrially derived weathered sediments into the aquifers. The type of water in the study area is Ca-Na- HCO_3^- type. More toxic and soluble As (III) is present in shallow groundwaters (<30 m). High

concentrations of As (V) and As_(t) are observed high in shallow and intermediate depth wells (<150 m). The most probable number based on the Colilert test and qPCR result for *E.coli* suggest that unprotected surface waters are harbingers for high microbial population compared to hand pumped wells. However, the very low observed concentrations of cultured *E. coli* (<1-10 MPN/100 mL) and *E. coli* DNA (<40 Copies/100 mL) in the wells indicates that the abundance of *E.coli* cells decrease rapidly with residence time in oligotrophic aquifers. Thus, it may be suggested that more humic DOC in shallow and intermediate groundwaters may be involved in complexation or other biogeochemical reactions that may mobilize As in groundwater. The non-indigenous bacteria can be the primary producers of DOC in the aquifers which can be utilizing surface derived DOC.

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Dedication

To People of Bangladesh

Chapter 1 - Introduction

Safe drinking water scarcity and water pollution are among the greatest environmental threats in some developing countries like Bangladesh and some other SE Asian countries. Over the last few decades, the majority of people in Bangladesh shifted their drinking water supply from surface water bodies (ponds and rivers) to groundwaters and consequently above 10 million new private wells have been installed to provide drinking water for over 130 million people (Harvey et. al., 2006). Groundwater has been utilized as a dependable source of drinking water rather than surface water. Typically surface water has been contaminated with microorganisms causing a significant risk of water-borne diseases and mortality, especially infant mortality. Therefore, groundwater from hand-pumped tubewells is the most popular drinking water supply in rural Bangladesh. However, a considerable switch of rural consumption to untreated groundwater supplied by millions of domestic wells over the past few decades has turned into a humanitarian disaster (Stute et al., 2007). Tragically, evidence of elevated arsenic (As) concentrations from drinking groundwaters (first reported during mid-1990) in the Ganges-Brahmaputra-Meghna Delta (GBMD) region of Bangladesh (Chakraborty and Saha, 1987; BGS and DPHE, 1999) initiating acute cases of arsenicosis and other related diseases. Several large scientific and social surveys demonstrate that high dissolved As concentrations are restricted to the upper 100 m of the aquifers and the distribution of As is spatially very heterogeneous within short distance (on scales of meters to kilometers) (BGS and DPHE, 2001; van Geen, et al., 2003b; Stute et al., 2007). The As concentrations in aquifers commonly exceed the World Health Organization (WHO) drinking water standard limit (10 µg/L) beneath the Holocene floodplains within the alluvial and deltaic plains of the GBM rivers. The As contamination issue is most common in the SE and NE of Bangladesh (McArthur et al., 2001). Higher percentage of shallow wells containing >10 µg/L As are observed in SE parts of Bangladesh and about 57% of the people from this specific region are more or less dependent on As contaminated water for drinking water purposes (Yu et. al., 2003). Three mechanisms have been proposed to explain As contamination of groundwater in the GMBD: (1) oxidation of arsenical pyrite in the alluvial sediments is contributing As release in groundwater as water table drawdown allows atmospheric O₂ to enter the aquifer (Mallick and Rajagopal, 1996; Mandal et al., 1998; Chowdhury et al., 1999); (2) absorption of anions within aquifer minerals promoting solubility of these ions into

solution by competitive chemical exchange of phosphate anions derived from over-usage of fertilizer to surface soils (Acharrya,1999); (3) reduction of iron oxyhydroxides (FeOOH) and release of dissolved As to solution under anoxic conditions (Bhattacharya et al., 1997; Nickson et al., 1998 and 2000; McArthur et al., 2001). The first two mechanisms of As release into groundwater are called in to question, because pyrite (dissolved sulphides) in groundwater has not been observed in the groundwaters; the process would require oxidizing conditions. Therefore, this is not considered as a source of As in Bangladesh groundwaters.

The replacement of surface water with hand pumped domestic wells as a major source of drinking water is often presumed to have reduced diarrheal complications among the populations that derived their water by this method. But recent evidence does not reveal a reduction of diarrhoea in households that adopted domestic wells (Sommer and Woodward 1972; Levine et al., 1976; Curlin et al., 1977; Briscoe, 1978; Khan et al., 1978; Luby et al., 2008). These studies have suggested that above 40% of shallow wells in Bangladesh are contaminated with human fecal organisms (Hoque, 1999; Islam et al., 2001; Luby et al., 2006 and 2008). Bacteria in groundwater may originate from recharge sources to the groundwater. Excellent groundwater quality can be characterized as containing <1 coliform/100 mL. Heterotrophic bacterial population, which is often very sparse (<10 organisms/mL), can be stimulated at 15°C or more temperature (Alson, 1982; Geldreich and LeChevallier, 1999). Thus, microbial quality shows slight variation in groundwater because the groundwater aquifer is protected from surface contamination. Some groundwaters, however, are not insulated from surface contamination (Allen and Geldreich, 1975). Agricultural fertilizer runoff and improperly segregated landfills can contribute to introduction of nitrates and a variety of organics, including biodegradable ones. Under such situations, bacterial populations in groundwater can be extreme, resulting in heterotrophic bacteria/mL counts of 1000 to 10,000/mL (Geldreich and LeChevallier, 1999). In the groundwaters that are not well protected from contamination by surface runoff and wastewater effluents, - coliforms and pathogens (bacterial, viral, protozoan) may be introduced into them unless a treatment barrier is activated (Craun, 1985). Surface waters are subject to a variety of microbial contaminants introduced by surface runoff over watersheds and the upstream discharges of domestic, agricultural and industrial wastes (Geldreich and LeChevallier, 1999). The key factors that help microbial colonization within waters are: source of nutrients, protective habitat and water temperatures ($\geq 15^{\circ}\text{C}$) favoring the right conditions for rapid proliferation

(Geldreich et al., 1977; Water Research Centre, 1977; Bartram et al., 2003). Naturally occurring and man-made nutrients include phosphorus, nitrogen, trace metals, and carbon which may be introduced into source waters with varying concentrations. Generally, microbiological activity in groundwater is often more stable than surface water (Katayama, 2008). As untreated groundwater is a communal source of drinking waters in rural Bangladesh, growing evidence of prevalent fecal contamination of groundwater is a major concern along with health risks. Eleven percent of all deaths are estimated to be caused by diarrheal diseases in Bangladesh (Streatfield et al., 2001).

The mechanisms of releasing dissolved As content along with finding fecal indicator bacteria growth in aquifers, are controversial topics by themselves. A widely held view is that, under anaerobic conditions- a geogenic contaminant As is released into groundwater following the reductive dissolution of Fe-oxide phases onto which As is primarily adsorbed (Nickson et al., 1998; McArthur et al., 2001). These processes are usually microbially mediated and the presence of labile organic carbon in aquifers is a rate-limiting constituent for the As release process in groundwater (Islam et al., 2004; Lawson et al., 2013). Additionally, it may be thought that assimilation of such mutable organic carbon may be acting as one of the sources of energy for fecal indicator bacteria (*E. coli*) growth in aquifers. The present study has been conducted to understand the possible impact of labile organic carbon on progressively shallow to deep groundwater chemistry (14-240 m) in relation to dissolved As and the co-occurrence of fecal indicator bacteria (*E. coli*) within Matlab of SE Bangladesh.

Chapter 2 - Background

The Ganges-Brahmaputra-Meghna (GBM) river basin is a transboundary river basin with a total area of over 1.7 million km², distributed between India (64 %), China (18 %), Nepal (9 %), Bangladesh (7 %) and Bhutan (3 %) (AQUASTAT Water Report 37, 2011) (Table 2.1). The headwaters of the Ganges and Brahmaputra originate in the Tibetan China area of the Himalayan mountain range. The Ganges river flows SW into India, then turns SE, joining with numerous major tributaries. The Ganges joins with the Brahmaputra and Meghna rivers to flow into the Bay of Bengal as the Padma and Meghna rivers in Bangladesh, respectively (McEwen, 2008; AQUASTAT Water Report 37, 2011). Bangladesh occupies the part of the GBM riverine system and lies mostly within the Bengal Basin (Fig 2.1). The GBM riverine system carries the large total sediment load in the world. The GBM delta was produced from erosion of the Himalayas and is producing the largest fluvio-deltaic system in the world. This fluvial-deltaic system forms prolific fresh water aquifers in most parts of Bangladesh and eastern India. The unconsolidated near-surface sediments are Pleistocene to recent in age. Fluvial and estuarine sediments underlie most parts of Bangladesh and the groundwater is predominantly withdrawn from these Quaternary strata. Bangladesh demonstrates enormous surface water resources due to frequent rains and favorable monsoonal climate spanning almost 5-6 months in a year. Until the 1970's

Figure 2.1 Map of the GBM catchments draining into the Bay of Bengal (Whitehead et al., 2015)

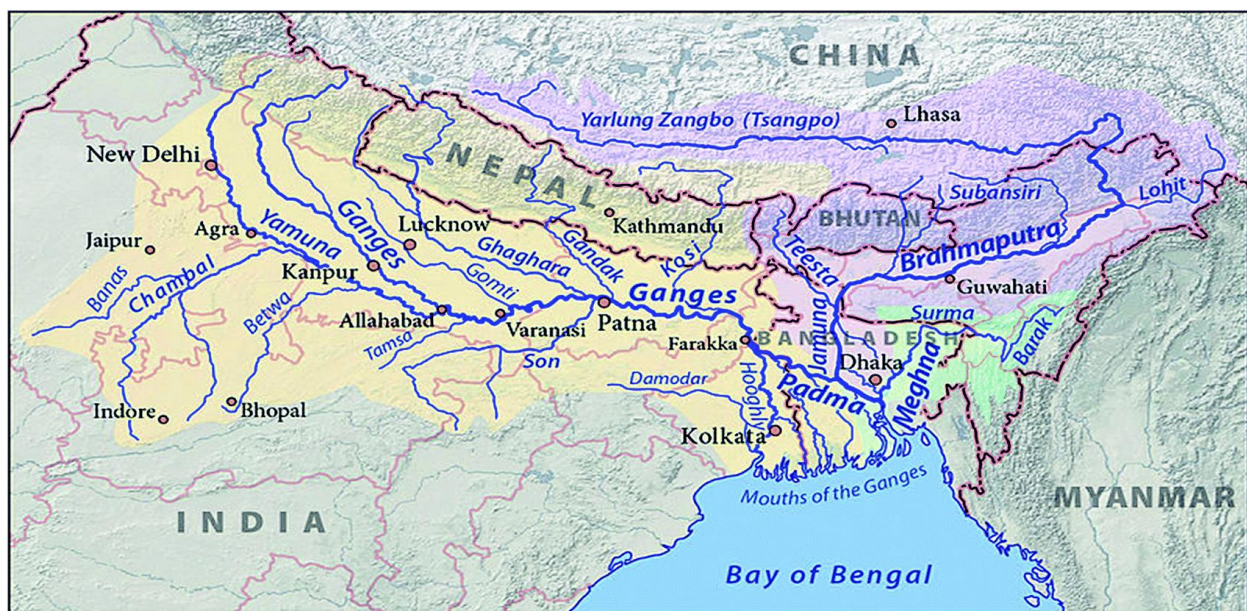


Table 2.1 Country areas in the Ganga-Brahmaputra-Meghna (GBM) river basin (Joint Rivers Commission Bangladesh, 2011)

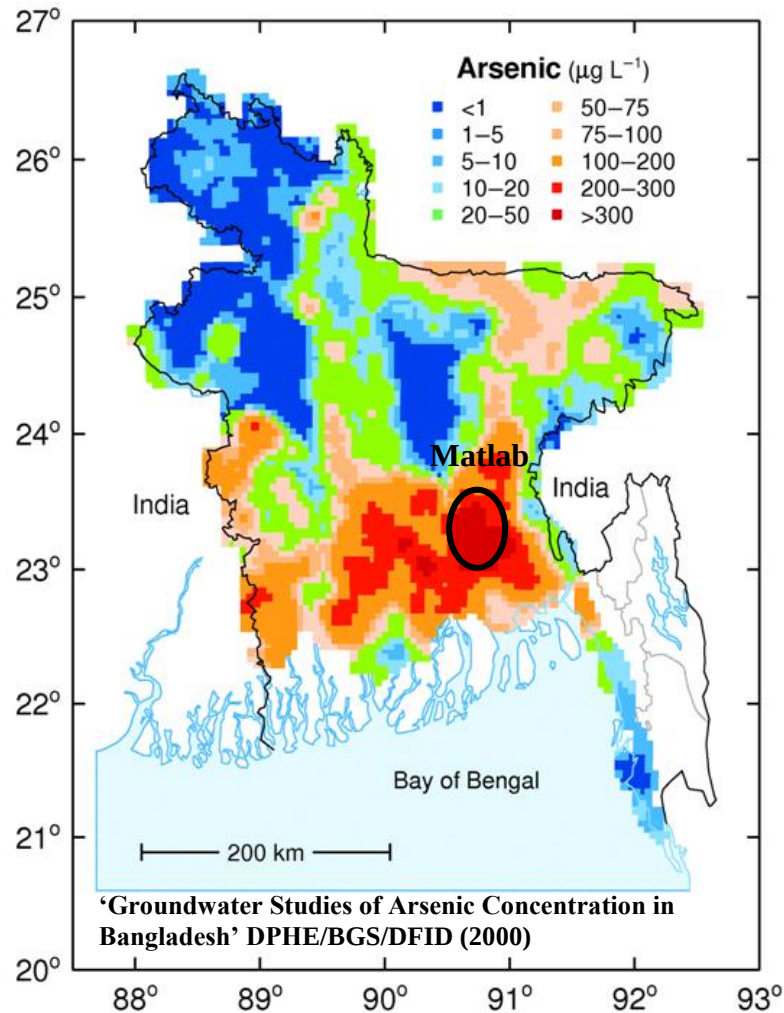
Basin	Area		Countries included	Area of country in basin (km ²)	As % of total area of the basin	As % of total are of the country
	km ²	% of Southeast Asia				
Ganges	1 087 300	5.2	India	860 000	79	26
			China	33 500	3	0.3
			Nepal	147 500	14	100
			Bangladesh	46 300	4	32
			Bhutan	-	-	-
Brahmaputra	543 400	2.7	India	195 000	36	6
			China	270 900	50	3
			Nepal	-	-	-
			Bangladesh	39 100	7	27
			Bhutan	38 400	7	100
Meghna	82 000	0.4	India	47 000	57	1
			China	-	-	-
			Nepal	-	-	-
			Bangladesh	35 000	43	24
			Bhutan	-	-	-
Total	1 712 700	8.3	India	1 102 000	64	33
			China	304 400	18	3
			Nepal	147 500	8	100
			Bangladesh	120 400	7	83
			Bhutan	38 400	3	100

Table 2.2 Simplified stratigraphic succession of Bangladesh (After Alam et al., 1990; Khan, 1991 and DPHE, 1999) (Ravenscroft et al., 2004)

Age	Stratigraphic units	Lithology	Notes
Late Pleistocene–Holocene	Chandina Formation Dhamrai Formation Unclassified deposits	Upward fining, grey micaceous, medium and coarse sand to silt with organic mud and peat.	Forms major aquifers beneath recent floodplains. Probably <150 m thick.
Lower Pleistocene	Madhupur Clay Barind Clay	Tough, red-brown to grey, silty-clay; residual deposits; kaolinite and iron oxide.	Often absent beneath Holocene floodplains. Thickness 6 to 60 m.
Plio-Pleistocene	Dupi Tila Formation Dihing Formation	Yellowish-brown to light grey, medium and coarse sand to clay; very weakly consolidated; depleted in mica and organic matter.	Forms major aquifers beneath the terraces and hills, and deeper aquifers beneath the Holocene floodplains. Hundreds to thousands of metres thick
Tertiary	Tipam Group	Yellowish-brown, weakly consolidated sandstone and mudstone.	Minor aquifers in hills
Mesozoic	Surma Series	Consolidated sandstone and shale	No significant aquifers
	Barail Series	Consolidated sandstone and shale	
	Jaintia Group	Shale, limestone and sandstone	
	Sylhet Traps	Basalt, shale and sandstone	

this surficial water was mainly used as drinking waters for the majority of the population of Bangladesh (Zahid et al., 2006). But bacteriological contamination resulted in multiple water-borne diseases such as cholera and dysentery that caused millions of deaths in the region (Ravenscroft et al., 2004). To resolve this problem approximately 6 to 11 million hand-pumped private wells have been installed in Bangladesh during last few decades partly driven by the UN International Decade for Water Supply and Sanitation (Kinniburgh et al., 2003). Unfortunately, the majority parts of Bangladesh have high As levels in groundwater above the Bangladesh drinking water standard limit of As (50 µg/L) and World Health Organization (WHO) drinking

Figure 2.2 Arsenic distributions at shallow depth wells in Bangladesh (BGS, 2001)

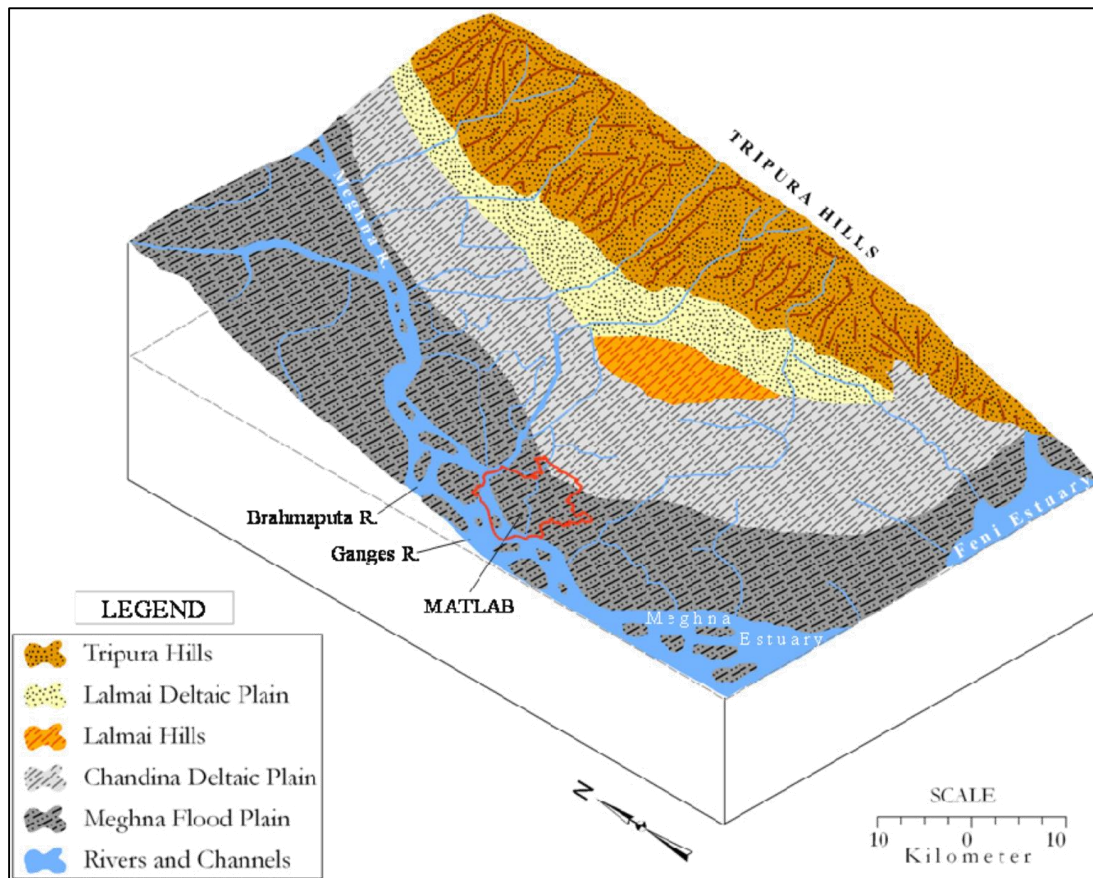


water standard limit of As ($10 \mu\text{g/L}$) (Rahman et al., 2002). Approximately 30 % of the domestic wells exceed the Bangladesh Drinking Water Standard (BDWS) limit of As, $50 \mu\text{g/L}$ (BGS and DPHE, 2001). Millions of people previously considered to have access to safe water are now known to be exposed to high As through drinking untreated waters (Smith et al., 2000; BGS and DPHE, 2001; Smedley and Kinniburgh, 2002; von Brömssen, 2012). Several studies suggested that dissolved As in groundwater occurs below the Holocene floodplains (GBM), within the Chandina and Dhamrai formations (Burgess and Ahmed, 2006) (Table 2.2). The maximum thickness of these aquifers is about 100 m. The Holocene sediments are dark-grey, highly micaceous, unweathered and organic matter is present in concentrations of up to $\sim 6 \text{ wt}\%$. Low hydraulic gradients are somewhat responsible for the flushing of the Holocene sediments since their time of deposition (Burgess and Ahmed, 2006). In Bangladesh, the As concentration is

above BDWS $>50 \mu\text{g/L}$ in those wells which are located in the area occupied by the young floodplains and deltaic sediments. On the other hand, the dissolved As content is lower in wells installed in Holocene coarse fan deposits and negligible in wells developed within Pleistocene and older sediments (BGS and DPHE, 2001). In Bangladesh, high As groundwater was officially recognized in 1993 (Smith et al., 2000; BGS and DPHE, 2001; Smedley and Kinniburgh, 2002; von Brömssen, 2012). Since then, it has been recognized that most parts of Bangladesh are at risk from elevated As concentrations in their drinking waters. The results of the BGS survey (BGS and DPHE, 2001) showed that the greatest number of high As wells are observed in the S and the SE parts of Bangladesh (Berser, 2007) (Fig 2.2). Matlab is one of the areas highly affected by As in SE Bangladesh. The As concentration ranges from <1 to $3644 \mu\text{g/L}$, and more than 70% of functioning tubewells exceeded the WHO guideline of $10 \mu\text{g/L}$ of dissolved As in Matlab (Rahman et. al., 2006). The surroundings of Matlab are composed of thick floodplain deposits of Holocene age and unconformably overlying the Plio-Pleistocene Dupi Tila Formation (after Bakr, 1977). The groundwater flow systems in the study area may be explained by the following ways: (i) presence of the recharge areas and deeper regional horizontal flow system as seen at the Tripura Hills area to the east of the study area and ii) presence of local groundwater recharge and small-scale local flow systems mostly driven by local topography (von Brömssen, 2012) (Fig 2.3). These local flow systems extend to approximately 30 m below ground level (bgl) and young groundwater (below 1,000 yr) should be expected within about 25 m bgl. Groundwater flow at certain depths (below this local flow system) for natural and undisturbed system is very slow. Groundwater pumping for irrigation usage is responsible for more than 85 % of the groundwater withdrawal (BGS and DPHE, 2001; von Brömssen, 2011). However, the patterns of local flow can be noticeably changed by irrigation wells during the irrigation seasons as a result of induce a vertical flow. Hence, groundwater abstraction may increase due to extensive irrigation pumping (von Brömssen, 2011).

The contamination of drinking water sources by chemical contaminants has been a common scenario in densely populated countries like Bangladesh. Both ground water and surface water may be microbiologically contaminated by various means, including introduction of agricultural runoff, poor sanitation etc. (Geldreich, 1990; Grabow et al., 1996; WHO, 2008). Unprotected surface waters are harbingers of higher microbial populations compared to extracted water from hand-pumped wells. Fecal contamination of groundwater may be reduced because of

Figure 2.3 The geomorphic units in and around the study area (Bakr, 1977) (Source: Mozumder, 2011)



filtration through aquifer sands (van Geen et al., 2011). Microbial contamination of groundwater is generally attributed to percolation of water containing human or livestock feces into the underlying aquifers. However, microbes attached to surfaces inside the pump or the well casing can also partially contribute to increase fecal contamination within hand pumped wells. The usage of contaminated water for periodic priming of the hand pumps is also one of reasons for such contamination (Ferguson et al., 2011). Population growth along with sanitation difficulties means that morbidity due to diarrheal diseases (Emch, 1999; Escamilla et al., 2011) is very high in rural Bangladesh, resulting in an estimated 11% of all deaths in the country (Streitfield et al., 2001). The majority of people in rural Bangladesh have been using shallow hand-pumped wells in sandy aquifers for drinking water usage; hence it may be assumed that the high level of diarrheal disease might be attributable to emergence of fecal contaminated well waters (Islam et al., 2007; Leber et al., 2011; Wu et al., 2011). Recent studies showed that the occurrence of fecal indicator bacteria (*E. coli*) in hand pumped domestic well water is frequent especially during the

monsoon periods (van Geen et al., 2011; Leber et al., 2011). However, the origin of *E. coli* into the aquifer may be attributed to vertical infiltration from near-surface sources (*e. g.*, latrines) or through lateral percolation of fecal contaminated ponds (Knappett et al., 2011 and 2012a).

The condition that leads to As mobilization in groundwater and fecal contamination in Bangladesh aquifers have been formulated in several ways. It is thought that in most cases As is released through microbial reduction of iron oxyhydroxides which releases to groundwater with changing redox conditions (Korte and Fernando, 1991) and labile organic carbon is helping to drive the microbial reduction process in groundwater (Chapelle and Lovely, 1992; Nealson, 1997). In this scenario, several sources for the organic matter have been postulated, *e.g.*, presence of peat layers or disseminated organic matter in soils (Ravenscroft et al., 2001). It has been suggested that during aquifer recharge from ponds biologically degradable organic carbon is carried down into the shallow aquifers. This drawdown may be facilitated by irrigation pumping and pond/surface waters are transported to that depth where the As concentrations are highest. In contrast, recharge from irrigated rice fields may contain predominantly recalcitrant organic carbon (Neumann et al., 2010). The cycling of Fe and dissolved organic matter (DOM) has been postulated to accelerate As mobilization in these sedimentary aquifers (Mladenov et al., 2010). The implication can be demonstrated in two ways: (i) labile DOM can aid as a source of energy (electrons) for Fe- and humic-reducing microbial communities (Tufano et al., 2008). The probable sources of labile DOM are terrestrial (plant/soil) organic matter in these aquifers, such as the presence of peat all the way through the aquifer sediments (McArthur et al., 2004); DOM in surface water may be transported to depth by natural flow or irrigation pumping (Polizzotto et al., 2005; Harvey et al., 2002; van Geen et al., 2003). (ii) DOM and Fe-reduction are related via the capacity for transferring electrons (electron shuttling) of humic substances (Mladenov et al., 2010). Moreover, the involvement of microbially mediated reductive processes and the oxidation of labile organic carbon are broadly considered to offer a critical mechanism for As release in shallow groundwaters. Dissolved organic carbon can be drawn into aquifer systems upto about 100 m (Lawson et. al., 2013). The aquifer redox condition is controlled by advected organic carbon to allow As release by natural process (Mailloux et al., 2013).

The frequency of *E. coli* detection in groundwaters increases with population in Bangladesh and decreases with the As content in the aquifer. Along with an increase in fecal waste discharged to the environment through leaking latrines (Knappett et al., 2011) the reason

might be attributable to downward transport of *E. coli* associated with local recharge (van Geen et al., 2011). Hand-pumped wells could potentially influence drinking water quality acting as persistent reservoirs for microbial indicator bacteria (Ferguson et al., 2011). Latrine polluted ponds may serve as one of sources of fecal contamination that infiltrate into shallow unconfined aquifers. Improper sealing of private hand-pumped well annuli may also contribute to significant enhancements in microbial contamination in drinking water (Knappett et al., 2012 and 2012b). Organic carbon is often a growth limiting nutrient. Organic carbon is exploited by heterotrophic bacteria for production of new cellular components (assimilation) and as an energy source (dissimilation) (LeChevallier et al., 1996). Most organic carbon in water originates via natural process and derived from living and decaying vegetation (Geldreich and LeChevallier, 1999). Organic matter in treated waters is essentially the biodegradable fractions. (LeChevallier, 1990; LeChevallier et al., 1991; Mathieu et al., 1992; Servais et al., 1987; Servais et al., 1992; Volk et al., 1994). Some typical events (algal bloom, rainfall, etc.) are capable of altering organic matter quality in untreated waters and may act as a catalyst for coliform growth (Boualam et al., 2002; LeChevallier et al., 1990; Lowther et al., 1984, Bouteleux et al., 2005).

Chapter 3 - Hypothesis and Objectives

Hypotheses

The hypotheses of this study to be tested are:

Young labile organic carbon may potentially accelerate As release in shallow reducing aquifers. Mobilization of As into groundwaters will be facilitated as long as As-bearing iron-oxides are available for reduction and labile organic carbon is available to drive the process.

As stated by Lawson et al., (2013), the occurrence of As in groundwaters under anaerobic conditions follow the reductive dissolution of iron oxide phases onto which As is primarily adsorbed (Nickson et al., 1998; McArthur et al., 2001). These processes are microbially mediated and labile organic carbon is a rate-limiting component of the As release mechanism (Islam et al., 2004). The role of the organic carbon which is responsible for driving As release in groundwaters remains a controversy (Harvey et al., 2002; McArthur et al., 2004 and 2011; Neumann et al., 2010; Fendorf et al., 2010). Extensive groundwater pumping along with drawdown of surface waters containing young labile organic matter (OM) may potentially accelerate As release into shallow reducing aquifers. This concept has attracted significant attention (Aggarwal et al., 2003; van Geen. et al., 2003; Michael et al., 2008; Datta et al., 2011; Burgess et al., 2010; Harvey et a., 2002; Lawson et a., 2013).

In addition, assimilation of organic carbon may lead to fecal bacterial growth in groundwaters (Geldreich and LeChevallier, 1999). Generally, the microbial quality of groundwater pumped from wells is better than unprotected surface waters, but in many cases well discharge may comprise significant fecal indicator bacteria (*E. coli*) levels (as shown by Islam et al., 2001, Hoque et al., 2006, Leber et al., 2011, van Geen et al., 2011).

Geldreich and LeChevallier, (1999) suggested that organic carbon is favorable for heterotrophic bacteria as an energy source (dissimilation) to generate fresh cellular elements (assimilation) in water (LeChevallier, et al., 1996). Additionally, Bouteleux et al., (2005) postulated that as OM is the source of carbon and energy for heterotrophic bacterial growth including coliforms in water (LeChevallier, 1990; LeChevallier et al., 1991; Mathieu et al., 1992; Servais et al., 1987; Servais et al., 1992; Volk et al., 1994). The characteristics of OM in untreated water can be acting as catalyst for coliform including fecal indicator (*E. coli*) growth (Boualam et al., 2002; LeChevallier et al., 1990; Lowther et al., 1984).

Hence the objectives of this study are:

- (1) To explore sources and characteristics of dissolved labile organic carbon that liberate As from iron oxyhydroxides within an aquifer.
- (2) To investigate water chemistry variation and source of recharge within shallow through deep aquifers in the study area and explore whether there are any correlations with the types of DOC found.
- (3) To examine the extent of co-occurrence of culturable and molecular (DNA) fecal indicator bacteria (*E. coli*) with labile organic carbon within shallow to deep groundwaters in the studied aquifers (14-240 m).
- (4) To sample the indigenous microbial community DNA in groundwater and surface water to identify the known genes involved in reductive dissolution of iron oxyhydroxides.

Chapter 4 - Study Area

The study area Matlab upazila is situated in SE Bangladesh which is divided into North and South parts. Matlab is located in the floodplain of Meghna River Basin from 23°15' to 23°30'N latitude and 90°36' to 90°50'E longitude near the confluence of Ganges, Brahmaputra and Meghna rivers with an aerial extent of about 409.22 km² in Bangladesh. A local river named Dhanagoda flows across Matlab (Fig 4.1). The study area encompasses a triangular-shaped tract known as Chandina Deltaic plain bounded by the Meghna River in the west, Lalmai Hills in the east and Old Meghna estuary at its south. The topographic feature is represented by a vast expanse of deltaic plain and old Meghna estuarine flood plain deposits. Physiographically, Matlab is situated in Meghna estuarine floodplain area (Fig 4.2 (a)). The Chandina deltaic plain is referred to as the Tipperah surface (Morgan and McIntyre, 1959), older alluvial surface (Umitsu, 1987 and 1993) and old Meghna estuarine surface (Brammer, 1996). The unit consists of silt, silty loam, silty clay and grayish clay and has been named as Chandina formation. The sediments resembling those of the recent Meghna flood plain are more compacted, decomposed and oxidized (after Bakr, 1977) (Table 4.1). Most parts of Bangladesh are covered with Quaternary sediments deposited by the GBM river systems. The sediments are thick, with most areas having a good water bearing capacity (Rahman, 2013). Alluvial aquifers are the main source of groundwater in the study area. The aquifers are mostly unconfined to semi-confined in nature. The unconfined water table occurs at shallow depths 2-5 m below ground surface. The groundwater table reaches its maximum level during the monsoon period (June-October) and its minimum level during the dry season (November-May) (Pasupuleti, 2005). The study area is located in the SE hydrologic regions as per National Water Management Plant (Fig 4.2 (b)) and in zone 'G' (UNDP, 1982). The main aquifer was considered for only deep tube-well development with discharge up to 2 cubic sec. The climate is tropical according to the Köppen-Geiger system (Aw). The average temperature in Matlab is 26.0 °C and in a year, the average rainfall is 2130 mm. The monsoon has a good deal of rainfall, while the dry season has very little. The driest month is December, with 6 mm of precipitation. Most of the precipitation falls in July, averaging 442 mm (<http://en.climate-data.org/location/969823/>).

Figure 4.1 Location map of the study area

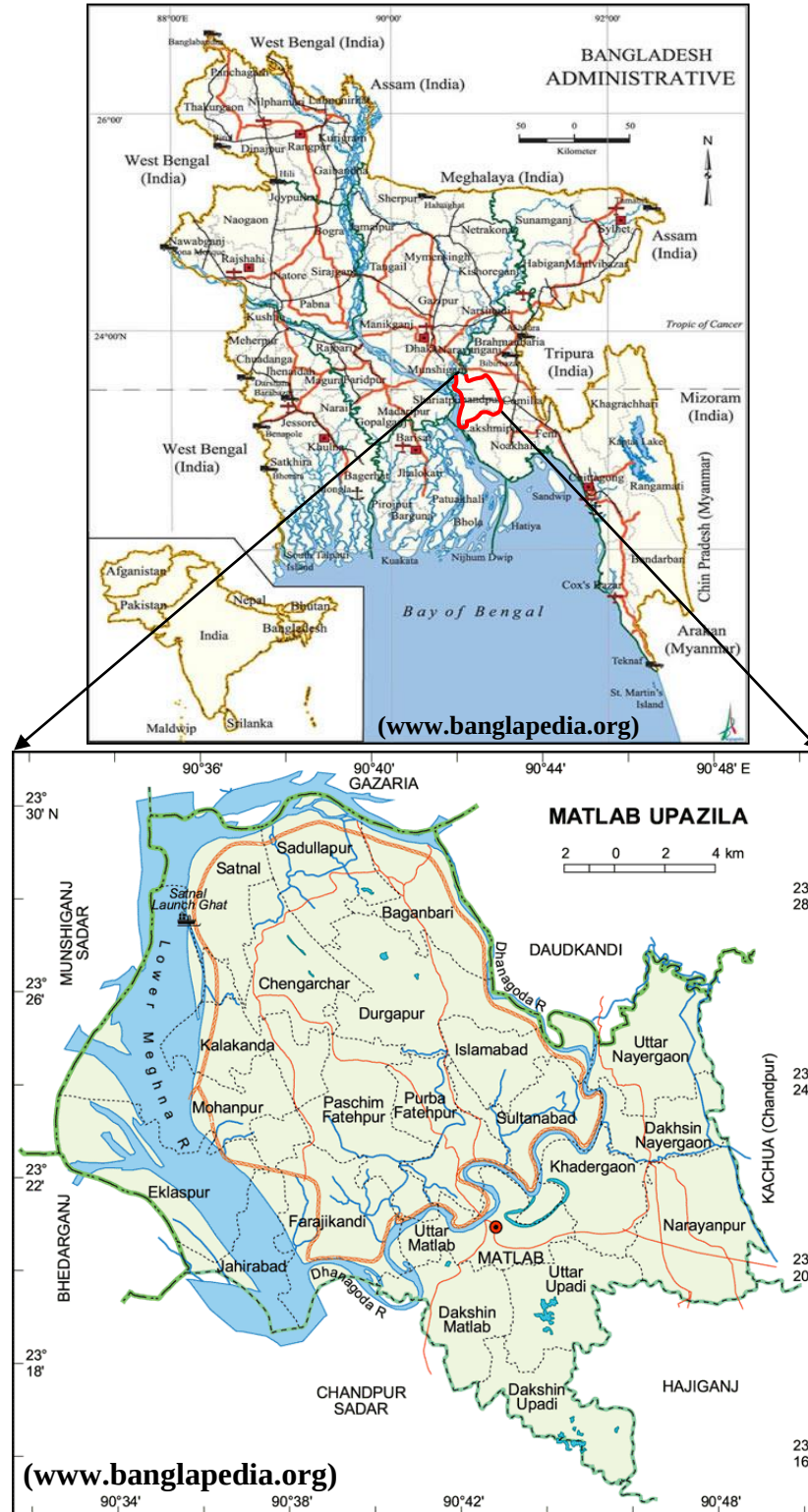
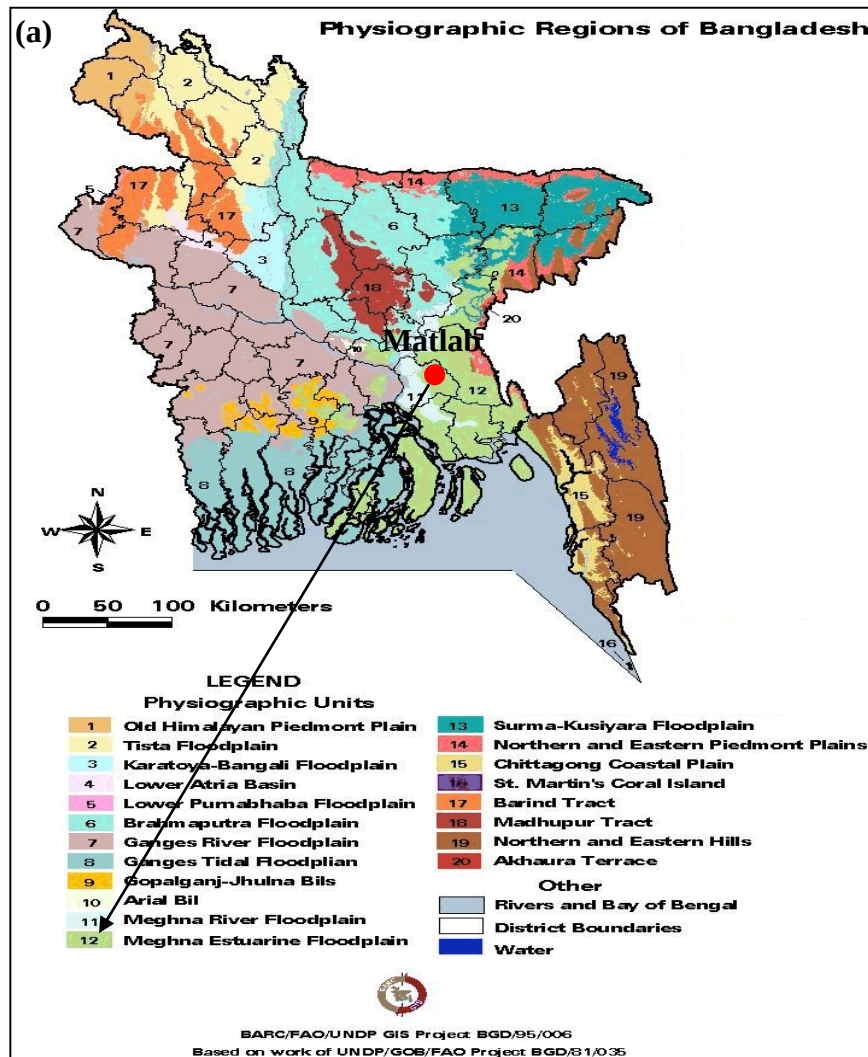
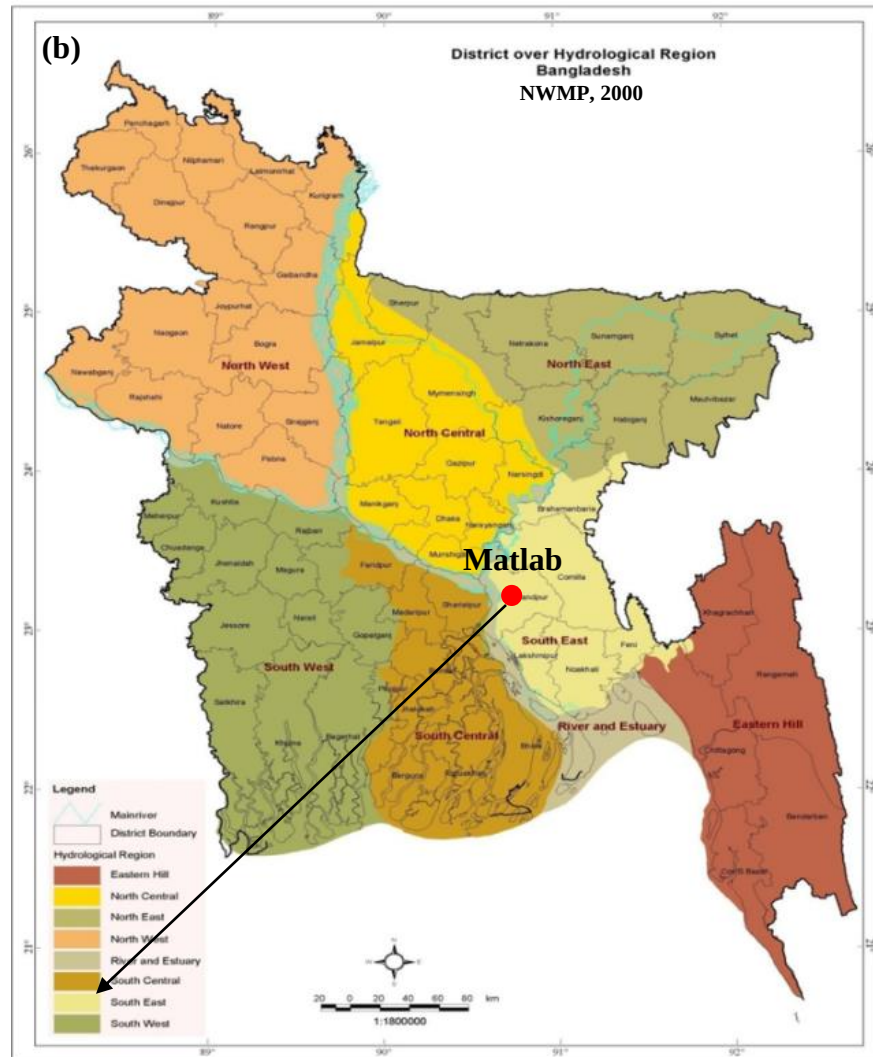


Table 4.1 General geological settings in Matlab (after Bakr, 1977)

Age	Geologic Unit	Lithology
<i>Holocene</i>	Meghna flood plain deposits Chandina formation (Chandina deltaic plain deposits)	Alluvial sand and silt Upper sandy sequence Lower silty sequence
<i>Pleistocene</i>	Madhupur clay formation (Lalmal deltaic plain)	Red-brown silty clay (residuum)
<i>Pliocene</i>	Dupitila formation	Grey fine to coarse sandstone with thick layers of grey to bluish grey, soft plastic and sticky clay

Figure 4.2 (a) Physiographic and (b) Hydrological region maps of Bangladesh (red dot indicates the study area)





Chapter 5 - Methods and Materials

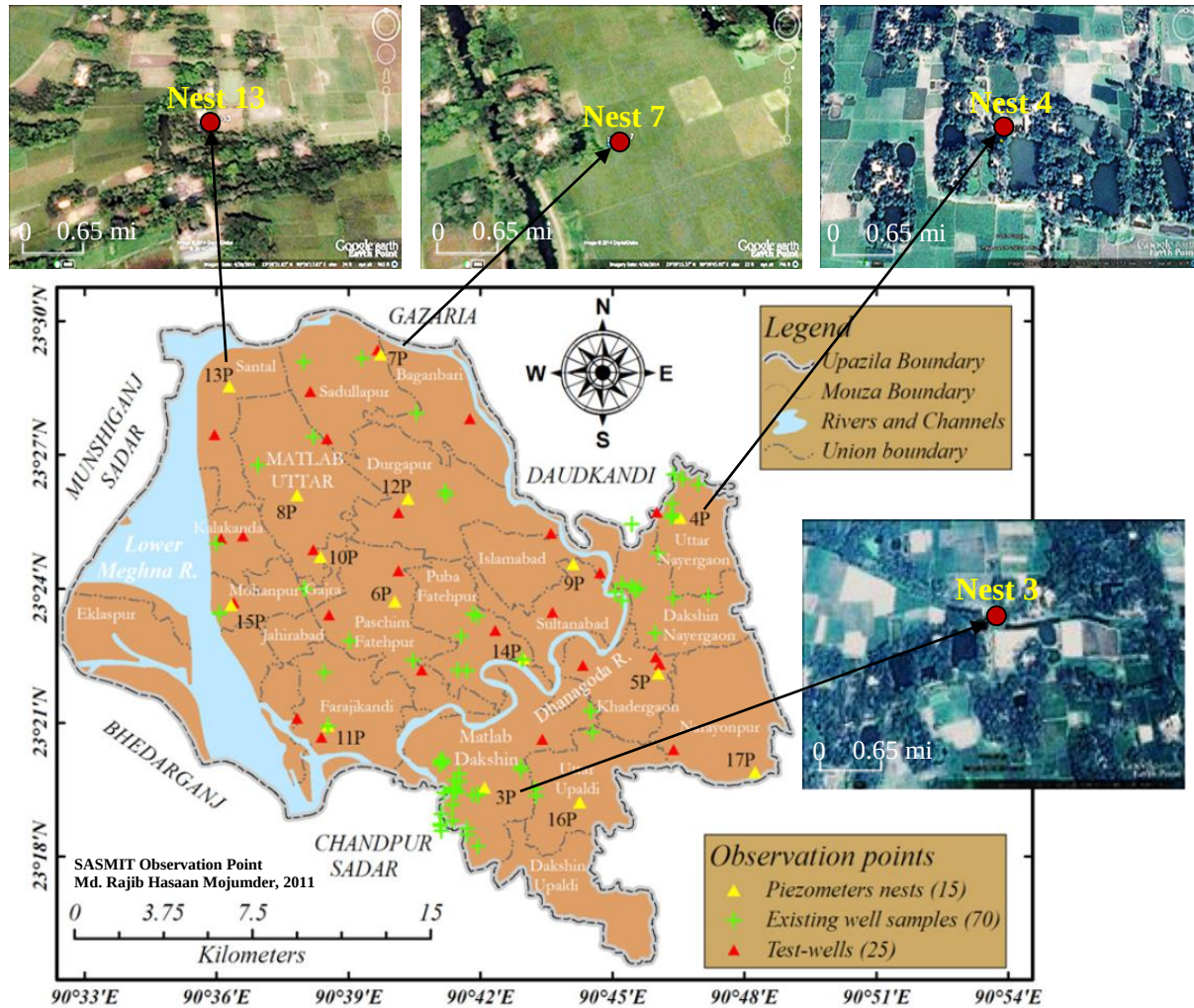
Water Sample Collection

Nineteen groundwater samples (depth ranging from 14m to 240 m) and nine surface water samples (8 ponds and one canal proximal to the piezometer nests) were collected from four different nests in Matlab during monsoon months (Jun-Jul, 2014). Nest 7 and 13 are located in north Matlab, whereas, nests 3 and 4 are located in south Matlab (Fig 5.1).

- Each nest consists of a group of piezometers drilled at the different depths at same location, *e.g.*, nest 3 has 6 piezometers at different depths (17-240 m) (Fig 5.2).
- SASMIT project in Bangladesh has been installed a large number of piezometer in the study area and the groundwater samples were collected among piezometer nests of the SASMIT project. Therefore, for the study, the depth of groundwater has divided into three ranges following by the SASMIT project depth range for piezometers (von Brömssen et al., 2011; Hossain et al., 2014) as <30 m – shallow well, >30 to <150 m – intermediate well, >150 m – deep well.
- The groundwater samples were collected by using 1" diameter water pump (HONDA WX-10, Tokyo, Japan) with 8 m long plastic tubing and 1" check valve (Fig 5.3).
- All piezometers were purged for 15 minutes to obtain fresh water sample from the main aquifer.
- Every sample bottle was rinsed three times with sample water (except charged HgCl_2 vials for dissolved inorganic carbon analysis) before collecting samples and filled up to the brim of the bottles without retaining any headspace. All water samples were preserved at 4°C in a cooler during field work.

Groundwater and surface water samples were stored in different sample bottles meant for different analyses. The following procedures and the acidification processes were followed- conventional method of preservation of water was acidified by 0.2 % (2 mL/L) of concentrated ultra-pure HNO_3 acid for cation analysis and HCl acid for As speciation, DOC and UV-absorbance analyses. There is a possibility to precipitation of the dissolved constituents and high bicarbonate or other inorganic carbon concentration in the water, hence, the water samples were acidified to lower the pH value (<2).

Figure 5.1 Location point of sampling in the study area



Cations

- The water sample was filtered via 0.45 μm hydrophilic polyether sulfone millipore syringe filter.
- 19 groundwater and 9 surface water samples were collected in 20 mL scintillation vials.
- 0.04 mL of ultra-pure HNO_3 acid was added to each sample

As-Speciation

- 6 M HCl was prepared from 36.5-38 % of laboratory grade HCl (Appendix H3).
- The groundwater samples were filtered via 0.45 μm hydrophilic polyether sulfone millipore syringe filters, exercising care during the filtration process. Because anoxic water may contain high concentrations of soluble iron and manganese that rapidly

Figure 5.2 The location of piezometers and surface water bodies in each nest within the study area (the red arrow indicates the distance between piezometer and surface water bodies)



precipitate when exposed to air. Iron and manganese hydroxyl/oxides precipitates remove dissolved As from water.

- 19 groundwater samples were collected in 20 mL scintillation vials.
- 0.04 mL of 6 M HCl acid was added to each sample.

Anions

- Unfiltered and unacidified 19 groundwater and 9 surface water samples were collected in 125 mL high density polyethylene amber plastic bottles.

Dissolved Organic Carbon (DOC)

- 0.45 µm hydrophilic polyether sulfone milipore syringe filter was pre-rinsed with 200 mL of fresh water prior to sampling in order to avoid bleeding of fluorescent compounds and contaminate the samples.
- 19 groundwater and 9 surface water samples were in 60 mL clear soda lime glass bottles.
- 0.12 mL of 10.2 M HCl acid was added to each sample.

Ultraviolet-Visible (UV) Absorbance

- The 0.45 µm hydrophilic polyether sulfone milipore syringe filter was pre-rinsed with 200 mL of fresh water prior to sampling to avoid bleeding of fluorescent compounds and contaminate the samples.
- 19 groundwater and 9 surface water samples were collected in 20 mL clear borosilicate glass vials.
- 0.04 mL of 10.2 M HCl acid was added to each sample.
- Each vial was sealed by rubber stopper and crimper.

Carbon-14 (C-14)

- The sample was filtered by 0.45 µm Nalgene nitrocellulose filter.
- 4 shallow groundwater samples (14-26 m) (one shallow well sample from each nest) were collected from four nests in 1 L clear polypropylene glass bottles.
- Each bottle was wrapped up by aluminum foil paper to prevent penetration of sunlight through the bottle that may alter carbon content.

Dissolved Inorganic Carbon (DIC)

- 1.4 g solid HgCl₂ (99.5+%, American Chemical Society reagent, Code#423935000, New Jersey, USA) were measured and mixed with 140 mL distilled water to prepare HgCl₂ solution.
- 5 mL of HgCl₂ solution was poured in each vial.
- Each vial was placed on hot plate at 80-100°C; evaporating to dryness and remove organic carbon until a visible solid residue of HgCl₂ solution was seen at the bottom of the vial.
- 19 groundwater and 9 surface water samples were collected in 20 mL clear borosilicate charged HgCl₂ glass vials.
- Each vial was sealed with crimp lid.

$\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$

- The sample was filtered by 0.45 μm hydrophilic polyether sulfone milipore syringe filter to reduce unusual quantity of suspended particles for examining $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$.
- 19 groundwater and 9 surface water samples were collected in 1 mL clear glass vials for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ analyses.
- 19 groundwater and 4 surface water (one pond water sample from each nest) samples were collected from four nests in 5 mL clear polypropylene centrifuge tube for measuring $\delta^{13}\text{C}$.

$^{87}\text{Sr}/^{86}\text{Sr}$

- 20 mL sample was filtered by 0.45 μm hydrophilic polyether sulfone milipore syringe filter for rinsing each bottle.
- New 100 mL sample was filtered with the same clean 0.45 μm hydrophilic polyether sulfone milipore syringe filter.
- 4 shallow groundwater (14-26 m) (one shallow water sample from each nest) and 4 pond water (one pond water sample from each nest) samples were collected from four nests in 125 mL amber polypropylene glass bottles.

Table 5.1 Details list of products and analysis

Product	Manufacturer	Location	Catalog No.	Analysis
HCl acid	Macron Fine Chemicals	Center Valley, PA, USA	2612-46	As speciation, DOC, UV-absorbance
HNO_3 acid	Fisher Scientific	Pittsburgh, PA, USA	A200S-212	Cations
0.45 μm PES syringe filter	Fisher Scientific	Pittsburgh, PA, USA	10326353	Cations, As speciation, UV-absorbance, Stable Isotopes, $^{87}\text{Sr}/^{86}\text{Sr}$
5 mL clear polypropylene centrifuge tube	Fisher Scientific	Pittsburgh, PA, USA	02-215-457	$\delta^{13}\text{C}$
20 mL scintillation vials with plastic cap	Fisher Scientific	Pittsburgh, PA, USA	03-337-23C	Cations, As speciation
20 mL clear borosilicate glass vials	Fisher Scientific	Pittsburgh, PA, USA	02-912-522	UV-absorbance, $\delta^{13}\text{C}$
60 mL clear soda lime glass bottles	Fisher Scientific	Pittsburgh, PA, USA	00-059-700	DOC
125 mL HDPE amber plastic bottles	Fisher Scientific	Pittsburgh, PA, USA	02-923-5C	Anions
125 mL amber polypropylene glass bottles	Fisher Scientific	Pittsburgh, PA, USA	00-054-562	$^{87}\text{Sr}/^{86}\text{Sr}$

Total Coliform and *E. coli*

- All devices of the water pump were soaked and circulated into the pump for 5 minutes in a mixture of cleaning solution consisting of 5 g Chlorox powder and 5 mL TWEEN-80 (T164-500, Fisher Scientific, Pittsburgh, PA, USA) in approximately 20 L hand-pumped well water (Fig 5.3).
- The process was followed preceding water sampling for fecal indicator bacteria test by rinsing with 20 L hand-pumped well water containing 5 g of Sodium Thiosulfate Anhydrous solution (S446-500, Fisher Scientific, Pittsburgh, PA, USA) for 5 minutes to devour any dissolved Chlorox powder in all tools within the water pump (Fig 5.3).

- 10 groundwater and 7 surface water samples from targeted four nests were collected in 120 mL Shrink-banded Vessels with Sodium Thiosulfate (98-09220-00, IDEXX Laboratories, Inc. Maine, USA).

Figure 5.3 Process showing cleaning of water pump and filtering water sample in field



- Surface water samples were diluted 1:100 before examining the frequency of bacteria to avoid exceedance of quantifiable maximum of 2419.6 bacteria/100 mL of the assay (Table 5.2).
- The underlying assumption is that the surface water from which the 100 mL duplicate samples were taken was mixed, and that the true concentration of bacteria in each 100-mL sample was the same (Knappett et al., 2011).
- For enumeration of fecal indicator bacteria (*E. coli*) genes, 6 (± 1) L of groundwater and 100 (± 50) mL of surface water samples were filtered onto 0.45 μm Nalgene nitrocellulose filters.
- The filters with petri dishes were kept frozen and transported on dry ice to Texas A&M University, College Station, USA for DNA extraction and qPCR analysis.
- The filters were removed from the plastic filter unit and placed in sterile petri dishes.

Table 5.2 Number of water sample collected at different depths with dilution factors for measuring concentration of culturable total coliform and *E. coli* from three nests-

Nest	Piezometer	Dilution Factor	Depth (m)
3	1	$\times 1$	17
	2	$\times 1$	29
	Pond 1	$\times 100$	2
	Pond 2	$\times 100$	1
7	2	$\times 1$	26
	5	$\times 1$	232
	Pond 1	$\times 100$	2
	Pond 2	$\times 100$	2
	Canal	$\times 100$	2
13	1	$\times 1$	14
	2	$\times 1$	33
	3	$\times 1$	85
	5	$\times 1$	237
	6	$\times 1$	124
	Private Well (PW)	$\times 1$	21
	Pond 1	$\times 100$	2
	Pond 2	$\times 100$	4

On Site Parameter Measurement

Field based On Site Parameters

- The Solinst water level meter was used to measure water level of each piezometer after and before pumping and each sample point was measured using GARMIN GPS (GPSmap 62s, Schaffhausen, Switzerland).
- The wellbore volume in L and the flow rate/L in second were calculated for each piezometer using 15 L bucket and water pump depending on well diameter, depth and water level to investigate the variation of volume with discharge rate per liter from shallow to deep wells in each nest (Fig 5.4).

$$D= 1 \text{ inch}= 2.54 \text{ cm} \quad r= D/2 = 1.27 \text{ cm} \quad A= \pi r^2 h = 3.14 (1.27)^2 \text{ cm}^2 = 5.1 \text{ cm}^2$$

$$D= 1.5 \text{ inch}= 3.81 \text{ cm} \quad r= D/2 = 1.905 \text{ cm} \quad A= \pi r^2 h = 3.14 (1.905)^2 \text{ cm}^2 = 11.4 \text{ cm}^2$$

$$D= 2 \text{ inch}= 5.08 \text{ cm} \quad r= D/2 = 2.54 \text{ cm} \quad A= \pi r^2 h = 3.14 (2.54)^2 \text{ cm}^2 = 20.3 \text{ cm}^2$$

$$\text{Volume} = \{(\text{Well Depth} - \text{Water Level}) \times \text{Cross Sectional Area}/1000\} \text{ L}$$

$$\text{Flow Rate/L} = (\text{Flow Rate (15 L)} \times \text{Volume}/15) \text{ sec/L}$$

- The portable METTLER TOLEDO multimeter (SG3, 51302530, Schwerzenbach, Switzerland) was used for recording temperature (°C), total dissolved solids (TDS) (g/L), electrical conductivity (EC) (mS/cm), salinity (ppt) and resistivity (Ωcm) and oxidation-reduction potential (ORP) was evaluated using HACH HQ40d ORP meter (Colorado, USA) (Fig 5.4).
- All the readings were taken until every value was stabilized and the water was clear. Both meters were calibrated by listed below standard solutions once before metering each parameter (Table 5.3).

Table 5.3 The standard solution for ORP, EC and pH

Parameter	Std. Solution
ORP	$\pm 220.2 \text{ mV}$ (Zobels)
EC	1.413 mS/cm
pH	7.13

- HACH field test kits were used to measure dissolved oxygen (DO), manganese (Mn), arsenic (As) and chloride (Cl^-) concentrations.
- SO_4^{2-} concentration was analyzed using HACH Pocket Colorimeter.

Parameter	HACH Product Colorado, USA	Range
DO	146900	0.2-20 mg/L
Mn	146700	0-3 mg/L
As	2800000	0-500 ppb
Cl ⁻	2063500	10-8,000 mg/L
SO ₄ ²⁻	5870029	2-70 mg/L

Colilert Test

The most probable number (MPN) based Colilert test was applied to determine the concentration of total coliform and *E. coli* in 100 mL well water samples using US-EPA approved commercial culture kit (Colilert IDEXX Laboratories, Inc.) following manufacturer's protocols (www.idexx.com)-

Figure 5.4 On site parameter measurement and MPN based Colilert test



Colilert simultaneously detects total coliforms and *E. coli* in water. It is based on IDEXX's patented Defined Substrate Technology (DST). When total coliforms metabolize Colilert's nutrient-indicator, *ortho*-Nitrophenyl- β -galactoside (ONPG), the sample turns yellow. When *E. coli* metabolize Colilert's nutrient-indicator, beta-Glucuronidase (MUG), the sample also fluoresces. Colilert can simultaneously detect these bacteria at 1 colony forming unit (cfu)/100 mL within 24 hours even with as many as 2 million heterotrophic bacteria per 100 mL present. Duplicate aqueous samples were collected in sterile, 120 mL plastic bottles. Samples were placed in cooler at 4°C prior to analysis, if not analyzed immediately. The holding time was 6 hours to arrive at laboratory plus 2 hours to analyze from time of sample collection.

Presence/Absence Procedure of Fecal Indicator Bacteria (*E. coli*)

1. Added contents of one pack to a 100 mL sample in a sterile, transparent, nonfluorescing vessel.
2. Capped vessel and shake until all contents dissolved properly.
3. Incubated at $35\pm 0.5^{\circ}\text{C}$ for 24 hours.

Quanti-Tray Enumeration Procedure

1. Added contents of one pack to a 100 mL water sample in a sterile vessel.
2. Capped vessel and shake until dissolved.
3. Poured sample/reagent mixture into a Quanti-Tray/2000 (Fig 5.4) and sealed in an IDEXX Quanti-Tray Sealer.
4. Placed the sealed tray in a $35\pm 0.5^{\circ}\text{C}$ incubator for 24 hours.
5. Counted the number of positive wells and referred to the MPN table provided with the trays to obtain a MPN which is based on 95% confidence limits of lower and upper bound (Fig 5.4).
6. Compared appearance with the comparator; *e.g.*, less yellow appearance than the comparator indicates negative for total coliforms and *E. coli*; yellow equal to or greater appearance than the comparator point out that positive for total coliforms; yellow and fluorescence appearance equal to positive for *E. coli* or greater than the comparator (Fig 5.4).
7. Observed for fluorescence with a 6-watt, 365-nm UV light within 5 inches of the sample in the dark room. Face of UV light keep away from eyes and towards the sample.
8. Colilert results are definitive if processed within 24–28 hours. In addition, positives for both total coliforms and *E. coli* observed before 24 hours and negatives observed after 28 hours are also valid.
9. The MPN value of diluted samples was multiplied by the dilution factor to obtain the quantified result of fecal indicator bacteria (*E. coli*).

Calculation of MPN for IDEXX Quanti-Tray/2000

- Quanti-Tray/2000 MPN was originally derived as described by: Hurley M.A. & Roscoe M.E. 1983.
- Small wells of Quanti-Tray/2000 have a mean volume of 0.186 mL (Fig 5.4).
- Large wells of Quanti-Tray/2000 have a mean volume of approximately 1.86 mL (ten times larger than the small wells) (Fig 5.4).
- Formula used to calculate the Quanti-Tray/2000 MPN table (Table 5.4).

$$\sum_{i=1}^K \frac{V_i d_i P_i}{1 - e^{-V_i d_i MPN}} = \sum_{i=1}^K V_i d_i n_i$$

K = no. of dilution level, n_i = no. of wells at level i, P_i = no. of positive wells at level i

d_i = dilution factor at level i (e.g. 0.01 for 1:100 dilution) V_i = volume of wells at level i 95%

Confidence Interval calculation (where S.E. is Standard Error)

Lower, upper = MPN $\pm$ 1.96 * S.E. of MPN

S.E. of MPN is

$$\frac{1}{\sqrt{MPN^2 \sum_{i=1}^K \frac{V_i^2 d_i^2 n_i^2}{e^{-V_i d_i MPN} - 1}}}$$

Table 5.4 Examples for calculating total coliform and E. coli using single and duplicate spreadsheet with above formulae-

Total Coliform (Single)					
Sample ID	big wells (+)	sm. wells (+)	95L	MPN	95H
N3/Pond 1	49	30	401.18	613.14	879.21
N3/Pond 1	49	47	1630.37	2419.57	4716.1
N7/P2	49	20	218.87	344.8	520.66
N7/P2	49	16	185.65	275.51	416.76
N7/Canal	49	48	1439.5	>2419.6	infinite
N7/Canal	49	19	206.64	325.54	498.08
N13/P1	25	0	21.95	33.55	48.93

E. coli (Single)					
Sample ID	big wells (+)	sm. wells (+)	95L	MPN	95H
N3/Pond 1	21	3	19.36	30.51	44.77
N3/Pond 1	47	12	119.49	172.33	242.22
N7/P2	8	1	4.45	9.69	17.16
N7/P2	10	2	7.1	13.23	22.01
N7/Canal	48	18	172.58	248.9	350.24
N7/Canal	28	3	30.59	44.12	62.52
N13/P1	1	0	0.05	1	5.49

Total Coliform (Duplicate)							
Sample ID	LARGE1	SMALL1	LARGE2	SMALL2	MPN	LB	UB
N3/P1	49	29	46	12	238.359	183.855	309.02
N7/P2	25	1	28	3	39.474	30.344	51.353
N7/P5	46	12	49	13	176.943	139.446	224.523
N13/P1	27	1	3	0	18.186	12.792	25.855
N13/P2	49	24	33	27	153.331	121.807	193.013
N13/PW	45	12	47	17	164.127	129.927	207.329
N13/Pond 1	49	30	49	12	320.949	243.817	422.482
N13/Pond 2	47	3	47	2	120.875	96.781	150.967

<i>E. coli</i> (Duplicate)							
Sample ID	LARGE1	SMALL1	LARGE2	SMALL2	MPN	LB	UB
N3/P1	6	1	0	0	3.603	1.717	7.563
N7/P2	1	0	1	0	1.009	0.253	4.034
N7/P5	3	1	4	0	4.138	2.068	8.279
N13/P1	0	0	0	0	<0.5	<0.07	<3.564
N13/P2	30	9	33	21	74.062	59.065	92.867
N13/PW	4	0	26	0	17.585	12.307	25.125
N13/Pond 1	20	12	15	16	39.148	30.072	50.963
N13/Pond 2	33	3	27	4	49.581	38.767	63.413

Laboratory Analyses

Ions

- Cations (Ca, K, Mg, Na, Fe, Si, Sr) and trace elements (As, Mn) were analyzed using high resolution inductively coupled plasma mass spectroscopy (HR ICP MS) at Actlabs in Ontario, Canada.
- Dissolved total iron (Fe_(t)) was also analyzed to cross check results using HR ICP MS at University of Kansas and inductively coupled plasma optical emission spectrometry (ICP OES) at Department of Agronomy laboratories in Kansas State University.
- Ion chromatography (IC) was used to measure anions (Cl⁻, Br⁻, NO₃⁻, PO₄³⁻, SO₄²⁻) at Department of Geology in Kansas State University.
- HCO₃⁻ concentrations were measured using the titration method (Standard H₂SO₄) (HACH Product# 2444301, Colorado, USA).

As-speciation

All As species are not toxic. Therefore, the ability to measure the different forms is important. The different forms of As (III), (V), monomethyl arsenic (MMA) and dimethyl arsenic (DMA) were measured using high performance liquid chromatography with inductively coupled plasma mass spectrometry (HPLC/ICP-MS) in Actlabs (Ontario, Canada). HPLC separates the forms and ICP-MS detects them as they elute from the column.

DOC Analyses

- The total concentration of organic carbon was determined in triplicate using TOC-5000 analyzer (Shimadzu, Kyoto, Japan) with a confidence interval of ± 0.02 mg Carbon (C)/L.
- 20 mL clear glass vials were pre-rinsed with about 100 mL distilled water. After that all vials were covered by aluminum foil paper and combusted in a muffle furnace for 4 hours at 450°C to remove any trace organic carbon from each vial.
- Five ultrapure water vials were placed in auto sampler which was flushed the tubing, needles before actual samples are analyzed.
- One ultra-pure water sample was placed after five samples interval in auto sampler to avoid any traces being carried for earlier sample to the next one and standard 1 mg/L, 2 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 50 mg/L were used to calibrate the instrument.

Fluorescence Spectroscopy

- The HORIBA Scientific Aqualog (Kyoto, Japan) instrument was used to characterize DOC and the data was processed by Aqualog V3.6 software.
- The fluorometer lamp of the instrument was allowed for approximately 45 minutes to warm up before testing all samples.
- The clean quartz cuvette was rinsed ~20 times with distilled water.
- All the sides of 3-Q-10 sealed water sample and starna quinine sulfate sample were cleaned up to remove dust particles around the cuvette prior to test each sample.
- The cuvette was checked to look for any peaks between emission 300 and 400 nm which are not noise and record the highest peak between emission 300 and 400 nm in the Aqualog logbook.xls (Appendix C).
- The water Raman scan was checked to record the Raman peak at ~397 nm (Raman peak X and Y) in the Aqualog logbook.xls and calculate the area under the Raman peak (Appendix C).

- First an ultrapure water sample ran to check for any contamination on the cuvette. After that to acquisition 3D EEM all samples were performed for three times to cross match the results (Appendix C).
- All Aqualog fluorescence raw data were exported as ASCII file format and corrected using MATLAB R2013a to correct excitation emission matrices and calculate indices.

Isotope and C-14 Analyses

- $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were measured using PICARRO Cavity Ring Down Spectrometer (L1102-i, Santa Clara, CA, USA) to understand the interaction between groundwater and surface water in Department of Biology at Kansas State University.
- $\delta^{13}\text{C}$ analyses were done by conventional off-line methods consisting of chromatographic separation followed by combustion and dual-inlet isotope ratio mass spectrometry to investigate recharge sources of groundwater and relevance to surface water bodies at ISOTECH Laboratories Inc. Illinois, USA.
- Triton multi-collector mass spectrometer was performed to determine the relative abundance of Sr isotopes in water samples as well as to evaluate the circulation rate between groundwater and surface water at Actlabs in Ontario, Canada. During the analysis the ratios $^{87}\text{Sr}/^{86}\text{Sr}$ of NBS 987 standard was 0.710246 ± 0.000007 .
- Carbon-14 was determined by accelerator mass spectrometry (AMS) to calculate the percentage of carbonate species that originated from living plants in the aquifer outcrop and the atmosphere as opposed to that added by ancient carbonaceous deposits in the aquifer matrix. All sample preparations were done at Actlabs in Ontario, Canada and then purified carbon dioxide was submitted to an established radiocarbon dating laboratory for the final AMS analysis.

Quantitative Polymerase Chain Reaction (qPCR)

Quantitative Polymerase Chain Reaction analysis was performed for 8 groundwater and 4 surface water samples to measure copies of genes for *E. coli* using assays and laboratory methods in Texas A&M University. DNA extraction and purification were performed on 1/2 or 1/4 of each filter using a DNA soil extraction kit following the manufacture's protocols (FastDNA[®] SPIN for Soil Kit, MP Biomedicals, Solon, Ohio). Initial concentrations of gene copies of each marker microorganism per nanogram of DNA extracted were obtained by qPCR (Layton et al., 2006, Knappett et al., 2011).

Chapter 6 - Results

The role of DOC and its fluorescence properties in water

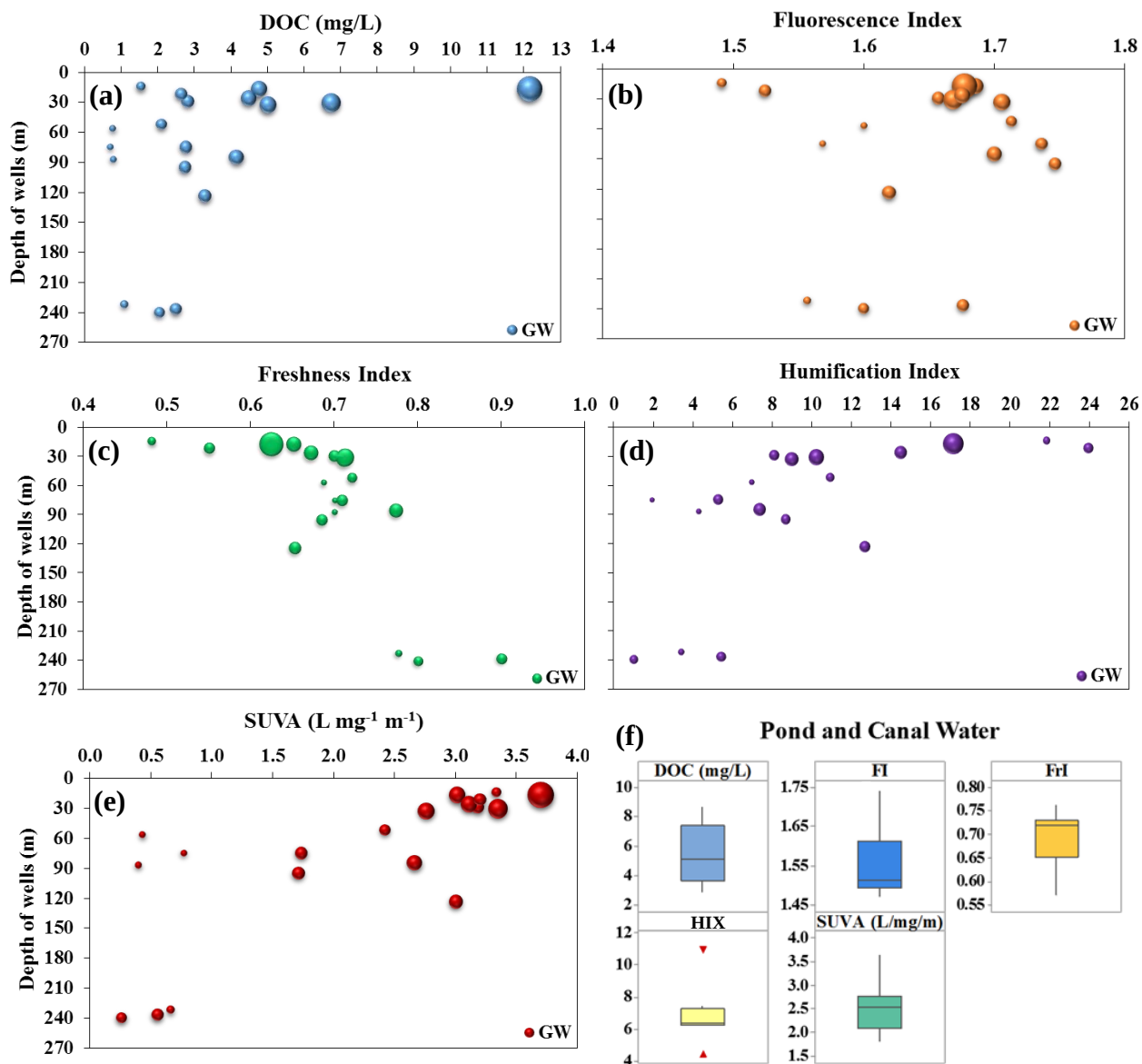
In the study area, concentrations of DOC vary widely from 0.7 to 12.2 mg/L at shallower to deeper depth wells (Fig 6.1 (a)) and from 2.9 to 8.7 mg/L in surface water bodies (pond and canal) (Fig 6.1 (f)). The highest and lowest values are 12.2 mg/L and 0.7 mg/L observed at 14 m and 75 m depths respectively (Fig 6.1 (a)); this indicates that the DOC concentration is high in shallow wells (14-30 m) compared to intermediate and deeper wells (33-240 m) (Fig 6.1 (a)). The mean DOC level is 5.5 mg/L ($n = 9$; STDEV = 2) higher in surface water than 3.3 mg/L ($n = 19$; STDEV = 2.7) in groundwater.

The fluorescence characterization of dissolved organic matter is a useful means of evaluating the chemical characteristics of DOC. Fluorescence spectroscopy can further be an indicator for determining the sources of DOC in a various range of settings (McKnight et al., 2001). On the basis of spectrofluorometric analyses, a range of indices have been employed from detailed excitation-emission matrices (EEMs) to explain DOC characteristics.

The fluorescence index (FI) is computed as the ratio of emission intensity at 470 nm to that of 520 nm for a fixed excitation wavelength of 370 nm (Cory and McKnight, 2005). The value of FI varies as a function of DOC concentrations at different depths in the groundwater samples in this study (Fig 6.1 (b)). The mean FI is 1.6 ($n = 18$; STDEV = 0.07) from shallow to deep groundwaters (14-240 m) and 1.6 ($n = 9$; STDEV = 0.09) in pond and canal water (Fig 6.1 (f)).

The study of EEMs is useful technique to understand the composition, origin and processing of DOM (Johnson et al., 2011) by using diagnostic indices, such as freshness index (FrI or $\beta:\alpha$) values (Parlanti et al., 2000) and humification index (HIX) (Parlanti et al., 2000; Ohno, 2002). These indices use ratios of fluorescence intensity in different areas of the EEM (Fellman et al., 2010). The FrI is evaluated by the ratio of emission intensity at 380 nm divided by the emission intensity maximum observed between 420 and 435 nm, acquired at excitation 310 nm (Parlanti et al., 2000; Wilson and Xenopoulos, 2009). The HIX is determined by Zsolnay et al., (1999) as the peak area below the emission spectra in the range 435–480 nm divided by the peak area below the emission spectra in the range 300–445 nm, at excitation 254 nm. Ohno, (2002) modified the HIX later to be represented by the area below the emission spectra 435–480

Figure 6.1 Vertical distributions (a, b, c, d, e) and boxplot diagram (f) of DOC concentration and its properties in groundwater and surface water (bubble size indicates DOC concentration; bigger bubble size represents higher DOC concentration)



nm divided by the peak area 300–345 nm + 435–480 nm, at excitation 254 nm. The FrI value in groundwater increases with increasing depth, but that variation shows little correlation to DOC concentration (Fig 6.1 (c)). The mean FrI is (~ 0.7) ($n_{SGW} = 7$; $n_{IGW} = 9$; STDEV (SGW-IGW) = 0.07; $n_{SW} = 9$; STDEV = 0.06) from shallow to intermediate groundwaters (14-123 m) as well as in surface water (Fig 6.1 (f)). The mean FrI in deep groundwaters (232-240 m) is (~ 0.8) ($n = 3$; STDEV = 0.07) (Table 6.1). The highest and lowest HIX is 24.0 and 1.0 observed at 21 m and

240 m depth wells respectively (Fig 6.1 (d)). The range of HIX is 1.9-24.0 from shallow to intermediate groundwaters (14-123 m) and is 1.0-5.4 in deeper aquifer (232-240 m). The mean HIX is high (~16.1) at shallow wells (14-30 m) ($n = 7$; STDEV = 5.7) compared to pond and canal water (~6.9) ($n = 9$; STDEV = 2.2) (Table 6.1) (Fig 6.1 (f)).

Table 6.1 Statistical analyses of DOC concentration and its fluorescence properties for groundwater and surface water

Groundwater and Surface water															
	DOC (mg/L)			FI			FrI			HIX			SUVA (L/mg/m)		
	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV
Shallow GW (14-30 m)	7	5	3.6	7	1.6	0.08	7	0.6	0.08	7	16.1	5.7	7	3.3	0.2
Intermediate GW (33-123 m)	9	2.5	0.7	8	1.7	0.07	9	0.7	0.03	9	7.5	3.3	9	1.8	1
Deep GW (232-240 m)	3	1.9	0.7	3	1.6	0.06	3	0.8	0.07	3	3.3	2.2	3	0.5	0.2
Surface water	9	5.5	2	9	1.6	0.09	9	0.7	0.06	9	6.9	1.8	9	2.5	0.5

Surface water (boxplot summary of fig 6.1 (f))

<i>Parameter</i>	<i>N</i>	<i>Q1</i>	<i>Median</i>	<i>Q3</i>	<i>IQRange</i>	<i>Whiskers to</i>
DOC (mg/L)	9	3.6	5.1	7.4	3.7	2.9, 8.7
FI	9	1.5	1.5	1.6	0.1	1.5, 1.7
FrI	9	0.7	0.7	0.7	0.1	0.6, 0.8
HIX	9	6.3	6.3	7.3	1	6.2, 7.4
SUVA (L/mg/m)	9	2.1	2.5	2.8	0.7	1.8, 3.6

Variable	Groundwater (14-240 m)		
	Pearson 'r'	r²	Test Statistics ($\alpha = 0.05$)
DOC and FI	0.08	0.01	0.75 > 0.05
DOC and FrI	0.2	0.04	0.43 > 0.05
DOC and HIX	0.4	0.15	0.1 > 0.05
DOC and SUVA	0.6	0.41	0.003 < 0.05
FrI and HIX	0.8	0.64	0.00004 < 0.05
HIX and SUVA	0.8	0.62	0.00007 < 0.05
HIX and Peak A	0.5	0.21	0.05 ≤ 0.05
HIX and Peak M	0.4	0.19	0.06 > 0.05
HIX and Peak C	0.4	0.2	0.05 ≤ 0.05
SUVA and Peak A	0.7	0.5	0.0007 < 0.05
SUVA and Peak M	0.7	0.51	0.0006 < 0.05
SUVA and Peak C	0.7	0.51	0.0005 < 0.05

Variable	Surface Water (Pond and Canal)		
	Pearson 'r'	r ²	Test Statistics ($\alpha = 0.05$)
DOC and FI	0.1	0.01	0.79 > 0.05
DOC and FrI	0.1	0.02	0.7 > 0.05
DOC and HIX	0.27	0.07	0.48 > 0.05
DOC and SUVA	0.02	0.0005	0.95 > 0.05
FrI and HIX	0.3	0.12	0.36 > 0.05
HI and SUVA	0.7	0.47	0.04 < 0.05
HIX and Peak A	0.1	0.02	0.72 > 0.05
HIX and Peak M	0.2	0.04	0.6 > 0.05
HIX and Peak C	0.2	0.06	0.53 > 0.05
SUVA and Peak A	0.3	0.09	0.45 > 0.05
SUVA and Peak M	0.3	0.06	0.51 > 0.05
SUVA and Peak C	0.2	0.06	0.54 > 0.05

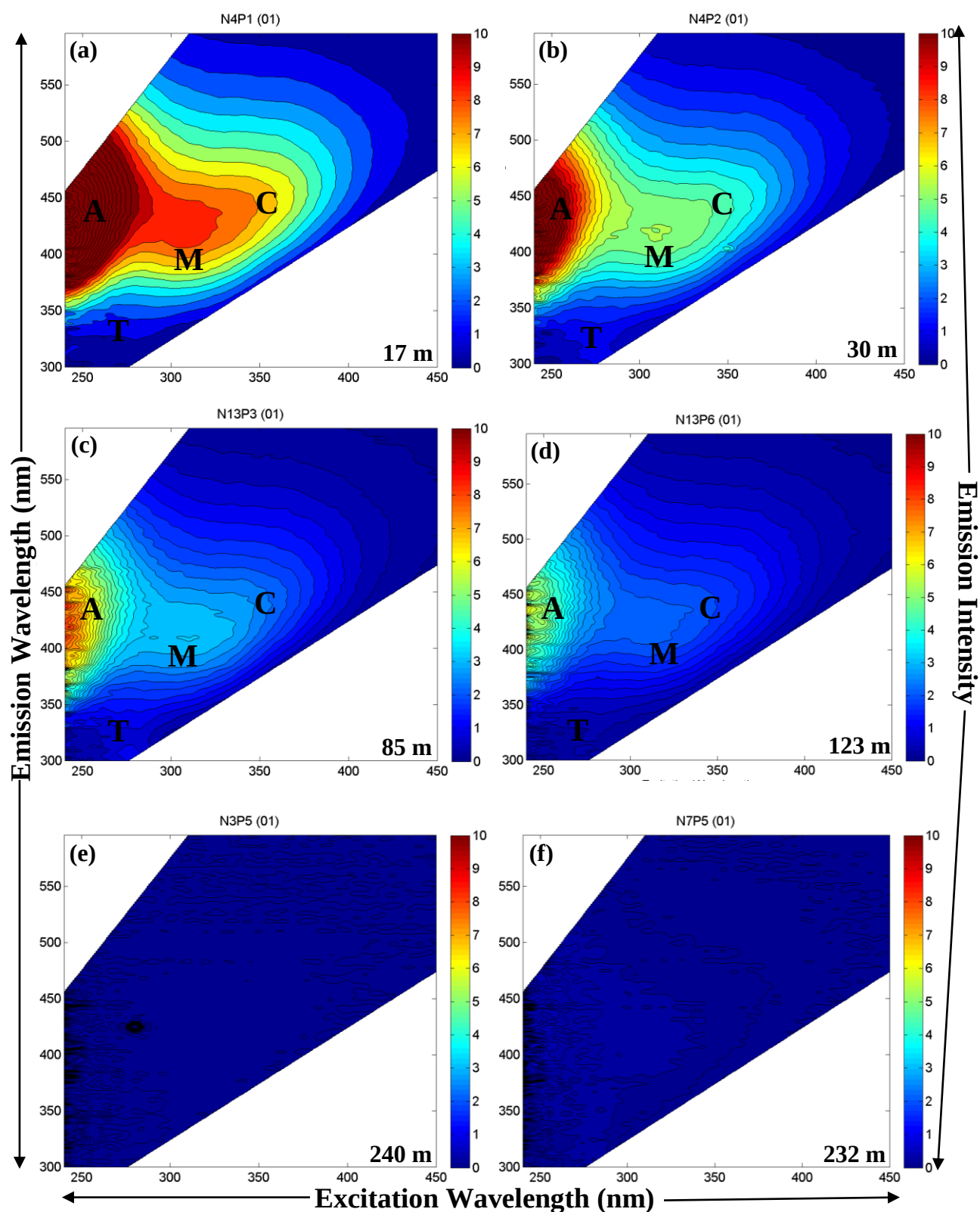
The aromatic character of DOC is described using specific UV absorbance (SUVA) measurements at 254 nm. The filtered sample is absorbed through a 0.01 m two ways quartz cuvette measured at 254 nm. This measurement is representative of the average absorbance at 254 nm of all of the organic molecules. The SUVA value for each sample is calculated by dividing the absorbance value by the concentration of DOC. SUVA indicates an average absorptivity for all the molecules which contain the DOC in water and has been used as a representative measurement for DOC aromaticity (Traina et al., 1990; Weishaar et al., 2003). The range of SUVA value is 0.3 to 3.7 from shallow to deep groundwaters (14-240 m) (Fig 6.1 (e)) and is 1.8 to 3.6 in surface water bodies (Fig 6.1 (f)). The mean SUVA value is 3.3 (n = 7; STDEV = 0.2) higher at shallow wells (14-30 m) compared to 2.5 (n = 9; STDEV = 0.5) in pond and canal water and is decreasing from 1.8 in intermediate wells (33-123 m) (n = 9; STDEV = 1) to 0.5 in deeper wells (232-240 m) (n = 3; STDEV = 0.2) with varying DOC concentration (Fig 6.1 (e)) (Table 6.1).

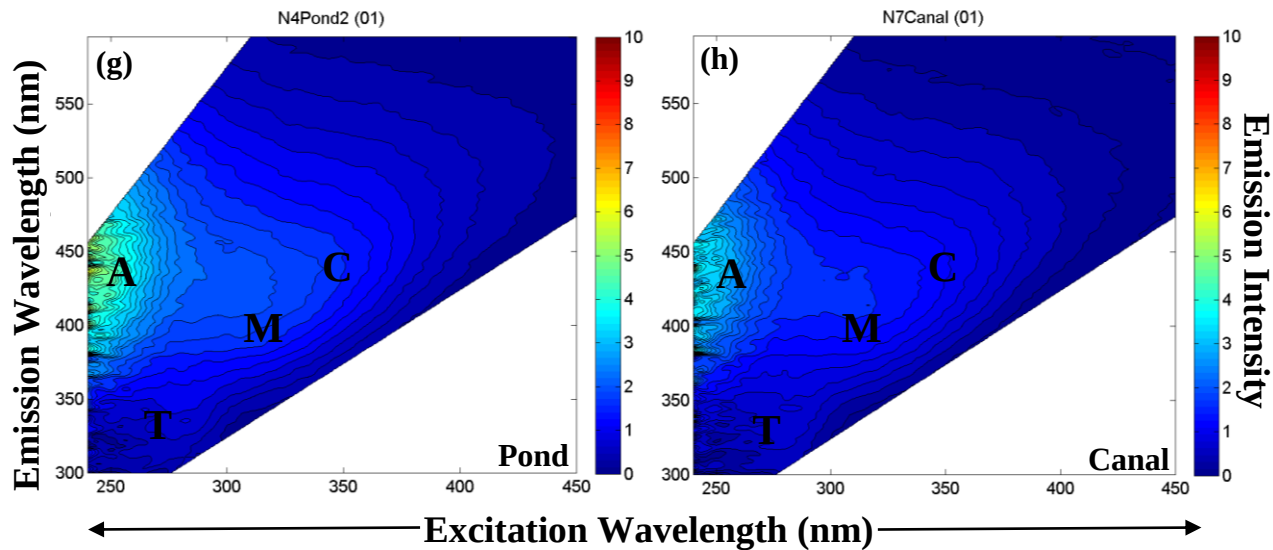
A significant relationship was between DOC concentration and SUVA in groundwater (p-value 0.003) (Table 6.2). The FrI and HIX were correlated with a high r² value, as were HIX and SUVA values (Table 6.1).

Fluorescence spectroscopic studies

The measurements of DOM fluorescence are often reported as 3D excitation-emission matrices (EEMs) (Coble et al., 1990; McKnight et al., 2001) EEMs are produced from many

Figure 6.2 EEMs maps showing four primary and unidentifiable peaks at different depths in groundwater (a, b, c, d, e, f) and surface water (g, h)





emission spectra combined at consecutively increasing excitation wavelengths (Fellman et al., 2010). The technique is used for visual inspection and analysis of EEMs or fluorescence peaks (Coble et al., 1990; Coble, 1996); it facilitates comparison of the intensity of individual peaks across a range of sample dates (Baker, 2001). Five primary peaks have been recommended within the large number of natural and anthropogenic fluorophores identified to date (Westerhoff et al., 2001; Coble, 2007; Hudson et al., 2007) - humic-like peaks A, C, and M and protein-like peaks B and T, because they have been deliberately connected to ecologically significant characteristics of DOM (Coble et al., 1990; Coble, 1996; Fellman et al., 2010).

The results about fluorescence peaks of aquatic DOM to characterize DOM is generalizing based on piezometer samples (N4/P1, N4/P2, N13/P3 and N13/P6) at different depths (17-123 m) and surface water samples (N4/Pond2 and N7/Canal) where four primary peaks and peak curves are meaningful. The EEMs maps show that three primary peaks (A, M, C and T) prominent from shallow to intermediate wells (17-123 m) (Fig 6.2 (a), (b), (c), (d)) and surface water bodies (Fig 6.2 (g), (h)). There are unknown fluorescence peaks at deeper wells (N3/P5, N7/P5 and N13/P5; 232-240 m) (Fig 6.2 (e), (f)) (Appendix C2, C4, C6).

Lithology and Mineral Saturation Index (MSI)

The study area is mostly composed of sand particles with some clay layers. The screens of all piezometers were installed in fine to medium sand layers in nest 3 (P1, P2, P3, P4, P6) except piezometer 6 where water infiltrates through medium to coarse sands. In nest 4, the screen lithology of two piezometers (P1, P2) is fine sand and water can percolate via medium sands in other two piezometers (P3, P4). The water penetrates through fine to medium sands in two

piezometers (P2, P5) of nest 7, whereas, the screen of piezometer 4 was set up in very fine sand layer. The lithology of filter is somewhat different in nest 13 than other three nests. Three screens (P1, P2, P5) of piezometers were installed in fine to medium sand strata. The aquifer quality of piezometer 3 is moderately good as water intrudes via fine to coarse sand particles. The only one exception in the context of screen layer is that water flows through medium sand with clay in piezometer 6 (Appendix D).

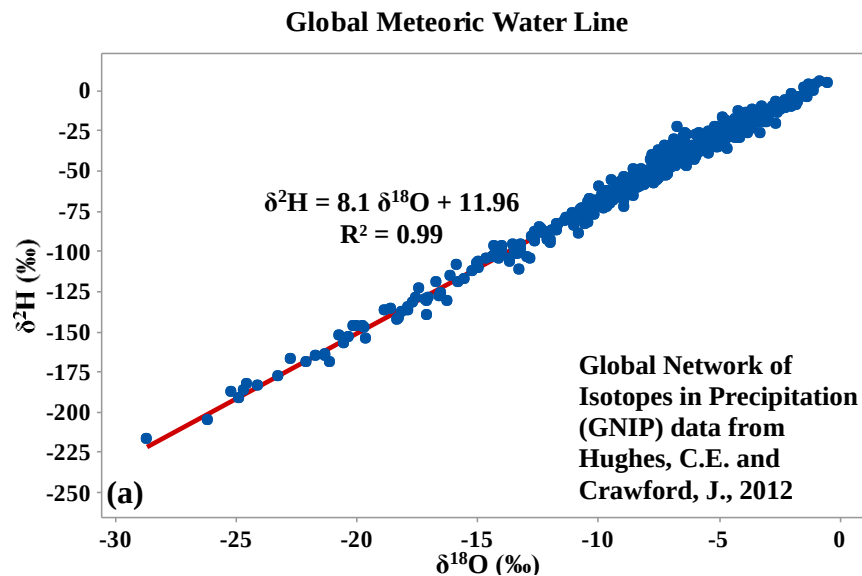
Geochemist's Workbench software (GWB10) and water chemistry data were used to calculate equilibrium constant (Q/K) and understand the state of mineral saturation in both groundwater and surface water. Saturation occurs at $Q/K = 1$; values greater than 1 are supersaturated and values less than 1 are undersaturated. The calculation of MSI point out that all minerals are supersaturated ($Q/K > 1$) in both groundwater and surface water bodies (Appendix E).

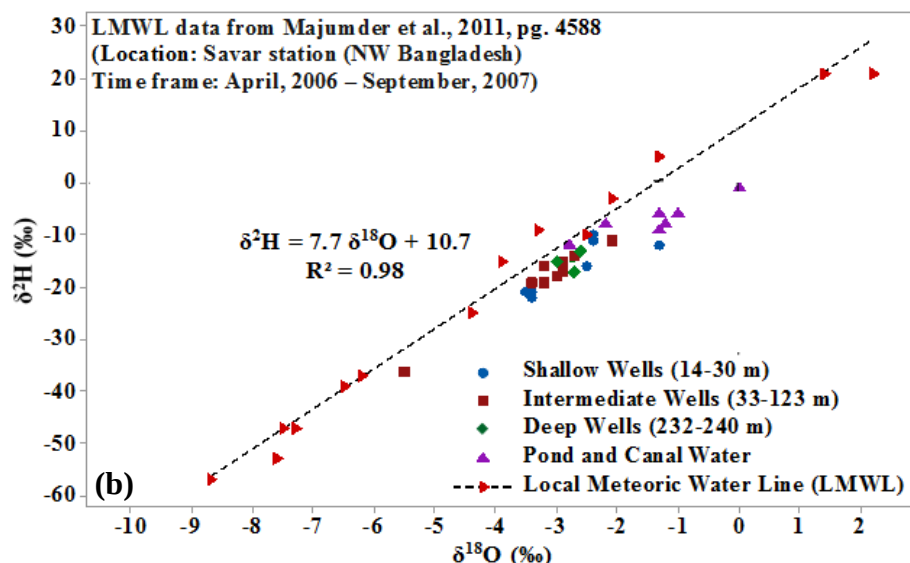
Water isotope results

δ^2H and $\delta^{18}O$

The Matlab groundwaters sampled in this study have stable oxygen ($\delta^{18}O$) isotope ratios ranging from -1.3 to -5.5 ‰ and 0 to -2.8 ‰, respectively, Hydrogen (δ^2H) isotope ratios range from -10 to -36 ‰ and -1 to -12 ‰, respectively for surface water samples (Fig 6.3 (b)). Most of

Figure 6.3 (a) Global Meteoric Water Line (GMWL) and (b) relation between δ^2H and $\delta^{18}O$ values of groundwater and surface water with referred local meteoric water line (LMWL)





the shallow samples (< 30 m) have stable oxygen isotope values between -1.3 and -3.5 ‰ (Fig 6.3 (b)). The intermediate depth (33 m) N13/P2 sample has more negative oxygen isotope value of -5.5 ‰ (Fig 6.3 (b)). Most of the surface water samples (N3/Pond2, N7/Pond1, N7/Pond2, N7/Canal, N13/Pond2) and one shallow groundwater (17 m) sample (N4/P1) show the most enrichment of $\delta^{18}\text{O}$ values ranging from -1 to -1.3 (Fig 6.3 (b)).

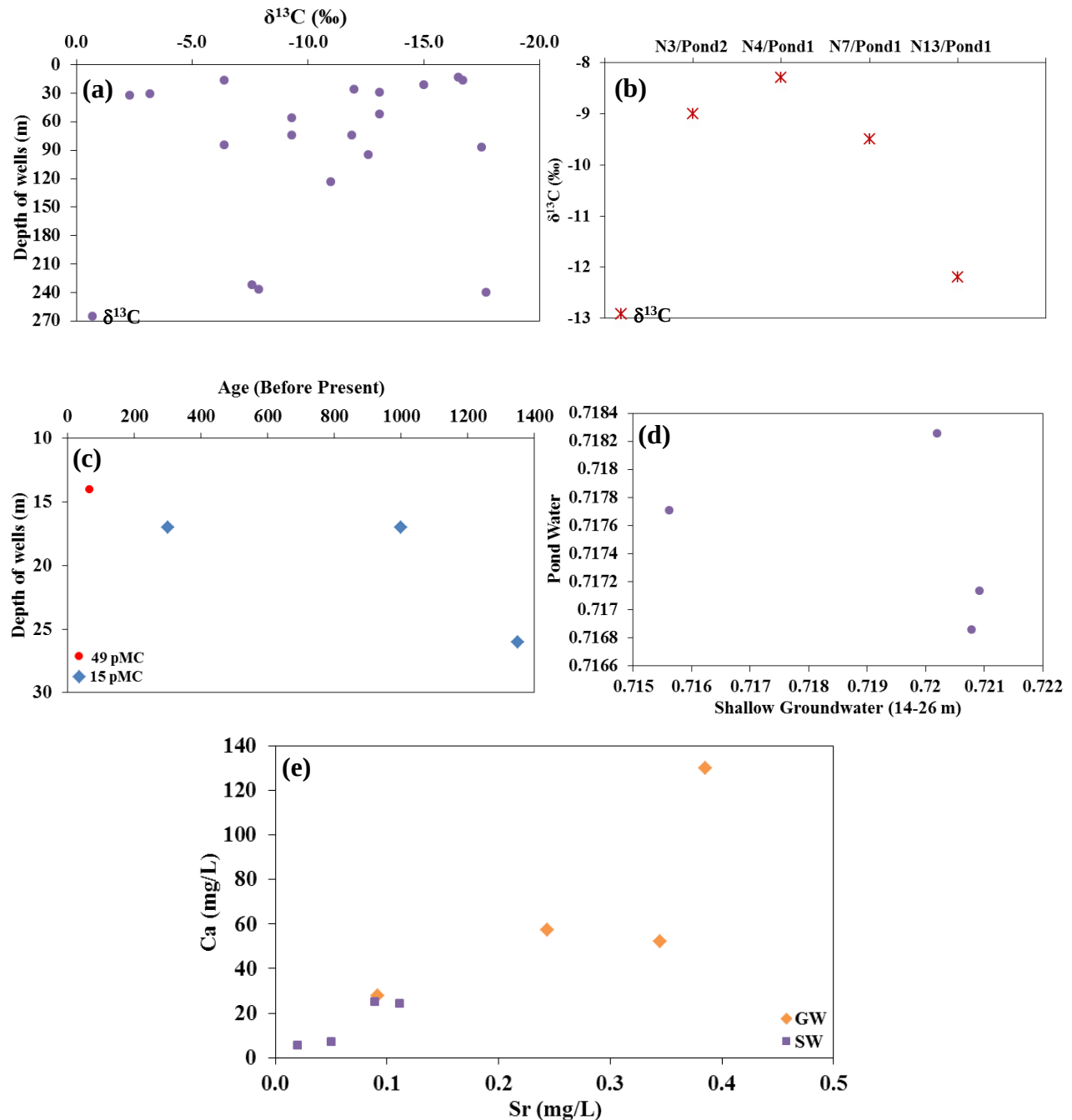
$\delta^{13}\text{C}$, Carbon-14 and $^{87}\text{Sr}/^{86}\text{Sr}$

The groundwater wells have a wide range of $\delta^{13}\text{C}$ from -2.3 to -17.7 ‰ with no consistent trend with depth (14-240 m) (Fig 6.4 (a)) and surface water bodies have a range of $\delta^{13}\text{C}$ from -8.3 to -12.2 ‰ (Fig 6.4 (b)). Two groundwater samples (N3/P4 and N3/P5) have more negative values of $\delta^{13}\text{C}$ 17.5 ‰ and 17.7 ‰ at 87 m and 240 m depths, respectively; whereas, one intermediate groundwater sample (N13/P2) at 33 m depth show more enriched $\delta^{13}\text{C}$ value -2.3 ‰ (Fig 6.4 (a)).

The ^{14}C activity in shallow groundwaters (14-26 m) ranged from 15 to 49 percent modern carbon (pMC) (Fig 6.4 (c)). Only one shallow groundwater sample (N13/P1) at 14 m depth has a higher pMC of 49, with the age of carbon being post-1950. The rest of the shallow wells contain 15 pMC, with ages ranging from 300 to 1350 (before present).

The ranges of Sr isotopic composition in shallow groundwater (14-26 m) and pond water are 0.7156 to 0.7209 and 0.7169 to 0.7183, respectively (Fig 6.4 (d)). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is higher in shallow groundwater than surface water. A high Sr-isotope ratio 0.7209 is observed at 26 m depth in groundwater (Fig 6.4 (d)) where the Ca and Sr concentrations are 57 mg/L and 0.2

Figure 6.4 (a) Vertical distribution of $\delta^{13}\text{C}$ signatures of DIC in groundwater (14-240 m), (b) $\delta^{13}\text{C}$ isotopic composition in surface water, (c) C-14 measurement (percent modern carbon) in shallow groundwaters (14-26 m), (d) Strontium isotope ratios in shallow wells (14-26 m) and pond water, (e) Calcium (Ca) and Strontium (Sr) concentrations (mg/L) in shallow groundwaters (14-26 m) and pond water



mg/L, respectively (Fig 6.4 (e)), whereas, one shallow groundwater sample (N4/P1) has a low Sr-isotope ratio of 0.7156 (Fig 6.4 (d)) where the concentrations of Ca and Sr are 52 mg/L and 0.3 mg/L, respectively (Fig 6.4 (e)).

Fecal Indicator Bacteria (E. coli)

The range of *E. coli* (MPN/100 mL) concentration is from 1,310 to 23,822 with averaging of 11,174 in pond and canal water (Table 6.2). This indicates that most probable number (MPN)/100 mL of *E. coli* is low across all depths (14-237 m) in groundwater (Fig 6.5 (a)) compared to surface water bodies (Fig 6.5 (b)). The *E. coli* DNA (Copies/100 mL) analyses indicate that copies/100 mL of *E. coli* DNA is below detection limit (<11) in groundwater (14-237 m) (Fig 6.5 (a)), whereas, high range of *E. coli* DNA (Copies/100 mL) from 13,538 to 116,138 with an average of 43,545 copies/100 mL present in surface water bodies (Fig 6.5 (b)) (Table 6.2).

Figure 6.5 (a) Vertical profile and (b) boxplot diagram of *E. coli* (MPN/100 mL) and *E. coli* DNA (Copies/100 mL) in groundwater and surface water respectively

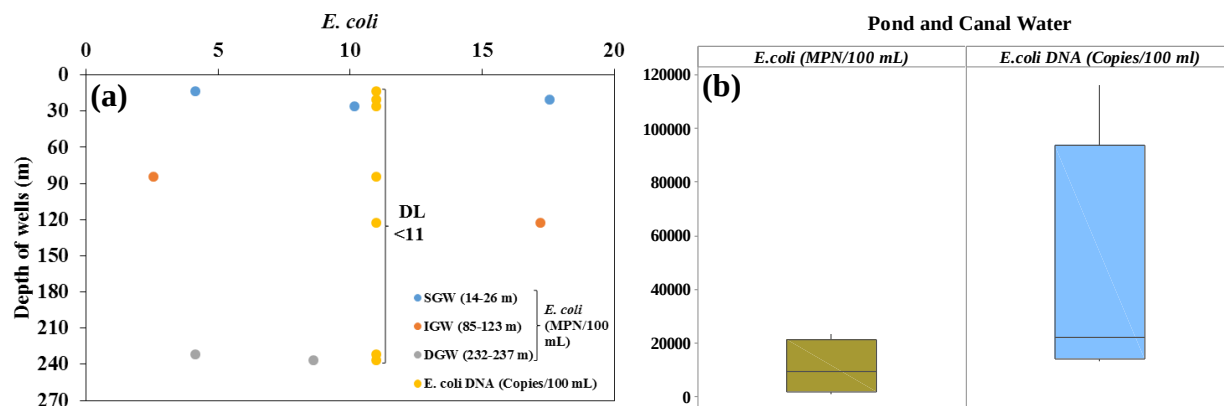


Table 6.2 Statistical analyses of concentration of fecal indicator bacteria (*E. coli*) for surface water

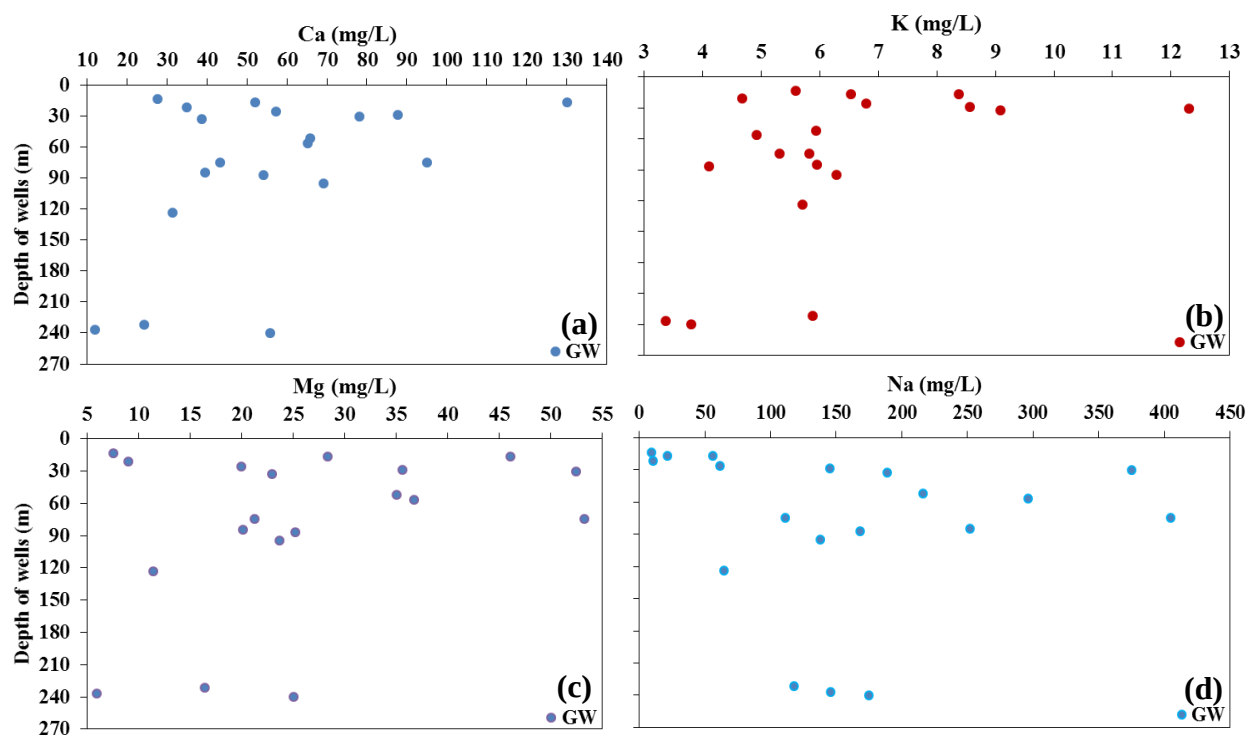
<i>Parameter</i>	<i>N</i>	<i>Q1</i>	<i>Median</i>	<i>Q3</i>	<i>IQRange</i>	<i>Whiskers to</i>
<i>E. coli</i> (MPN/100 mL)	4	2,085.5	9,782	21,654.5	19,569	1,310, 23,822
<i>E. coli</i> DNA (Copies/100 mL)	4	14,398.8	22,251	93,983.8	79,585	13,538, 116,138

Water Chemistry

Cation

The concentrations of Ca, K, Mg and Si were observed to be high, i.e. 130 mg/L (N3/P1), 12 mg/L (N4/P2), 53 mg/L (N4/P2) and 30 mg/L (N4/P1), respectively at shallow depth wells (14-30 m) (Fig 6.6 (a), (b), (c), (g)). An intermediate groundwater sample (N4/P4) also shows high Mg concentration (53 mg/L) at 75 m depth (Fig 6.6 (c)). On the other hand, the concentrations of Na, Mn, Fe_(t) and Sr were found to be high, i.e. 405 mg/L (N4/P4), 4.7 mg/L (N4/P3), 0.38 mg/L (N3/P6) and 0.7 mg/L (N4/P4), respectively, in intermediate groundwaters (33-123 m) (Fig 6.6 (d), (e), (f), (h)). Ca, K, Mg, Mn and Fe_(t) concentrations were observed to be low, i.e. 12 mg/L (N13/P5), 3 mg/L (N13/P5), 6 mg/L (N13/P5), 0 mg/L (N13/P5) and 0.01 mg/L (N7/P5), respectively, at deeper wells (232-240 m) (Fig 6.6 (a), (b), (c), (e), (f)). It is noticeable that the lowest concentrations of Fe_(t) (0.01 mg/L; N3/P2) and Sr (0.1 mg/L; N13/P1 and N13/PW) are also found in shallow groundwaters (14-30 m) (Fig 6.6 (f), (h)). The range of concentrations of all cations in both groundwater and surface waters indicate that only the concentration of K is high in pond and canal waters compared to groundwater (Table 6.3).

Figure 6.6 Vertical distribution of cation concentration in groundwater (a, b, c, d, e, f, g, h) and boxplot diagram of cation concentration in surface water (i)



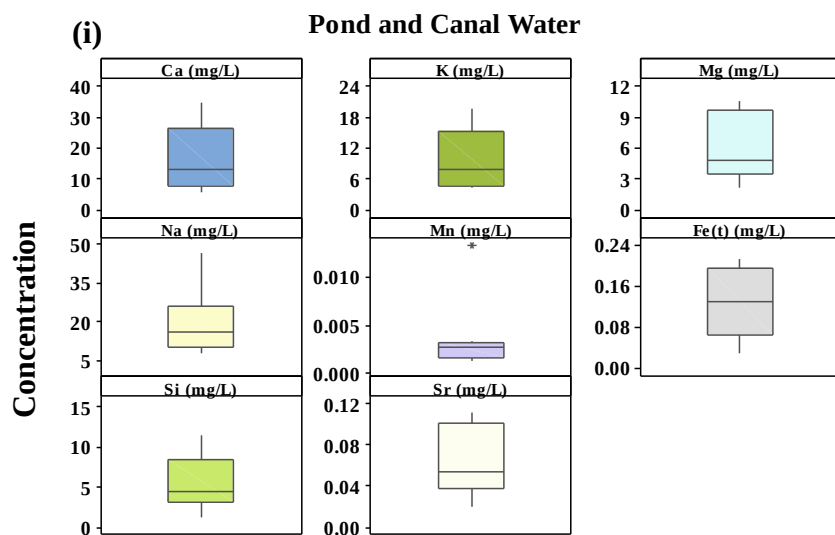
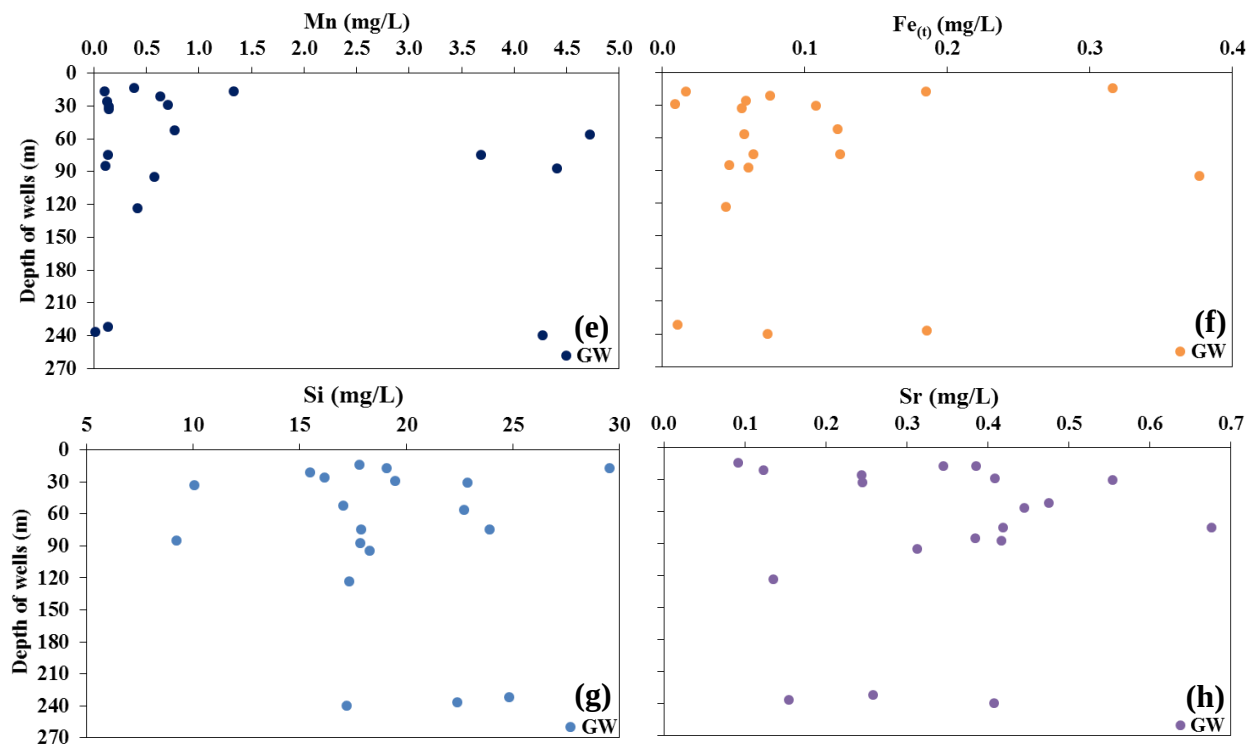


Table 6.3 The range of cation concentration in groundwater

Cation	Range (mg/L)	Cation	Range (mg/L)
Ca	12-130	Mn	0-4.7
K	3-12	Fe _(t)	0.01-0.38
Mg	6-53	Si	9-30
Na	9-405	Sr	0.1-0.7

Table 6.4 Statistical analyses of cation concentration for groundwater and surface water

Groundwater and Surface water

	Ca (mg/L)			K (mg/L)			Mg (mg/L)			Na (mg/L)			Mn (mg/L)			Fe _(t) (mg/L)			Si (mg/L)			Sr (mg/L)		
	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV
Shallow GW (14-30 m)	7	66.8	32.6	7	7.6	2.3	7	28.5	16.2	7	97	121.5	7	0.5	0.4	7	0.1	0.1	7	20.1	4.5	7	0.3	0.2
Intermediate GW (33-123 m)	9	55.8	20	9	5.69	1.4	9	27.8	12.3	9	204.4	103.3	9	1.7	2	9	0.1	0.1	9	17.1	4.9	9	0.4	0.2
Deep GW (232-240 m)	3	30.8	22.6	3	4.4	1.3	3	15.8	9.6	3	146.3	28.5	3	1.5	2.4	3	0.1	0.1	3	21.5	3.9	3	0.3	0.1
Surface water	9	17.4	10.7	9	9.53	5.7	9	6.1	3.2	9	19.4	12.4	9	0.004	0.004	9	0.1	0.1	9	5.4	3.4	9	0.1	0.03

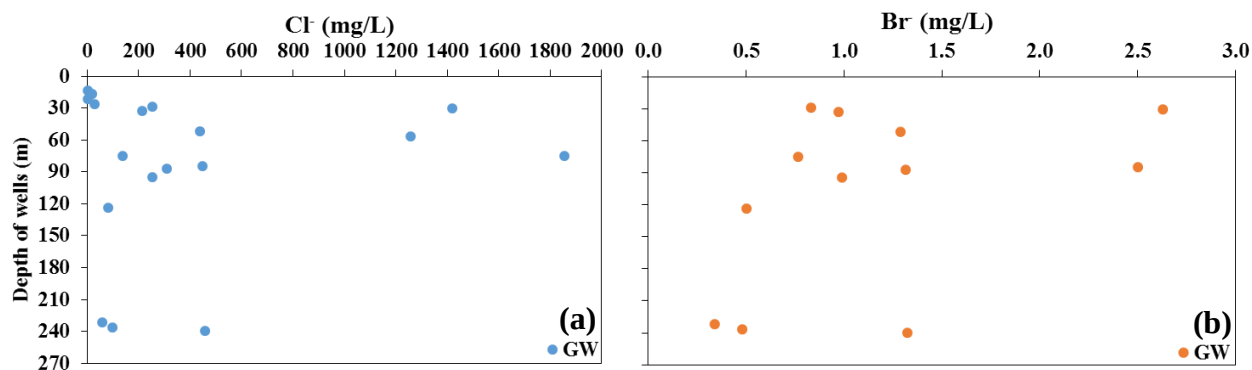
Surface water (boxplot summary of fig 6.6 (i))

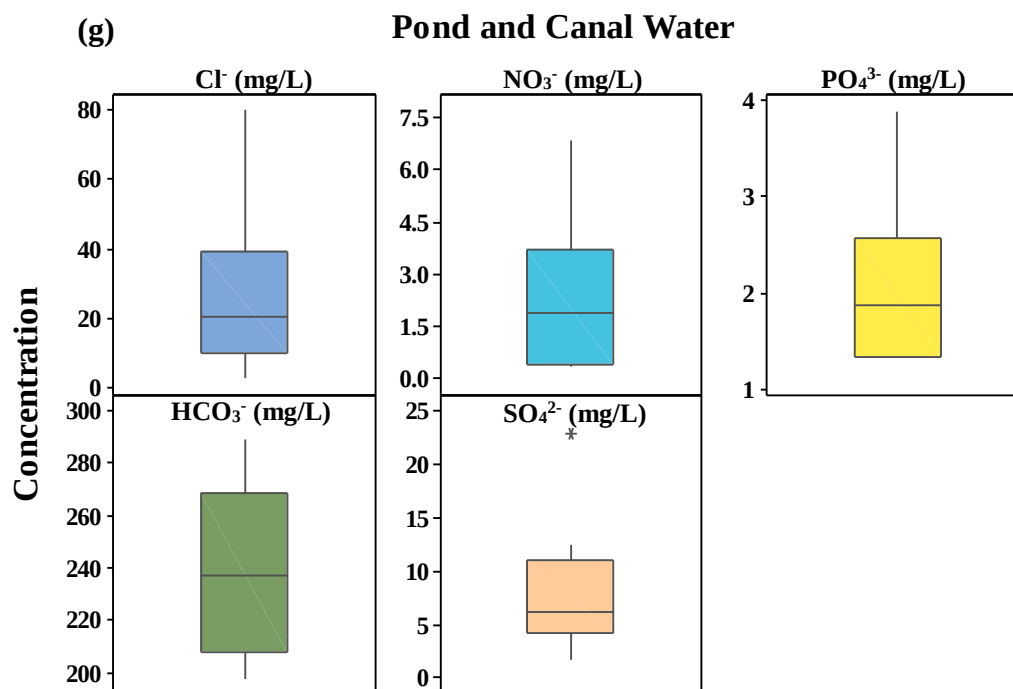
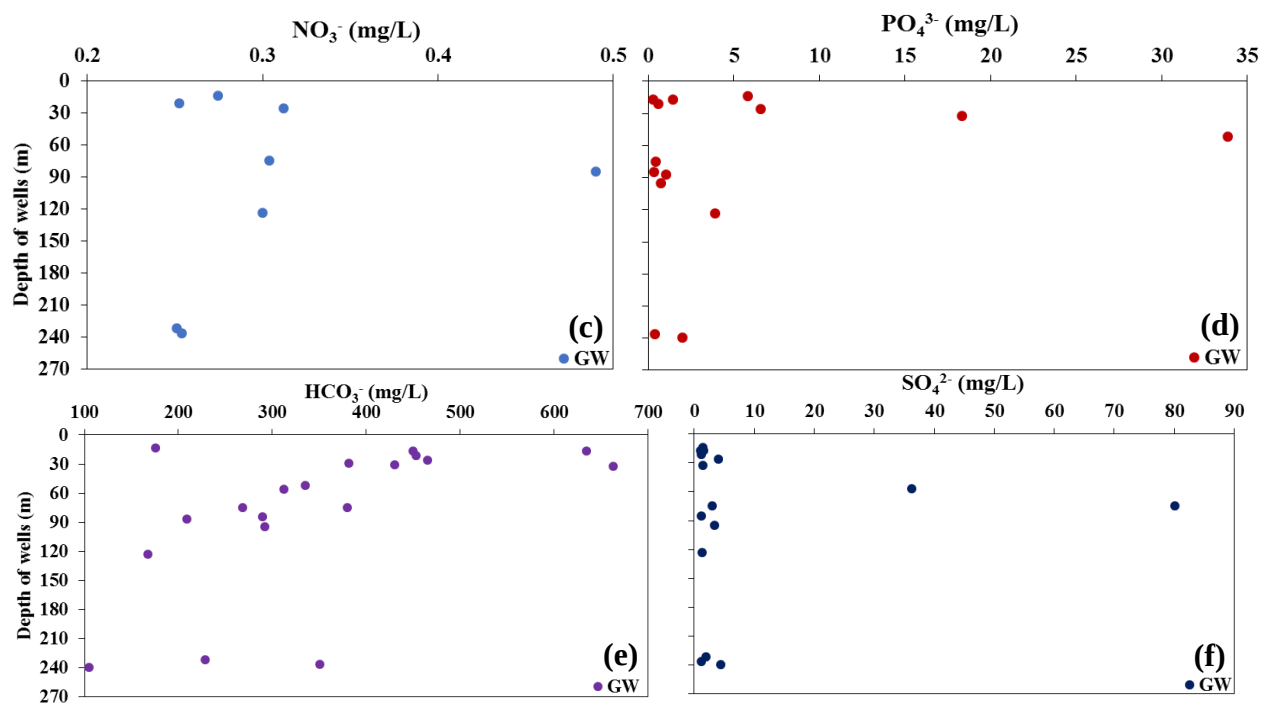
Cation	N	Q1	Median	Q3	IQRange	Whiskers to
Ca (mg/L)	9	7.365	13.1	26.45	19.085	5.26, 34.6
K (mg/L)	9	4.63	7.74	15.15	10.52	4.26, 19.6
Mg (mg/L)	9	3.44	4.81	9.67	6.23	2.04, 10.6
Na (mg/L)	9	10.38	16.3	26.3	15.92	7.91, 46.7
Mn (mg/L)	9	0.002	0.003	0.003	0.002	0.001, 0.003
Fe _(t) (mg/L)	9	0.066	0.13	0.195	0.129	0.031, 0.214
Si (mg/L)	9	3.06	4.4	8.485	5.425	1.256, 11.504
Sr (mg/L)	9	0.037	0.055	0.102	0.065	0.021, 0.112

Anion

The highest concentrations of Cl⁻ and HCO₃⁻ were 1857 mg/L (N4/P4) and 663 mg/L (N13/P2), respectively, observed in intermediate groundwaters (33-123 m), whereas, the lower concentration of Cl⁻ (3 mg/L; N13/P1 and N13/PW) and HCO₃⁻ (105 mg/L; N3/P5) were observed at shallower wells (14-30 m) and deeper depths (232-240 m) in groundwater, respectively (Fig 6.7 (a), (e)). Br⁻ concentration is high 2.6 mg/L (N4/P2) at shallow depths (14-30 m) and low 0.3 mg/L (N7/P5) at deeper wells (232-240 m) (Fig 6.7 (b)). Only one groundwater sample (N13/P3), which is at intermediate depth (85 m), shows a high NO₃⁻ concentration of 0.5 mg/L. The lowest concentration of NO₃⁻ (0.3 mg/L) was found at different depths in groundwater (Fig 6.7 (c)). It is noteworthy that only two groundwater samples, N3/P3

Figure 6.7 Vertical distribution of anion concentration in groundwater (a, b, c, d, e, f) and boxplot diagram of anion concentration in surface water (g)





and N4/P4, which occur at intermediate depths (33-123 m), have high PO_4^{3-} and SO_4^{2-} concentrations of 33.9 mg/L and 80.1 mg/L, respectively (Fig 6.7 (d), (f)) compared to rest of the groundwater samples. The lowest concentrations of PO_4^{3-} and SO_4^{2-} are 0.3 mg/L and 1 mg/L

found at different depths in groundwater wells (Fig 6.7 (d), (f)). Br^- was detectable ($>0.25 \text{ mg/L}$) in only one sample (N7/Pond1), which has a concentration of 0.3 mg/L (Appendix H4); all others are below detection limits ($<0.25 \text{ mg/L}$). The range of concentrations of all anions in both groundwater and surface water points to the fact that only NO_3^- concentration is high in surface water compared to other anions in groundwater (Table 6.5).

Table 6.5 The range of anion concentration in groundwater

Anion	Range (mg/L)	Anion	Range (mg/L)
Cl^-	3-1857	PO_4^{3-}	0.3-33.9
Br^-	0.5-2.6	HCO_3^-	198-289
NO_3^-	0.3-0.5	SO_4^{2-}	1.0-80.1

Table 6.6 Statistical analyses of anion concentration for groundwater and surface water

Groundwater and Surface water

	$\text{Cl}^- \text{ (mg/L)}$			$\text{NO}_3^- \text{ (mg/L)}$			$\text{PO}_4^{3-} \text{ (mg/L)}$			$\text{HCO}_3^- \text{ (mg/L)}$			$\text{SO}_4^{2-} \text{ (mg/L)}$			$\text{Br}^- \text{ (mg/L)}$		
	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV	n	Mean	STDEV
Shallow GW (14-30 m)	7	248.4	524.5	3	0.3	0.03	5	2.9	3	7	427	136.2	5	1.8	1.2	2	1.7	1.3
Intermediate GW (33-123 m)	9	554.3	600.1	3	0.4	0.1	7	8.4	13	9	324	142.1	7	18.1	30.2	7	1.2	0.6
Deep GW (232-240 m)	3	204.5	221.6	2	0.3	0.002	2	1.2	1.1	3	228	123	3	2.5	1.7	3	0.7	0.5
Surface water	9	27.2	23.9	7	2.5	2.4	6	2.1	1	9	239.6	32.9	9	8.4	6.3	bdl	bdl	bdl

Surface water (boxplot summary of fig 6.7 (g))

Parameter	N	Q1	Median	Q3	IQRange	Whiskers to
$\text{Cl}^- \text{ (mg/L)}$	9	9.714	20.298	38.735	29.022	2.629, 79.779
$\text{NO}_3^- \text{ (mg/L)}$	7	0.365	1.89	3.661	3.296	0.297, 6.803
$\text{PO}_4^{3-} \text{ (mg/L)}$	6	1.318	1.862	2.564	1.246	1.316, 3.863
$\text{HCO}_3^- \text{ (mg/L)}$	9	208	237	269	61	198, 289
$\text{SO}_4^{2-} \text{ (mg/L)}$	9	4.294	6.237	11.137	6.842	1.741, 12.466

Total As and As speciation

In nature, there are four oxidation states of As. Arsenite (III) and arsenate (V) are the two primary forms of inorganic As in the environment. For most of the groundwater samples the concentration of As (III) concentration is below detection limits ($<5 \mu\text{g/L}$), except for three samples (N3/P1, N13/P1, N13/PW). These samples have As (III) concentrations ranging from $13\text{-}23 \mu\text{g/L}$ from 14 to 21 m depth in groundwater (Fig 6.8 (a)). As (III), As (V) and $\text{As}_{(t)}$

concentrations decrease with increasing depth in groundwater (Fig 6.8 (a)). The highest concentrations of As (V) and As_(t) are 386 µg/L and 407 µg/L, respectively, observed in shallow

Figure 6.8 (a) Vertical distribution of inorganic As species and total As concentration (µg/L) from shallow to deep groundwaters (14-240 m) and boxplot diagram of total As concentration (µg/L) in surface water bodies (inset); (b) As species distribution in north and south Matlab

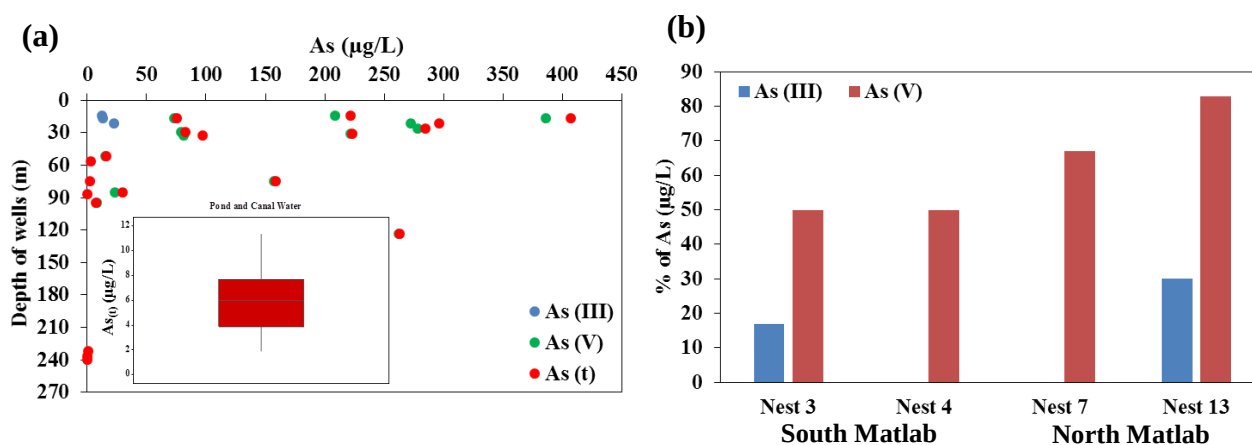


Table 6.7 Statistical analyses of As species and total As concentration for groundwater and surface water

Groundwater and Surface water									
	As (III) (µg/L)			As (V) (µg/L)			As _(t) (µg/L)		
	<i>n</i>	<i>Mean</i>	<i>STDEV</i>	<i>n</i>	<i>Mean</i>	<i>STDEV</i>	<i>n</i>	<i>Mean</i>	<i>STDEV</i>
Shallow GW (14-30 m)	3	16.1	5.8	7	217	112	7	227.3	118.6
Intermediate GW (33-123 m)	bdl	bdl	bdl	6	91.2	101.1	9	64.1	92.3
Deep GW (232-240 m)	bdl	bdl	bdl	bdl	bdl	bdl	3	0.4	0.3
Surface water	None	None	None	None	None	None	9	6	2.8

Surface water (boxplot summary of inset fig 6.8 (a))

<i>Parameter</i>	<i>N</i>	<i>Q1</i>	<i>Median</i>	<i>Q3</i>	<i>IQR</i>	<i>Whiskers to</i>
As _(t) (µg/L)	9	3.89	5.97	7.715	3.825	1.86, 11.4

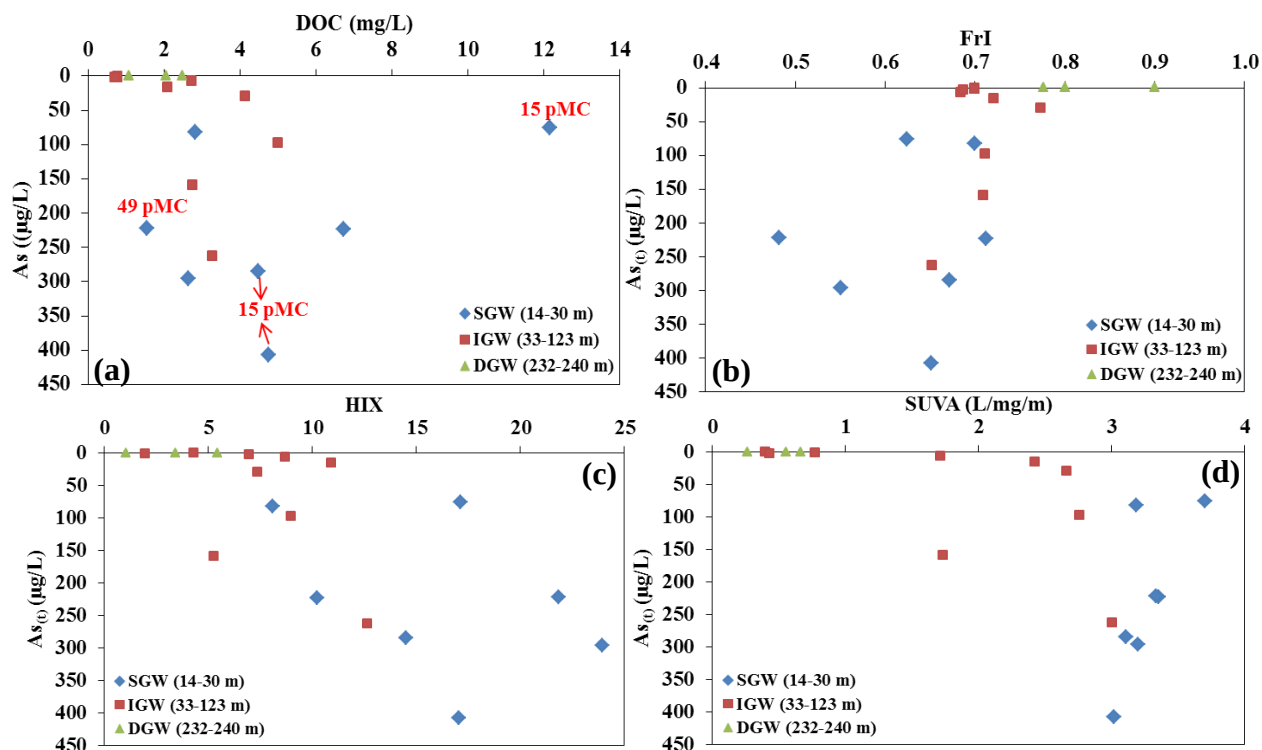
groundwater at a depth of 17 m (Fig 6.8 (a)). This indicates that As (V) and As_(t) are high in shallow aquifers. The mean As (V) and As_(t) concentrations are high 217 µg/L (*n* = 7; *STDEV* = 112) and 227.3 µg/L (*n* = 7; *STDEV* = 118.6) in shallow groundwaters (14-30 m) compared to intermediate and deep groundwaters (Table 6.7). It is also noticeable that most intermediate groundwater samples (N3/P3, N7/P4, N13/P2, N13/P3, N13/P6) have total As concentration

above the standard limit of WHO guideline (10 $\mu\text{g/L}$) with concentrations ranging from 16 to 263 $\mu\text{g/L}$ for depths of 33 to 123 m, whereas, in deeper wells and surface water bodies low As concentrations (Fig 6.8 (a)). More than 50 % of samples (twelve out of nineteen groundwater samples) from north and south Matlab show high As (V) concentrations. But the As (III) content is low in north and south Matlab as indicated by below 30 % samples (three out of nineteen groundwater samples) have detectable level of As (III) concentration (Fig 6.8 (b)). The As (V) content is high in north Matlab compared to south Matlab (Fig 6.8 (b)).

Co-occurrence of DOC with As in aquifer

The highest and lowest values are 12.2 mg/L and 0.7 mg/L observed at 14 m and 75 m depths respectively (Fig 6.9 (a)) indicating that the DOC concentration is higher in shallow wells (14-30 m) compared to intermediate and deeper wells (33-240 m). Shallow and intermediate groundwaters (14-123 m) are affected by As with concentration levels ranging from 16 to 407 $\mu\text{g/L}$ except four intermediate groundwater samples (N3/P4, N3/P6, N4/P3, N4/P4) (Fig 6.9 (a)). One of more the toxic and soluble inorganic forms of As is As (III), which is found in shallow groundwaters (14-21 m) with concentration ranging from 13-23 $\mu\text{g/L}$ (Fig 6.8 (a)). The analyses of ^{14}C for four shallow groundwater samples (14-26 m) indicate that the percent of modern

Figure 6.9 Relationship between (a) $\text{As}_{(t)}$ ($\mu\text{g/L}$) and DOC (mg/L) along with the percent of modern carbon (pMC), (b) $\text{As}_{(t)}$ ($\mu\text{g/L}$) and FrI, (c) $\text{As}_{(t)}$ ($\mu\text{g/L}$) and HIX, (d) $\text{As}_{(t)}$ ($\mu\text{g/L}$) and SUVA (L/mg/m) in groundwater (14-240 m)



carbon is overall low in the shallow groundwaters (14-26 m) (Fig 6.9 (a)). The mean FrI is unlikely low (~ 0.7) from shallow ($n = 7$; $STDEV = 0.7$) to intermediate groundwaters (14-123 m) (Fig 6.9 (b)). The degree of humification and level of aromaticity are high from shallow to intermediate groundwaters (14-123 m) but low in deeper aquifers (232-240 m) (Fig 6.9 (c), (d)). The fluorescence study suggests that the characteristics of DOC are mostly UVA and UVC humic like components along with tryptophan-like components in shallow and intermediate groundwaters (14-123 m) (Fig 6.2 (a), (b), (c), (d)).

Chapter 7 - Discussions

Comparison of results between north and south Matlab

In south Matlab, the DOC concentration is high (12.2 mg/L) in samples from shallow well depths (17 m), whereas, the concentration of DOC is comparatively low (1.1-5 mg/L) in north Matlab at similar depths (Fig 6.1 (a)). The values of FI (~1.7) and FrI (~0.7) are similar throughout the study area (Fig 6.1 (b), (c)). The degree of humification (HIX) is noticeably high in north Matlab compared to south Matlab (Fig 6.1 (d)). Additionally, high aromaticity was observed in north Matlab compared to south Matlab (Fig 6.1 (e)). The fluorescence studies suggest that both groundwater (except deeper groundwaters) and surface water bodies contain mostly UVA and UVC like humic components along with tryptophan like components in the study area (Fig 6.2 (a), (b), (c), (d)). The trends of all isotopic compositions, including hydrogen and oxygen, are similar in north and south Matlab. Moreover, a high percentage of modern carbon (49 %) (Fig 6.4 (c)) observed in north Matlab indicating that the aquifer sediment is fresher and/or more recently recharged in north Matlab than south Matlab. Generally, the water type in Matlab is Ca-Na-HCO₃⁻ type (Fig 6.6 and 6.7). The percentage of total dissolved As increases from shallow to intermediate groundwaters (14-26 m) in north Matlab (Fig 6.8 (a), (b)). The MPN-based *E. coli* test and qPCR suggests that very little culturable *E. coli* and *E. coli* DNA are present in the groundwater, respectively (Fig 6.5 (a)). On the other hand, the microbial population is very high in unprotected surface water bodies in the whole study area (Fig 6.5 (a), (b)).

Effect of DOC and its properties in waters

Dissolved organic carbon (DOC) is a quantitative measure of the organic carbon dissolved in water. Organic carbon occurs as a result of decomposition of plant or animal material and OC present in soil or water bodies may then dissolve when contacted by water. This DOC moves with both ground and surface waters. Soil/sediments produce much of the soil organic matter (SOM) in pore waters through leaching or microbial oxidation of SOM. In contact with water, SOM may leach ad into solution or become mobilized from sediments and form DOC (Söderberg, 2013). Dissolved organic carbon concentrations tend to be high in groundwater (14-240 m) than surface water bodies, as indicated by the mean of DOC concentration in the study area (Fig 6.1 (a), (f)). A high flow rate may increase DOC concentration by changing water

flow path, with more runoff routed through shallow, organic rich soil horizons, relative to deeper mineral horizons in which DOC adsorption is greatest (Cronan and Aiken, 1985; McDowell and Likens, 1988). Additionally, rainfall and runoff distribution may also affect both DOC production and transport processes.

High FI values (~ 1.8) are indicative of DOC consisting of microbially-derived substances (extracellular release and leachate from bacteria), while low FI values (~ 1.2) suggest that water contains terrestrially-derived substances (terrestrial plant and soil organic matter) (McKnight et al., 2001). Intermediate values suggest contributions from a combination of DOC sources. The mean FI is ~ 1.6 (nGW = 18; STDEV = 0.09; nSW = 9; STDEV = 0.09) in groundwater (14-240 m) and surface water, respectively, indicating that both groundwater and surface water may consist of both microbially and/or terrestrially derived substances. Surface waters may receive allochthonous carbon and other terrestrial organic matter from the surrounding area (plant material, soil carbon after rainfall) that make the FI of the surface water bodies decrease (~ 1.6) (Fig 6.1 (f)). In addition, surface water exposure to sunlight acts to decrease the FI. The high FI in shallow groundwater (14-30 m) may be due to the activity of microbes exuding organic compounds. However, the high FI in groundwater is not expected and contradicts the high aromaticity and HIX values, which are more consistent with a terrestrial source of DOC in shallow groundwater (14-30 m).

FrI is the indicator of the contribution of recently produced DOM (Fellman et al., 2010) and HIX is the indicator of humic substance content. Higher values of HIX indicate an increasing degree of humification (Fellman et al., 2010). The FrI is low (~ 0.7) in shallow and intermediate groundwaters (14-123 m) (Fig 6.1 (c)) and in surface water (Fig 6.1 (f)), suggesting that much of the DOC there is older/decomposed components. The HIX is high (~ 16.1) at shallow wells (14-30 m) (Fig 6.1 (d)) compared to pond and canal water (~ 6.9) (Fig 6.1 (f)), indicating that the shallow reducing aquifers have a high degree of humification-which may, in turn, cause the lower FrI at shallow depths (14-30 m). Additionally, the shallow to intermediate aquifers (14-123 m) and surface water bodies may have more microbially-degraded and recalcitrant organic matter that may act to decrease the FrI value. On the other hand, a low degree of humification and FrI in deeper groundwaters (232-240 m) (Fig 6.1 (c), (d)) indicate that the DOC in deep aquifer contains less humic content. Collectively the data suggest a greater contribution of humic

materials in shallow (14-30 m), intermediate aquifers (33-123 m) and surface water bodies (possibly from peat or dispersed sedimentary materials).

The mean SUVA value is higher 3.3 ($n = 7$; STDEV = 0.2) in shallow wells (14-30 m) compared to pond and canal waters (2.5) ($n = 9$; STDEV = 0.5). A high mean SUVA value in shallow wells (14-30 m) and surface water bodies implies that both shallow groundwaters (14-30 m) and surface water bodies may contain more aromatic and humic components. Hence, it has been suggested that both shallow groundwaters (14-30 m) and surface water bodies may receive more humic substances leached from soil and/or from the cellular constituents and exudates of indigenous aquatic organism sources. On the other hand, low degree of humification and FrI in deeper groundwaters (232-240 m) (Fig 6.1 (c), (d)) indicate that the DOC in the deep aquifer (232-240 m) is less humic. The mean SUVA value decreases from 1.8 ($n = 9$; STDEV = 1) to 0.5 ($n = 3$; STDEV = 0.2) in intermediate and deeper wells (33-240 m) respectively (Fig 6.1 (e)), which supports less aromatic nature of DOC in the deep aquifer.

Fluorescence spectroscopic studies

Peaks A and C are considered to be derived primarily from vascular plant sources, aromatic in nature, highly conjugated with higher molecular weight fraction of the DOM pool (Coble et al., 1998). Peak M was originally used as a marker for endogenous DOM production because it was presumed to be derived completely from marine planktonic production. Peak T has been used to predict DOM lability (biogeochemical tracers) (Fellman et al., 2009a) and to signature DOM derived from microbial sources (Hood et al., 2009). But several studies suggested that it originated in terrestrial and freshwater environments (Stedmon and Markager, 2005a; Murphy et al., 2008; Balcarczyk et al., 2009). The variations in the contribution of these humic-like fluorescence groups can be used to differentiate between terrigenous (derived from higher plant material) and autochthonous DOM (produced within the aquatic environment) (Fellman et al., 2010). The fluorescence study as part of this project indicates that the characteristics of DOC are predominantly UVA and UVC humic-like components (Table 7.1). Additionally, the tryptophan-like components are also present in shallow (14-30 m), intermediate groundwaters (33-123 m) and surface water bodies. Much of the DOC is of more aromatic humic in nature due to the presence of more humic contents in shallow groundwaters (14-30 m) as the mean of humification index (HIX) is high (~ 16.1) at shallow depths (14-30 m) (Table 6.1) (Fig 6.1 (d)). Intermediate wells (33-123 m) and surface water bodies may contain a mixture of less

and more aromatic humic DOC, as the degree of humification decreases with increasing depth from shallow to intermediate groundwaters (14-123 m) (Fig 6.1 (d); Fig 6.2 (c), (d), (g), (h)). The fluorescence peaks for deeper wells (232-240 m) are unknown (Fig 6.2 (e), (f)). Microbial processing along with reactions with allochthonous humic matter may cause a decrease in the level of aromaticity from shallow to intermediate groundwaters with depth (17-240 m). On the other hand, the presence of tryptophan-like components from shallow to intermediate wells (17-123 m) may suggest that some labile organic carbon may be derived from microbial sources, such as from pond microbial organic compounds (bacteria, algae, exudates from microorganisms).

Table 7.1 Summary of observed natural fluorescence peaks of aquatic DOM from shallow to intermediate groundwaters (17-123 m) and surface water bodies (pond and canal) (vide table 2 of Fellman et al., 2010, Coble et al., 1990 and 1998, Parlanti et al., 2000)

Component	Peak Name	Reference Excitation _{max} (nm)	Acquired Excitation _{max} (nm)	Reference Emission _{max} (nm)	Acquired Emission _{max} (nm)	Probable Sources
Tryptophan	T	270-280 (<240)	275	330-368	340	T, A, M
UVA Humic	M	290-325 (<250)	312	370-430	415-425	T, A, M
UVC Humic	A	<260	<260	448-480	450	T
UVC Humic	C	320-360	350	420-460	440-450	T

Note: T - Terrestrial plant or soil organic matter, A - Autochthonous production, M - Microbial processing

Inference from stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$), $\delta^{13}\text{C}$, ^{14}C and $\text{Sr}^{87}/\text{Sr}^{86}$

Intermediate groundwater samples (33-123 m) have different isotopic signatures from -14 to -36 $\delta^2\text{H}$ (‰) values and from -2.1 to -5.5 $\delta^{18}\text{O}$ (‰) values. A more negative oxygen isotope value -5.5 ‰ in intermediate depth wells (33 m) (Fig 6.3 (b)) may suggest that the progressive depletion of the vapor mass and thus of the precipitation by the condensation process, preferentially remove the H and O isotopes from the vapor. Many of the isotope values for shallow water samples (14-30 m) from Matlab are more or less similar to rainfall isotopic compositions in Savar region (LMWL). The more enriched isotopic values of $\delta^{18}\text{O}$ for surface water samples are impacted by evaporation before or during infiltration (Fig 6.3 (b)). Most of the surface water samples and one shallow groundwater sample (17 m) show enriched $\delta^{18}\text{O}$ values denoting that the waters may be affected by evaporation prior to entering into the surface (Fig 6.3 (b)). All groundwater and surface water samples from Matlab plot below the global and local

meteoric water line, indicating an origin from local rain and surface water bodies (for groundwater), with or without some evaporation before infiltration (Fig 6.3 (a), (b)).

The average $\delta^{13}\text{C}$ value of -11.8‰ in shallow groundwaters (14-30 m) (Fig 6.4 (a)) is similar to the $\delta^{13}\text{C}$ values for C_4 plants (average about -12‰ of $\delta^{13}\text{C}$ value) that may be indicated that terrestrial plant materials may utilize photosynthetic reaction (Deines, 1980). In the absence of vegetation, atmospheric CO_2 and heavy rainfall may contribute to dissolved inorganic carbon (DIC) through rock weathering, resulting in $\delta^{13}\text{C}$ values greater than $-7 \pm 2\text{‰}$ from shallow to deep wells (14-240 m) and surface water bodies (Fig 6.4 (a), (b)). Moreover, the major sources of carbon contributing to DIC in natural waters are CO_2 derived from the decay of organic matter in continental soils and from the dissolution of carbonate, while in general the contribution of atmospheric CO_2 is negligibly small. Processes usually involved in the removal of DIC include photosynthesis, carbonate precipitation and air-water exchange. On the other hand, precipitation of carbonate minerals from solution may take place rapidly, far from chemical equilibrium, introducing the possibility of isotopic disequilibrium between dissolved inorganic carbon and precipitated carbonate (Mook and Tan, 1991).

A high percentage of modern carbon, 49 % was found at 14 m depth in groundwater with an age of post-1950 (Fig 6.4 (c)), and represents a relatively recent recharge of this groundwater. In contrast, the remaining shallow wells contain a low percentage of modern carbon 15 %, with the ages ranging from 300 to 1350 (before present), and reflects an older, more refractory DOC pool retained within the groundwater (Fig 6.4 (c)). Hence, the variation of percentage of modern carbon shallow depths (14-26 m) may be affected by extensive cycling and reworking of the labile DOC taking place in these catchment soils during surface runoff and infiltration of rain water.

Fecal indicator bacteria (E. coli) and probable role

High concentrations of *E. coli* (MPN/100 mL) in surface water compared to groundwater indicate that the microbial population is high compared to extracted water from hand-pumped wells. *E. coli* genes are not transported at all in groundwater (Fig 6.5 (c)), whereas, surface water bodies contain culturable *E. coli* with *E. coli* genes (Fig 6.5 (d)). The presence of *E. coli* (MPN/100 mL) in groundwater and culturable *E. coli* with genes in surface water indicate that quantitative fecal contamination. The study area is predominantly composed of sand particles so it may suggest that low microbial density in groundwaters by lateral and/or vertical transport

from adjacent surface water bodies may affect by collision with sand particles or low to moderate porous medium.

Water chemistry of Matlab groundwaters

Most of the dissolved cations and anions analyzed in this study are soluble in water. All cations and anions may dissolve from weathering of rock-forming minerals (carbonate minerals etc.) as water percolates into soils and rocks and thereby carries chemical constituents into aquifer. The fluctuation of the concentration of different chemical elements from shallower to deeper groundwaters (14-240 m) and surface water bodies may be affected by the different weathering rates along flowpaths and stabilities of minerals in the weathering environment. One of the major observations in the study area is that very low total Fe concentration was noticed in almost all piezometers of the four nests. Three different but precisely calibrated instruments (HR ICP MS (2) and ICP OES) were used to measure $\text{Fe}_{(t)}$. The $\text{Fe}_{(t)}$ concentration was lower in comparison to previous results in the same piezometer (Appendix H2). This may be accounted for as precipitation of Fe-carbonate minerals that can be massive to decrease dissolved Fe along the groundwater flowpath under high Eh and pH (Stumm and Morgan, 1996; Huntsman-Mapila et al., 2011). But there is no distinct correlation observed between the relations of Fe- HCO_3^- and Eh-pH in groundwater (Appendix H2).

As speciation of Matlab groundwaters

The most toxic and mobile form of inorganic As, As (III), was found to range from 13-23 $\mu\text{g/L}$ in shallow wells (14-21 m). As (V) and $\text{As}_{(t)}$ are also high at shallow depths indicating that shallow groundwaters (14-30 m) are highly contaminated by dissolved As content (Fig 6.8 (a)). Intermediate groundwaters are also affected by high range of As concentration (0.3-263 $\mu\text{g/L}$), whereas deeper wells and surface water bodies have low As concentration (DGW: 0.2-0.8 $\mu\text{g/L}$; SW: 1.9-11.4 $\mu\text{g/L}$) (Fig 6.8 (a)). As (V) is mostly bound to iron oxides on mineral surfaces (Matera et al., 2003), while As (III) is more soluble. The concentrations of total As and As (V) are remarkably high in north and south Matlab (Fig 6.8 (b)). On the other hand, more toxic and soluble As (III) is found in the study area with concentrations ranging from 12-23 $\mu\text{g/L}$. One of the key factors leading to an increase in As concentration in groundwaters is thought to be bioreduction of As (V) and As-bearing iron oxides (Wang et al., 2014). The BGS survey showed that the As concentration is remarkably high in S and SE Bangladesh (BGS and DPHE, 2001) (Fig 2.2). Since As-transforming microbes along with the physicochemical conditions of the

environment, can alter the valence state and mobility of As in an aquifer by natural processes (Oremland and Stolz, 2005; Stolz et al., 2006), it may suggest that there is a high possibility to increase As pollution in the study area.

Relation between DOC and its properties with As

The DOC level is high in groundwater from shallow wells (14-30 m), with the mean DOC concentration of 5.5 mg/L (Fig 6.9 (a)). Shallow and intermediate groundwaters (14-123 m) have dissolved As contents above 10 µg/L (Fig 6.8 (a)). Much of the DOC in shallow to intermediate wells is older/decomposed whereas DOC seems to be less humic in deeper groundwaters. The characteristics of DOC are predominantly UVA and UVC humic like components in shallow and intermediate groundwaters (14-123 m) but tryptophan-like components are also present in both groundwaters (Fig 6.2 (a), (b), (c), (d)). The percent of modern carbon is 49 (Post-1950) observed at 14 m depth (from recently recharged groundwater), whereas, the remaining shallow groundwater samples contain only 15 percent modern carbon (Fig 6.4 (c)). Thus, it may suggest that high As is associated with older more humic DOC in shallow and intermediate groundwater as the percentage of modern carbon is low and much of the DOC are older/decomposed in these groundwaters.

Chapter 8 - Conclusions

The As speciation analyses suggest that As (III) is present in shallow groundwaters (14-30 m). The concentrations of As (V) and As_(t) decrease with increasing depths in the aquifer. The highest concentrations of As (V) and As_(t) are observed at shallower depths, indicating that overall As content is very high in shallow aquifers. It is also noticed that intermediate groundwaters are also affected by As as the concentration is above As standard limit of WHO guideline (10 µg/L), whereas deeper wells and surface water bodies have low As concentration (<10 µg/L).

The overall water chemistry data represents that only the range of K and NO₃- concentrations of the pond and canal waters are high compared to groundwaters. The concentrations of Ca, K and Mg are higher in shallow depth wells (14-30 m). On the other hand, the concentrations of Na, Mg, Mn and Sr are found higher in intermediate groundwaters (33-123 m). Ca, K, Mg, Mn and Fe_(t) concentrations are lower in deeper wells (232-240 m) with relatively high Si concentrations. The highest concentrations of Cl⁻ and HCO₃⁻ are observed in intermediate groundwaters (33-123 m), whereas, the lowest concentrations of Cl⁻ and HCO₃⁻ are observed in deeper wells (232-240 m).

The analyses of DOC properties (FI, FrI, HIX and SUVA) suggest that both groundwater and surface water may comprise of microbially and/or terrestrially derived organic materials. Shallow to intermediate groundwaters (14-123 m) and surface water contain older/decomposed DOC but DOC in deeper groundwaters (232-240 m) is less humic. More microbially-degraded and recalcitrant organic matter is present in shallow to intermediate aquifers (14-123 m) and surface water bodies. Both shallow groundwaters (14-30 m) and surface water bodies may obtain a significant proportion of humic substances leached from soil and/or from the cellular constituents and exudates of indigenous aquatic organisms. The fluorescence spectroscopic studies demonstrate that four primary peaks are prominent A, M, C and T from shallow to intermediate wells (14-123 m) and surface water bodies indicating that DOC are enriched in UVA and UVC humic like components along with tryptophan like components. Much of the DOC is more aromatic in nature, whereas, intermediate wells (33-123 m) and surface water bodies may contain mixture of less and more humic DOC.

The stable isotope ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) analyses indicate that the recharge source of groundwater in the study area is from local rain and local surface water bodies, with or without some evaporation before infiltration. The $\delta^{13}\text{C}$ analyses suggest that the trend of $\delta^{13}\text{C}$ signatures of DIC is not the same in groundwater (14-240 m) and surface water. The $\delta^{13}\text{C}$ isotopic composition may be controlled in the following ways: (1) in the absence of vegetation; (2) low atmospheric CO_2 concentrations; (3) heavy rainfall; (4) decay of organic matter in continental soils. It may also suggest that precipitation of weathering secondary minerals may take place rapidly in solution which may be introduced to cause $\delta^{13}\text{C}$ isotopic disequilibrium. The activity of ^{14}C in groundwaters (14-26 m) shows a decreasing trend and the overall percentage of modern carbon is low in very shallow depth wells (14-26 m). The variations of ^{14}C activity in very shallow groundwaters (14-26 m) may be affected by extensive cycling of the labile DOC in sediments during surface runoff and infiltration of rain water.

The most portable number (MPN) based Colilert test for fecal indicator bacteria (*E. coli*) indicates that the concentration of *E. coli* (MPN/100 mL) is low at almost all depths in groundwater compared to surface water bodies. Similarly, qPCR results denote that *E. coli* genes are below detection limit in all groundwater samples. In contrast, unprotected surface water bodies are harbinger of high microbial density compared to groundwaters.

Hence the following findings can be formulated: (a) DOC concentration are high in shallow wells; (b) degree of humification and level of aromaticity are high in shallow wells; (c) variable pMC within shallow waters; (d) dissolved As concentration are high in shallow and intermediate depths. More humic DOC in shallow and intermediate groundwaters may be involved in complexation or other biogeochemical reactions which may aid in mobilizing As in groundwaters. (e) *E. coli* transport from ponds is limited in extent even in sandy sediment. In many cases it would not occur at all because the fine grain sediment filters it out. There is no need for bacteria to be transported from the surface, however. Many studies have shown that thousands of species of endogenous bacteria are alive and well in aquifers. These bacteria may be utilizing DOC coming from the surface.

References

- Acharyya, S. K. (1999). Comment on Nickson et al., 1998, Arsenic poisoning of Bangladesh groundwater *Nature*, 401, 545.
- Aggarwal, P. K.; Basu, A. R.; Kulkarni, K. M. (2003). Arsenic Mobility and Groundwater Extraction in Bangladesh: Comment. *Science*, 300, 584.
- Alam, M. K.; Hassan, A. K. M. S.; Khan, M. R.; Whitney, J. W. (1990). Geological Map of Bangladesh. Geological Survey of Bangladesh.
- Allen, M. J. and Geldreich, E. E. (1975). "Bacteriological Criteria for Ground-water Quality." *Ground Water*, 13, 45–52.
- Aravena, R.; Schiff, S. L.; Trumbore, S. E.; Dillon, P. J. and Elgood, R. (1992). Evaluating dissolved inorganic carbon cycling in a forested lake watershed using carbon isotopes. *Radiocarbon* 34(3), 636–645.
- AQUASTAT Survey–2011. Irrigation in Southern and Eastern Asia in figures. FAO Water Reports 37, ISBN 1020-1203.
- Bakr, M. (1977). Quaternary geomorphic evolution of the Brahmanbaria-Noakhali area. Geological Survey of Bangladesh, pp. 10.
- Baker, A. (2001). Fluorescence excitation–emission matrix characterization of some sewage-impacted rivers. *Environ. Sci. Technol.* 35: 948–953, doi:10.1021/es000177t.
- Balcarczyk, K. L.; Jones, Jr. J. B.; Jaffe, R. and Maie, N. (2009). Stream dissolved organic matter bioavailability and composition in watersheds underlain with discontinuous permafrost. *Biogeochemistry* 94: 255–270, doi:10.1007/s10533-009-9324-x.
- Bartram, J.; Cotruvo, J.; Exner, M.; Fricker, C.; Glasmacher, A. (2003). Heterotrophic Plate Counts and Drinking-water Safety. The Significance of HPCs for Water Quality and Human Health, World Health Organization 2003, ISBN: 92 4 156226 9 (WHO).
- Berset, E. (2007). Groundwater in Bangladesh: A review of the proposed Mechanisms leading to Arsenic Release. Term Paper in Biogeochemistry and Pollutant Dynamics.
- Bhattacharya, P. D.; Chatterjee and Jacks, G. (1997). Occurrence of arsenic contaminated groundwater in alluvial aquifers from the Delta Plain, eastern India: Options for a safe drinking water supply, *Water Res. Dev.*, 13, 79-92.
- Bouteleux, C.; Saby, S.; Tozza, D.; Cavard, J.; Lahoussine, V.; Hartemann, P. and Mathieu, L. (2005). *Escherichia coli* Behavior in the Presence of Organic Matter Released by Algae Exposed to Water Treatment Chemicals. *Appl Environ Microbiol.*, 71(2): 734–740.

- Boualam, M.; Mathieu, L.; Fass, S.; Cavard, J. and Gatel, D. (2002). Relationship between coliform culturability and organic matter in low nutritive waters. *Water Res.* 36:2618-2626.
- Brammer, H. B. (1996). *The Geography of the Soils of Bangladesh*. University Press Limited, Dhaka, Bangladesh, 287p
- Briscoe, J. (1978). The role of water supply in improving health in poor countries (with special reference to Bangla Desh). *Am J Clin Nutr*, 31, 2100–2113.
- British Geological Survey (BGS) and Department of Public Health and Engineering (DPHE). (1999). *Groundwater Studies for Arsenic Contamination in Bangladesh Phase I: Rapid Investigation Phase, Main Report*. British Geological Survey and Mott MacDonald Ltd.
- British Geological Survey (BGS) and Department of Public Health Engineering (DPHE). (2001). *Arsenic Contamination of Groundwater in Bangladesh*. In: Kinniburgh, D.G., Smedley, P.L. (Eds), *British Geologic Survey Report WC/00/19*, Vol. 1-4.
- Brooks, P. D. and Lemon, M. M. (2007). Spatial variability in dissolved organic matter and inorganic nitrogen concentrations in a semiarid stream, San Pedro River, Arizona. *J Geophys Res* 112:G03S05. doi:10.1029/2006JG000262.
- Burgess, W.; Ahmed, K. M. (2006). Arsenic in aquifers of the Bengal Basin: From sediment source to tube-wells used for domestic water supply and irrigation. In Naidu R, Smith E, Owens G, Bhattacharya P and Nadebaum P (Eds) *Managing arsenic in environment*, CSIRO Publishing, Collingwood VIC, Australia, p. 31-56.
- Burgess, W. G.; Hoque, M. A.; Michael, H. A.; Voss, C. I.; Breit, G. N.; Ahmed, K. M. (2010). Vulnerability of deep groundwater in the Bengal Aquifer System to contamination by arsenic. *Nat. Geosci.*, 3 (2), 83–87.
- Castillo, C. E. D. and Avril, B. (1998). Distribution and optical properties of CDOM in the Arabian Sea during the 1995 SW monsoon. *Deep-Sea Res. II* 45: 2195–2223, doi:10.1016/S0967-0645(98)00068-X.
- Chakraborti, A. K. and Saha, K. C. (1987). Arsenical dermatosis from tubewell water in West Bengal. *Ind. J. Med. Res.* 85, 326-334.
- Chapelle, F. H. and Lovley, D. R. (1992). Competitive-exclusion of sulphate reduction by Fe (III)-reducing bacteria - a mechanism for producing discrete zones of high-iron groundwater. *Ground Water*, 30, 29-36.
- Chowdhury, R. T. et al. (1999) Comment on Nickson et al. (1998). Arsenic Poisoning of Bangladesh groundwater, *Nature*, 401, 545-546.

- Coble, P. G.; Green, S. A.; Blough, N. V. and Gagosian, R. B. (1990). Characterization of DOM in the Black Sea by fluorescence spectroscopy. *Nature* 348: 432–435, doi:10.1038/348432a0.
- Coble, P. G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation–emission matrix spectroscopy. *Mar. Chem.* 51: 325–346, doi:10.1016/0304-4203(95)00062-3.
- Coble, P. G. (2007). Marine optical biogeochemistry: The chemistry of ocean color. *Chem. Rev.* 107: 402–418, doi:10.1021/cr050350+.
- Craun, G. F. (1985). “A Summary of Waterborne Illness Transmitted Through Contaminated Ground-water.” *Jour. Environ. Health*, 43, 122.
- Cronan, C. S. and Aiken, G. R. (1985), Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York, *Geochim. Cosmochim. Acta*, 49, 1697–1705.
- Curlin, G. T.; Aziz, K. M. A. and Khan, M. R. (1977). The Influence of Drinking Tubewell Water on Diarrhea Rates in Matlab Thana, Bangladesh. Bangladesh: Dhaka, International Centre for Diarrhoeal Disease Research, Bangladesh.
- Datta, S.; Neal, A. W.; Mohajerin, T. D.; Ocheltree, T.; Resenheim, B. E.; White, C. D.; Johannesson, K. H. (2011). Perennial ponds are not an important source of water or dissolved organic matter to groundwaters with high arsenic concentrations in West Bengal, India. *Geophys. Res. Lett.*, 38, L20404 DOI: 10.1029/2011GL049301.
- Degens, E. T. (1969). Biogeochemistry of stable carbon isotopes. In: Eglinton, G. and Murphy, M. T. J. (Eds) *Organic Geochemistry, Methods and Results*, Springer Verlag, Heidelberg, pp. 304-29.
- Deines, P. (1980). The isotopic composition of reduced organic carbon. In: P. Fritz and J.C. Fontes (Eds.), *Hand book of Environmental Isotope Geochemistry*. Elsevier, Amsterdam, pp. 329-406.
- DPHE. (1999). Groundwater studies for arsenic contamination in Bangladesh. Rapid Investigation Phase. Final Report. Mott MacDonald Ltd and British Geological Survey. Report for the Department for Public Health Engineering and the Department for International Development.
- Escamilla, V.; Wagner, B.; Yunus, M.; Streatfield, P. K.; van Geen, A. & Emch, M. (2011). Effect of deep tubewell use on childhood diarrhoea in Bangladesh. *Bull. WHO* 89, 521–527.
- DPHE/BGS/DFID. (2000). ‘Groundwater Studies of Arsenic Concentration in Bangladesh’
- Escamilla, V.; Knappett, P.; Yunus, M.; Streatfield, P. K. & Emch, M. (2013). Influence of latrine proximity and type on tubewell water quality and diarrheal disease in Bangladesh. *Ann. Assoc. Am. Geogr.* In Press.

- Fendorf, S.; Michael, H. A.; van Geen, A. (2010). Spatial and temporal variations of groundwater arsenic in south and southeast Asia. *Science*, 328, 1123–1127.
- Feighery, J.; Mailloux, B. J.; Ferguson, A. S.; Ahmed, K. M.; van Geen, A. and Culligan, P. J. (2013). Transport of *E. coli* in aquifer sediments of Bangladesh: Implications for widespread microbial contamination of groundwater. *Water Resources Research*, Vol. 49, 1–15, doi:10.1002/wrcr.20289.
- Frost, C.D.; Toner, R.N. (2004). *Ground Water*, 42, 418-432.
- Galy, A.; France-Lanord, C.; Derry, L. A. (1999). The strontium isotopic budget of Himalayan Rivers in Nepal and Bangladesh. *Geochimica et Cosmochimica Acta*, Vol. 63, No. 13/14, pp. 1905-1925.
- Geldreich, E. E. (1975). *Handbook for Evaluating Water Bacteriological Laboratories*. EPA-670/9-75-006. Cincinnati, Ohio: U.S. Environmental Protection Agency.
- Geldreich, E. E.; Nash, H. D. and Spino, D. (1977). “Characterizing Bacterial Populations in Treated Water Supplies: A Progress Report.” *Proc. AWWA Water Quality Tech. Conf.*, Kansas City, Missouri, December 4–7.
- Geldreich, E. E. (1990). Microbiological quality of source waters for water supply. p. 3-31. In: G. A. McFeters, edited. *Drinking Water Microbiology*. Springer-Verlag, New York.
- Geldreich, E. E. and LeChevallier, M.W. (1999). Microbial water quality in distribution systems. In *Water Quality and Treatment*, 5th edn (ed. R.D. Letterman), pp. 18.1–18.49, McGraw-Hill, New York.
- Grabow, W. O. K. (1996). Water borne Diseases: Update on water quality assessment and control. *Water SA*. 22: 193-202.
- Fellman, J., B.; Hood, E.; D’Amore, D., V.; Edwards, R., T. and White, D. (2009a). Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate watersheds. *Biogeochemistry* 95: 277–293, doi:10.1007/s10533-009-9336-6.
- Fellman, J. B.; Hood, E. and Spencer, R. G. M. (2010). Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review. *Limnol. Oceanogr.*, 55(6), 2452–2462.
- Ferguson, A., S.; Mailloux, B., J.; Ahmed, K., M.; van Geen, A.; McKay, L., D.; Culligan, P., J. (2011). Hand-pumps as reservoirs for microbial contamination of well water, *Journal of Water and Health*, 09.4, 707-717.
- Harvey, C. F.; Swartz, C. H.; Badruzzaman, A. B. M.; Keon-Blute, N.; Yu, W.; Ashraf Ali, M.; Jay, J.; Beckie, R.; Niedan, V.; Brabander, D.; Oates, P. M.; Ashfaq, K. N.; Islam, S.; Hemond, H. F.; Ahmed, M. F. (2002). Arsenic mobility and groundwater extraction in Bangladesh. *Science*, 298, 1602–1606.

- Harvey, C. F.; Ashfaq, K. N.; Yu, Winston; Badruzzaman, A. B. M.; Ali M. Ashraf; Oates, P. M.; Michael, H. A.; Neumann, R. B.; Beckie, R.; Islam, S.; Ahmed, M. F. (2006). Groundwater dynamics and arsenic contamination in Bangladesh, *Chemical Geology* 228, 112-136.
- Hoque, B. (1999). Biological Contamination of Tubewell Water (In 8th Annual Scientific Conference). Dhaka, Bangladesh: ICDDR. B.
- Hoque, B. A., Hallman, K., Levy, J., Bouis, H., Ali, N., Khan, F., Khanan, S., Kabir, M., Hossain, S. & Alam, M. S. (2006). Rural drinking water at supply and household levels: quality and management. *Int. J. Hyg. Environ. Health* 209, 451–460.
- Hood, E.; Fellman, J., B.; Spencer, R., G., M.; Hernes, P., J.; Edwards, R., T.; D' Amore, D., V. and Scott, D. (2009). Glaciers as a source of ancient and labile organic matter to the marine environment. *Nature* 462: 1044–1048, doi:10.1038/nature08580.
- Hossain, Mohammed; Bhattacharya, P.; Frape, S., K.; Jacks, G.; Islam, M., M.; Rahman, M., M.; von Brömssen, M.; Hasan, M., A.; Ahmed, K., M. (2014). Sediment color tool for targeting arsenic-safe aquifers for the installation of shallow drinking water tubewells. *Science of the Total Environment* 493 (2014) 615–625.
- Hudson, N.; Baker, A. and Reynolds, D. (2007). Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—A review. *River Res. Applic.* 23: 631–649. doi:10.1002/rra.1005.
- Hughes, C. E. and Crawford, J. (2012). A new precipitation weighted method for determining the meteoric water line for hydrological applications demonstrated using Australian and global GNIP data: *Journal of Hydrology*, 464–465, 344-351.
- Hurley, M. A. and Roscoe, M. E. (2008). Automated statistical analysis of microbial enumeration by dilution series. *Journal of Applied Bacteriology*, 55(1), 159–164.
- Huntsman-Mapila, P.; Nsengimana, H.; Torto, N.; Diskin, S. (2011). Arsenic distribution and geochemistry in groundwater of a recharge wetland in NW Botswana. In: IYPE (Eds.), *Groundwater*. Springer.
- Islam, M. S.; Brooks, A.; Kabir, M. S.; Jahid, I. K.; Islam, M. S.; Goswami, D.; Nair, G. B.; Larson, C.; Yukiko, W.; Luby, S. (2007). Faecal contamination of drinking water sources of Dhaka city during the 2004 flood in Bangladesh and use of disinfectants for water treatment. *Appl. Environ. Microbiol.*, 103 (1), 80–87.
- Islam, F. S.; Gault, A. G.; Boothman, C.; Polya, D. A.; Charnock, J. M.; Chatterjee, D.; Lloyd, J. R. (2004). Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature*, 430, 68–71.
- Islam, M. S.; Siddika, A.; Khan, M. N.; Goldar, M.; Sadique, M., Kabir, A.; Huq, A. and Colwell, R. (2001). Microbiological analysis of tube-well water in a rural area of Bangladesh. *Appl Environ Microbiol*, 67, 3328–3330.

- Johnson, M. S.; Couto, E. G.; Abdo, M.; Lehmann, J. (2011). Fluorescence index as an indicator of dissolved organic carbon quality in hydrologic flowpaths of forested tropical watersheds. *Biogeochemistry*, Springer. 105:149–157.
- JRCB. (2011). About Joint Rivers Commission Bangladesh.
- Katayama, H. (2008). Detection of microbial contamination in groundwater, in *cSUR-UT Series: Library for Sustainable Urban Regeneration*, vol. 2, edited by Satoshi Takizawa, pp. 151–169, Springer, Japan.
- Khan, M.; Mosley, W.H.; Chakraborty, J.; Sardar, A. M. and Khan, M. R. (1978). *Water Sources and the Incidence of Cholera in Rural Bangladesh*. Bangladesh: Dhaka, International Centre for Diarrhoeal Disease Research, Bangladesh.
- Khan, F. H. (1991). *Geology of Bangladesh*. University Press, Dhaka.
- Kinniburgh, D. G.; Smedley, P. L.; Davies, J.; Milne C. J.; Gaus, I.; Trafford, J. M.; Burden, S.; Ihtishamul, Huq, S. M.; Ahmad, N.; Ahmed, K. M. (2003). The scale and causes of the groundwater arsenic problem in Bangladesh. In Welch AH, Stollenwerk KG (Eds) *Arsenic in Ground Water: Geochemistry and Occurrence*. Kluwer Academic Publishers, Boston, p. 211-257.
- Kinniburgh, D. G. and Smedley, P. L. (2001). Arsenic contamination of groundwater in Bangladesh. Volume 1: Summary. BGS Technical Report WC/00/19, British Geological Survey & Department of Public Health Engineering, p. 15.
- Knappett, P., S., K.; Escamilla, V.; Layton, A.; McKey, L., D.; Emch, M.; Williams, D., E.; Huq, R.; Alam, J.; Farhana, L.; Mailloux, B.; Ferguson, A.; Sayler, G., S.; Ahmed, K., M.; van Geen, A. (2011). Impact of population and latrines on fecal contamination of ponds in rural Bangladesh, *Science of the total environment*, 409, 3174-3182.
- Knappett, P., S., K.; McKey, L., D.; Layton, A.; Williams, D., E.; Alam, Md., J.; Huq, Md., R.; Feighery, J., E.; Culligan, P., J.; Mailloux, B., J.; Zhuang, J.; Escamilla, V.; Emch, M.; Perfect, E.; Sayler, G., S.; Ahmed, K., M.; van Geen, A. (2012). Implications of Fecal Bacteria Input from Latrine-Ponds for Wells in Sandy Aquifers, *Environ. Sci. Techno.*, 46, 1361-1370.
- Knappett, S. K. P.; McKay, L. D.; Layton, A.; Williams, E.; Alam, Md. J.; Mailloux, B. J.; Ferguson, A. S.; Culligan, P. J.; Serre, M. L.; Emch, M.; Ahmed, K. M.; Sayler, G. S. and van Geen, A. (2012b). Unsealed tubewells lead to increased fecal contamination of drinking water. *Journal of Water and Health*, 10.4, 565-578.
- Korte, N. E. and Fernando, Q. (1991). A review of arsenic (III) in groundwater. *Crit. Rev. In Environm. Control*, 21, 1-39.
- Layton, A. L.; McKay, D.; Williams, V.; Garrett, R.; Gentry, and G. Sayler. (2006). Development of Bacteroides 16S rRNA gene TaqMan-based real-time PCR assays for

- estimation of total, human, and bovine fecal pollution in water. *Applied & Environmental Microbiology* 72, no. 6: 4214–4224.
- Lawson, M.; Polya, D., A.; Boyce, A., J.; Bryant, C.; Mondal, D.; Shantz, A.; Ballentine, C., J. (2013). Pond-Derived Organic Carbon Changes in Arsenic hazard Found in Asian Groundwaters, *Environ. Sci. Technol.*, 47, 7085-7094.
- Leng, M. J. (2006). *Isotopes in Palaeoenvironmental Research*, Springer, ISBN-13 978-1-4020-2504-4 (e-book).
- Levine, R. J.; Khan, M. R.; D'souza, S. and Nalin, D. R. (1976). Failure of sanitary wells to protect against cholera and other diarrhoeas in Bangladesh. *Lancet*, ii, 86–89.
- LeChevallier, M. W. (1990). Coliform regrowth in drinking water: a review. *J. Am. Water Works Assoc.* 82:74-86.
- LeChevallier, M. W.; Schulz, W. and Ramon, L. G. (1991). Bacterial nutrients in drinking water. *Appl. Environ. Microbiol.* 57:857-862.
- LeChevallier, M. W.; Shaw, N. J. and Smith, D. B. (1996a). *Factors Limiting Microbial Growth in Distribution Systems: Full-Scale Experiments*. Denver, Colo.: AwwaRF and AWWA.
- Leber, J.; Rahman, M., M.; Ahmed, K., M.; Mailloux, B.; van Geen, A. (2011). Contrasting influence of geology on *E. coli* and arsenic in aquifers of Bangladesh. *Ground Water*, 49 (1), 111-124.
- Lowther, E. D. and Moser, R. H. (1984). Detecting and eliminating coliform regrowth. In *Proceedings of the Water Quality Technology Conference*. American Water Works Association, Denver, Colo.
- Luby, S. P.; Gupta, S. K.; Sheikh, M. A.; Johnston, R. B.; Ram, P. K. and Islam, M. S. (2008). Tubewell water quality and predictors of contamination in three flood-prone areas in Bangladesh. *Journal of Applied Microbiology*, 105 (4), 1002–1008.
- Luby, S.; Islam, M. S. and Johnston, R. (2006). Chlorine spot treatment of flooded tube wells, an efficacy trial. *J Appl Microbiol*, 100, 1154–1158.
- Majumder, R. K.; Halim, M. A.; Shimada, J.; Saha, B. B.; Zahid, A.; Hasan, M. Q.; Islam, M. S. (2011). Hydrochemistry and isotopic studies to identify Ganges River and riverbank groundwater interaction, southern Bangladesh. *Arab J Geosci.*, 6:4585–4591, doi: 10.1007/s12517-012-0767-3.
- Mailloux, B. J.; Trembath-Reichert, E.; Cheung, J.; Watson, M.; Stute, M.; Freyer, G. A.; Ferguson, A. S.; Ahmed, K. M.; Alam, Md. J.; Buchholz, B. A.; Thomas, J.; Layton, A. C.; Zheng, Y.; Bostick, B. C. and van Geen, A. (2013). Advection of surface-derived organic carbon fuels microbial reduction in Bangladesh groundwater. *PNAS*, 110(14), 5331-5335, doi: 10.1073/pnas.1213141110.

- Mallick, S. and Rajagopal, N. R. (1996). Groundwater development in the arsenic-affected alluvial belt of West Bengal—Some questions, *Curr. Sci.*, 70, 956-958.
- Mandal, B. K.; Chowdhury, T. R.; Samanta, G.; Mukherjee, D.; Chanda, C. R.; Saha, K. C. and Chakraborti, D. (1998). Impact of safe water for drinking on five families for 2 years in West Bengal, India, *Sci. Total Environ.*, 218, 185-201.
- Mathieu, L.; Paquin, J. L.; Block, J. C.; Randon, G.; Maillard, J. and Reasoner, D. (1992). Paramètres gouvernant la prolifération bactérienne dans les réseaux de distribution. *Rev. Sci. Eau* 5:91-112.
- Matera, V.; Hecho, I.; Laboudigue, A.; Thomas, P.; Tellier, S.; Astrue, M. (2003). A methodological approach for the identification of arsenic bearing phases in polluted soils. *Environ Pollut*, 126:51-64.
- McArthur, J. M.; Ravenscroft, P.; Safiulla, S. and Thirlwall, M. F. (2001). Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resour. Res.*, 37 (1), 109-117.
- McArthur, J. M.; Banerjee, D. M.; Hudson-Edwards, K. A.; Mishra, R.; Purohit, R.; Ravenscroft, P.; Cronin, A.; Howarth, R. J.; Chatterjee, A.; Talukder, T.; Lowry, D.; Houghton, S.; Chadha, D. K. (2004). Natural organic matter in sedimentary basins and its relation to arsenic in anoxic groundwater: The example of West Bengal and its worldwide implications. *Appl. Geochem.*, 19, 1255–1293.
- McDowell, W. H.; Likens, G. E. (1988). Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. *Ecological Monographs* 58, 177e195.
- McKnight, D. M.; Boyer, E. W.; P. K. Westerhoff, P. T.; Kulbe, D. T. and Andersen, D. T. (2001). Spectrofluorometric characterization of DOM for indication of precursor material and aromaticity. *Limnol. Oceanogr.* 46: 38–48, doi:10.4319/lo.2001.46.1.0038
- Md. Golam Kibria. (2014). Hydrogeochemistry and Microbial Geochemistry of Different Depth Aquifer Sediments from Matlab Bangladesh: Relation to Arsenic Contamination in Groundwaters
- Michael, H. A; Voss, C. I. (2008). Evaluation of the sustainability of deep groundwater as an arsenic-safe resource in the Bengal Basin. *Proc. Natl. Acad. Sci., U. S. A.*, 105 (25), 8531–8536.
- Mladenov, N.; Zheng, Y.; Miller, M., P.; Nemergut, D., R.; Legg, T.; Simone, B.; Hageman, C.; Rahman, M., M.; Ahmed, K., M.; McKnight, D., M. (2010). Dissolved Organic Matter Sources and Consequences for Iron and Arsenic Mobilization in Bangladesh Aquifers, *Environ. Sci. Technol.*, 44, 123-128.

- Mook, W., G. and Tan, T., C. (1991). Scope 42 – Biogeochemistry of Major World Rivers. (11) Stable Carbon Isotopes in Rivers and Estuaries., Wiley Chichester, <http://www.scopenvironment.org/downloadpubs/scope42/chapter11.html>.
- Morgan, J. & McIntire, W. (1959). Quaternary geology of the Bengal Basin, East Pakistan and India. *Geol. Soc. America Bull.* 70: 319-342.
- Mozumder, M.R.H. (2011). Aqueous phase geochemical characterization and delineation of low-arsenic aquifers in Matlab Upazila, SE Bangladesh. TRITALWR Degree project 11:08, 38p.
- Murphy, K. R.; Stedmon, C. A.; Waite, T. D. and Ruiz, G. M. (2008). Distinguishing between terrestrial and autochthonous organic matter sources in marine environments using fluorescence spectroscopy. *Mar. Chem.* 108: 40–58, doi:10.1016/j.marchem.2007.10.003.
- Nealson, K. H. (1997). Sediment bacteria: Who's there, what are they doing, and what's new? *Annu. Rev. Earth Planet. Sci.*, 25, 403-434.
- Neumann, R. B.; Ashfaq, K. N.; Badruzzaman, A. B. M.; Ali, M. A.; Shoemaker, J. K.; Harvey, C. F. (2010). Anthropogenic influences on groundwater arsenic concentrations in Bangladesh. *Nat. Geosci.*, 3(1), 46–52.
- Nickson, R. T.; McArthur, J. M.; Burgess, W. G.; Ravenscroft, P.; Ahmed, K. M. and Rahman, M. (1998). Arsenic poisoning of Bangladesh groundwater, *Nature*, 395, 338.
- Nickson, R. T.; McArthur, J. M.; Ravenscroft, P.; Burgess, W. G.; Ahmed, K. M. (2000). Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *J Applied Geochemistry* 15 (4): 403-413.
- Nickson, R. T.; McArthur, J. M.; Ravenscroft, P.; Burgess, W. G. and Ahmed, K. M. (2000). Mechanism of arsenic poisoning of groundwater in Bangladesh and West Bengal, *A ppl. Geochem.* 1, 5, 403-413.
- Ohno, T. (2002). Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. *Environ. Sci. Technol.* 36: 742–746, doi:10.1021/es0155276.
- Oremland, R. S.; Stolz, J. F. (2005). Arsenic, microbes and contaminated aquifers. *Trends Microbial*, 13:45-49.
- Pasupuleti, P. K. (2005). Mobilization of Arsenic in Aquifer Sediments of Matlab Upazila, Southeastern Bangladesh. TRITA-LWR Master Thesis. KTH.
- Parlanti, E.; Worz, K.; Geoffroy, L. and Lamotte, M. (2000). Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. *Org. Geochem.* 31: 1765–1781, doi:10.1016/S0146-6380(00)00124-8

- Palmer S. M., Hope D., Billett M. F., Dawson J. J. C., and Bryant C. L. (2001). Sources of organic and inorganic carbon in a headwater stream: evidence from carbon isotope studies. *Biogeochemistry* 52, 321–338.
- Polizzotto, M. L.; Harvey, C. F.; Sutton, S. R.; Fendorf, S. (2005). Processes conducive to the release and transport of arsenic into aquifers of Bangladesh. *Proc. Natl. Acad. Sci. U.S.A.*, 102, 18819–18823.
- Rahman, M. M.; Mukherjee, D.; Sengupta, M. K.; Chowdhury, U. K.; Lodh, D.; Chanda, C. R.; Roy, S.; Selim, M.; Quamruzzaman, Q.; Milton, A. H.; Shahidullah, S. M.; Rahman, M. T.; Chakraborti, D. (2002). Effectiveness and reliability of arsenic field testing kits: Are the million dollar screening projects effective or not? *J Environmental Science & Technology* 36 (24): 5385-5394.
- Rahman, M. M.; Vahter, M. A.; Wahed, N.; Sohel, M.; Yunus, P. K.; Streatfield, et al. (2006). Prevalence of arsenic exposure and skin lesions. A 44 population based survey in Matlab, Bangladesh. *J Epidemiol Community Health*, 60(3): p. 242-8.
- Rahman, M. M.; Woobaidullah, A. S. M.; Ahmed, K. M.; Hasan, M. A.; Hossain, M.; Bhattacharya, P.; Bromssen, M. V.; Jacks, G. (2013). Assessment of Hydrogeological Conditions for Safe Drinking Water to Unprivileged Community in Regions with High Arsenic Groundwater at Matlab, Bangladesh. *The International Journal Social Sciences*, 14(1), 67-75.
- Ravenscroft, P.; Burgess, W. G.; Ahmed, K. M.; Burren, M.; Perrin, J. (2004). Arsenic in groundwater of the Bengal Basin, Bangladesh: Distribution, field relations, and hydrogeological setting. *Hydrogeology Journal*, Springer, 13:727–751.
- Ravenscroft, P.; McArthur, J. M.; Hoque, B. A. (2001). Geochemical and palaeohydrological controls on pollution of groundwater by arsenic. In Chapell WR, Abernathy CO, Calderon R (Eds) *Arsenic Exposure and Health Effects VI*. Elsevier Science Ltd, Oxford, p. 53-78.
- Sankar Manalilkada Sasidharan. (2013). Geochemical Significance of Arsenic and Manganese Toxicity in Groundwaters from Murshidabad District, West Bengal, India. Master of Science Published Thesis.
- Schiff, S. L.; Aravena, R.; Trumbore, S. E. and Dillon, P. J. (1990). Dissolved organic carbon cycling in forested watersheds: a carbon isotope approach. *Water Resour. Res.* 26, 2949–2957.
- Schiff, S. L.; Aravena R.; Trumbore, S. E.; Hinton, M. J.; Elgood, R. and Dillon, P. J. (1997). Export of DOC from forested catchments on the Precambrian shield of central Ontario: clues from ^{13}C and ^{14}C . *Biogeochemistry* 36, 43–65.
- Servais, P.; Billen, G. and Hascoet, M. C. (1987). Determination of the biodegradable fraction of dissolved organic matter in waters. *Water Res.* 21:445-450.

- Servais, P.; Billen, G.; Bouillot, P. and Benezet, M. (1992). A pilot study of biological GAC filtration in drinking water. *Aqua* 41:163-168.
- Smedley, P. L. and Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* 17(5): 517-568.
- Smith, A. H.; Lingas, E. O. and Rahman, M. (2000). Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. *Bulletin of the World Health Organization* 78(9):1093-1103.
- Sommer, A. and Woodward, W.E. (1972). The influence of protected water supplies on the spread of classical-Inaba and El Tor-Ogawa cholera in rural East Bengal. *Lancet*, ii, 985–987.
- Söderberg, L. (2013). Importance of dissolved organic carbon for transport of organic contaminants in groundwater. Published digitally at the Department of Earth Sciences, Uppsala University, Uppsala, ISSN 1401-5765.
- Stedmon, C. A. and Markager, S. (2005a). Resolving the variability in DOM fluorescence in a temperate estuary and its catchment using PARAFAC. *Limnol. Oceanogr.* 50: 686–697, doi:10.4319/lo.2005.50.2.0686.
- Streatfield, K.; Persson, L. A.; Chowdhury, H. R. & Saha, K. K. (2001). Disease Patterns in Bangladesh: Present and Future Needs. International Centre for Diarrhoeal Disease Research, Bangladesh, Dhaka, Bangladesh.
- Stumm, W. and Morgan, J. J. (1996). *Aquatic Chemistry, Chemical Equilibria and rates in Natural Waters* (3rd Edition), Environmental Science and Technology, A Wiley-Interscience of Texts and Monographs.
- Stute, M.; Zheng, Y.; Schlosser, P.; Horneman, A.; Dhar, R. K.; Datta, S.; Hoque, M. A.; Seddique, A. A.; Shamsudduha, M.; Ahmed, K. M.; van Geen, A. (2007). Hydrological Control of As Concentrations in Bangladesh Groundwater. *Water Resour. Res.*, 43 (9), doi: 10.1029/2005WR004499.
- Stolz, J. F.; Basu, P.; Santini, J. M.; Oremland, R. S. (2006). Arsenic and selenium in microbial metabolism. *Annu Rev* 12:349-365.
- Traina, S. J.; Novak, J.; Smeck, N. E. J. (1990). *Environ. Qual.*, 19, 151-153.
- Tufano, K. J.; Fendorf, S. 2008. Confounding impacts of iron reduction on arsenic retention. *Environ. Sci. Technol.*, 42, 4777–4783.
- Tyler McEwen. 21 February 2008. Ganges-Brahmaputra-Meghna/Barak Basin, CE 397 – Transboundary Water Resources

- Umitsu, M. (1987). Late Quaternary sedimentary environment and landform evolution in the Bengal Lowland. *Geographical Review of Japan, Series B.*, 60, 164-178.
- van Geen, A.; Ahmed, K., M.; Akita, Y.; Alam, Md., J.; Culligan, P., J.; Emch, M.; Escamilla, V.; Feighery, J.; Ferguson, A., S.; Knappett, P.; Layton, A., C.; Mailloux, B., J.; McKay, L., D.; Mey, J., L.; Serre, M., L.; Streatfield, P., K.; Wu, J.; Yunus, M. (2011). Fecal Contamination of Shallow Tubewells in Bangladesh Inversely Related to Arsenic, *Environ. Sci. Technol.*, 45, 1199–1205.
- van Geen, A.; Zheng, Y.; Stute, M.; Ahmed, K. M. (2003). Arsenic mobility and groundwater extraction in Bangladesh: Comment. *Science*, 300, 584.
- van Geen, A.; Zheng, Y.; Versteeg, R.; Stute, M.; Horneman, A.; Dhar, R.; Steckler, M.; Gelman, A.; Small, C.; Ahsan, H.; Graziano, J. H.; Hussain, I. and Ahmed, K. M. (2003b). Spatial variability of arsenic in 6000 tube wells in a 25 km² area of Bangladesh, *Water Resour. Res.*, 39(5), 1140, doi: 10.1029/2002WR001617.
- Volk, C. and Joret, J. C. (1994). Paramètres prédictifs de l'apparition des coliformes dans les réseaux de distribution d'eau d'alimentation. *Sci. Eau* 7:131-152.
- von Brömssen, M. (2012). Hydrogeological and geochemical assessment of aquifer systems with geogenic arsenic in southeastern Bangladesh – Targeting low arsenic aquifers for safe drinking water supplies in Matlab. PhD thesis, TRITA LWR PhD 1063, 46 p.
- von Brömssen, M.; Markussen, L.; Bhattacharya, P.; Ahmed, K. M.; Hossain, M.; Jacks, G.; Sracek, O.; Thunvik, R.; Hasan, M. A.; Islam, M.; Rahman, M. M. (2011). Hydrogeological investigations for assessment of the sustainability of low-As aquifers as a safe drinking water source in regions with high As groundwater in Matlab, Southeastern Bangladesh, *Manuscript*.
- Wang, Y.; Morin, G.; Ona-Nguema, G.; Brown, G. E. Jr. (2014). Arsenic(III) and arsenic(V) speciation during transformation of lepidocrocite to magnetite. *Environ Sci Technol.* 2014 Dec 16;48(24):14282-90.
- Wassenaar, L. I.; Aravena, R.; Fritz, P. and Barker, J. F. (1991). Controls on the transport and carbon isotopic composition of dissolved organic carbon in a shallow groundwater system, Central Ontario, Canada. *Chem. Geol.* 87, 39–57.
- Water Research Centre. (1977). “Deterioration of Bacteriological Quality of Water During Distribution.” In Notes on Water Research No. 6. Medmenham, England.
- Weishaar, J. L.; Aiken, G. R.; Bergamaschi, B. A.; Fram, M. S.; Fujii, R. and Moppe, R. (2003). Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon. *Environ. Sci. Technol.*, 37, 4702-4708.

- Westerhoff, P.; Chen, W. and Esparza, M. (2001). Fluorescence analysis of a standard fulvic acid and tertiary treated wastewater. *J. Environ. Qual.* 30: 2037–2046, doi:10.2134/jeq2001.2037.
- Whitehead, P. G.; Barbour, E.; Futter, M. N.; Sarkar, S.; Rodda, H.; Caesar, J.; Butterfield, D.; Jin, L.; Sinha, R.; Nicholls, R. and Salehin, M. (2015). Impacts of climate change and socio-economic scenarios on flow and water quality of the Ganges, Brahmaputra and Meghna (GBM) river systems: low flow and flood statistics. *Environ. Sci.: Processes Impacts*, 17, 1057-1069, doi: 10.1039/C4EM00619D.
- Wilson, H. F. and Xenopoulos, M. A. (2009). Effects of agricultural land use on the composition of fluvial dissolved organic matter. *Nature Geosci.* 2: 37–41, doi:10.1038/ngeo391.
- WHO (World Health Organization). (2008). Guidelines for Drinking Water Quality. WHO, Geneva, Switzerland.
- Wu, J.; van Geen, A.; Ahmed, K. M.; Akita, Y.; Alam, Md. J.; Culligan, P. J.; Escamilla, V.; Feighery, J.; Ferguson, A. S.; Knappett, P.; Mailloux, B. J.; McKay, L. D.; Serre, M. L.; Streatfield, P. K.; Yunus, M. & Emch, M. (2011). Increase in diarrheal disease associated with arsenic mitigation in Bangladesh. *PLoS One* 6, e29593.
- Yu, W. H.; Harvey, C. M.; Harvey, C., F. (2003). Arsenic in the groundwater in Bangladesh: a geostatistical and epidemiological framework for evaluating health effects and potential remedies. *Water Resour. Res.*, 39 (6) (Art. No. 1146).
- Zahid, A. and Ahmed, S. R. U. (2006). Groundwater Resources Development in Bangladesh: Contribution to Irrigation for Food Security and Constraints to Sustainability. No H039306, IWMI Books, Reports from International Water Management Institute <http://publications.iwmi.org/pdf/h039306.pdf>.
- Zsolnay, A.; Baigar, E.; Jimenez, M.; Steinweg, B. and Saccomandi, F. (1999). Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying. *Chemosphere* 38: 45–50, doi:10.1016/S0045-6535(98)00166-0.

Website

1. <http://en.climate-data.org/location/969823/>
2. www.banglapedia.org
3. www.idexx.com

Appendix A - On Site Parameters

Appendix A1 – GPS Location of Samples

Sample ID	Longitude (D)	Latitude (D)	Easting	Northing	Elevation (m)
N3P1	90.70171	23.32567	482073.8	4399822.3	3.4
N3P2	90.70171	23.32567	482073.8	4399822.3	3.4
N3P3	90.70171	23.32567	482073.8	4399822.3	3.4
N3P4	90.70171	23.32567	482073.8	4399822.3	3.4
N3P5	90.70171	23.32567	482073.8	4399822.3	3.4
N3P6	90.70171	23.32567	482073.8	4399822.3	3.4
N4P1	90.77570	23.42652	482080.3	4399947.0	4.3
N4P2	90.77570	23.42652	482080.3	4399947.0	4.3
N4P3	90.77570	23.42652	482080.3	4399947.0	4.3
N4P4	90.77570	23.42652	482080.3	4399947.0	4.3
N7P2	90.66227	23.48756	482028.1	4399824.8	3.1
N7P4	90.66227	23.48756	482028.1	4399824.8	3.1
N7P5	90.66227	23.48756	482028.1	4399824.8	3.1
N13P1	90.60495	23.47562	482078.9	4399879.0	3.4
N13P2	90.60495	23.47562	482078.9	4399879.0	3.4
N13P3	90.60495	23.47562	482078.9	4399879.0	3.4
N13P5	90.60495	23.47562	482078.9	4399879.0	3.4
N13P6	90.60495	23.47562	482078.9	4399879.0	3.4
N3Pond1	90.70171	23.32567	482073.8	4399822.3	3.4
N3Pond2	90.70171	23.32567	482073.8	4399822.3	3.4
N4Pond1	90.77570	23.42652	482080.3	4399947.0	3.1
N4Pond2	90.77570	23.42652	482080.3	4399947.0	3.1
N7Pond1	90.66227	23.48756	482028.1	4399824.8	3.1
N7Pond2	90.66227	23.48756	482028.1	4399824.8	3.1
N7Canal	90.66227	23.48756	482028.1	4399824.8	3.1
N13Pond1	90.60495	23.47562	482078.9	4399879.0	3.4
N13Pond2	90.60495	23.47562	482078.9	4399879.0	3.4

Appendix A2 – Measured Field Parameters

	Nest	Piezometer	Depth (m)	Water Level (m)	Time of WL Measurement	Well Diameter (inch)	Flow Rate (15 L)	Flow Rate (L)	Volume (L)
South Mallab	3	1	17	2.575	10.05 am	1.5	1 min 20 sec	1 min 28 sec	16.4
				2.446	9.59 am				
		2	29	2.571	10.05 am	1.5	44 sec	1 min 29 sec	30.1
				2.584	9.58 am				
		3	52	2.72	10.06 am	1.5	40 sec	2 min 30 sec	56.2
				2.601	9.56 am				
		4	87	3.962	10.06 am	1.5	40 sec	4 min 21 sec	94.7
				3.482/3.514	9.55 am				
		5 (Private Well)	240	L-shaped		1.5	41 sec		
		6	95	3.565	10.06 am	1.5	38 sec	4 min 40 sec	104.1
				3.455	9.57 am				
	4	1	17	2.885	12.11 pm	1.5	1 min 11 sec	1 min 28 sec	16.1
		2	30	2.999	12.12 pm	1.5	33 sec	1 min 13 sec	30.8
		3	56	5.075	12.13 pm	1.5	53 sec	3 min 43 sec	58.1
		4	75	5.025	12.14 pm	1.5	48 sec	4 min 26 sec	79.8
North Mallab	7	2	26	1.528	10.15 am	1.5	55 sec	1 min 43 sec	27.9
				1.41	12.05 pm				
				1.333	12.46 pm				
				1.655	1.10 pm				
				1.43	6.25 pm				
		4	75	4.42	1.10 pm	1.5	1 min	5 min 37 sec	80.5
				4.47	3.05 pm				
				4.34	8.00 pm				
		5	232	4.36	9.43 am	1.5	48 sec	13 min 84 sec	259.5
				4.4	1.16 pm				
				4.19	4.05 pm				
	13	1	14	1.442	10.23 am	1.5	40 sec	39 sec	14.3
				1.434	12.15 pm				
		2	33	1.528	10.16 am	1.5	44 sec	1 min 46 sec	35.9
				1.554	10.23 am				
				1.53	6.26 pm				
		3	85	4.376	10.16 am	1.5	1 min 4 sec	6 min 54 sec	91.9
				4.349	10.24 am				
				4.35	6.25 pm				
		5 (Private Well)	237	4.36	1.15 pm	2	51 sec	27 min 15 sec	472.3
		6	124	4.49	10.17 am	1.5	53 sec	8 min 2 sec	136.2
				4.46	10.24 am				
				4.456	12.16 pm				
		Private Well	21	1.185	12.30 pm	1.5	24 sec	37 sec	22.6

Suction Pump: Inlet = 0.75" Outlet = 1" Check Valve = 1" Pipe = 26/8 m

Diameter = 1 inch = 2.54 cm, radius = 1.27 cm, Area = $3.14 (1.27)^2 = 5.1 \text{ cm}^2$

Diameter = 1.5 inch = 3.81 cm, radius = 1.91 cm, Area = $3.14 (1.91)^2 = 11.4 \text{ cm}^2$

Diameter = 2 inch = 5.08 cm, radius = 2.54 cm, Area = $3.14 (2.54)^2 = 20.3 \text{ cm}^2$

Volume = ((Well Depth – Water Level)*A/1000) L

Flow Rate/L = (Flow Rate (15L)*V/15) sec/L

Appendix A3 – Physical and Chemical Parameters

Sample ID	Depth (m)	TDS (mg/L)	Salinity (ppt)	Resistivity (Ωcm)	EC (mS/cm)	ORP (mV)	pH	Temp (°C)
N3P1	17	472	0.47	1.05E+03	0.94	67.5	7.1	25.9
N3P2	29	643	0.64	7.77E+02	1.29	-147.2	6.9	26.2
N3P3	52	18250	23	2.74E+01	36.33	37.2	6.5	26.6
N3P4	87	8930	10.59	5.60E+01	19.39	77.4	6.6	26.7
N3P5	240	14250	17.57	3.51E+01	28.47	86	6.4	26.7
N3P6	95	8970	10.57	5.58E+01	24.74	87.5	6.4	25.3
N4P1	17	7420	8.63	6.74E+01	14.8	77.6	6.6	26.3
N4P2	30	31000	46.6	1.57E+01	64.77	61	6.6	22.1
N4P3	56	45.8	0.05	1.09E+04	65.37	89.8	6.5	27.5
N4P4	75	34600	46.4	1.47E+01	67.73	116.5	6.1	24.4
N7P2	26	419	0.41	1.19E+03	0.86	-118.4	6.9	26.3
N7P4	75	502	0.49	9.37	0.98	-46.4	6.7	26.8
N7P5	232	635	0.63	7.87E+02	1	2.1	6.6	25.8
N13P1	14	128	0.12	3.91E+03	0.26	-169.8	7.0	26.0
N13P2	33	1291	1.33	3.87E+02	1.15	-170.1	7.0	25.9
N13P3	85	985	1	5.08E+02	1.98	-113.9	6.9	27.6
N13P5	237	391	0.38	1.28E+03	0.78	-148	7.5	27.5
N13P6	124	320	0.31	1.56E+03	0.64	124.8	6.9	26.4
N13PW	21	160	0.15	3.12E+03	0.32	-102.1	6.9	26.7
N3Pond1	2	29	0.03	1.90E+04	60.5	-123.1	6.8	28.3
N3Pond2	1.2	499	0.5	9.63E+02	101	-90.8	6.6	28.4
N4Pond1	2	3300	3.6	1.49E+02	6.7	84.4	6.8	32.5
N4Pond2	1.5	2300	2.46	2.17E+02	4.63	95.6	7.1	32.4
N7Pond1	2	486	0.55	1.03E+02	0.5	9.4	7.3	26.3
N7Pond2	2	198	0.019	2.55E+03	0.4	-36.2	7.0	24.8
N7Canal	1.5	399	0.402	1.26E+02	0.25	275.5	6.8	23.5
N13Pond1	2	46	0.05	1.09E+04	0.10	-171	7.8	26.9
N13Pond2	4	131	0.13	3.83E+03	0.3	32.3	7.3	26.7

Sample ID	Depth (m)	DO (mg/l)	As (ppb)	Mn ²⁺ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)
N3P1	17	2	500	0.3		0
N3P2	29	2	250	0.2		0
N3P3	52	1	50-100	0.3		0
N3P4	87	3	0	0.5		17
N3P5	240	2	0	0.6		1
N3P6	95	1	50	0.2		1
N4P1	2	4	0	0		6
N4P2	1.2	2	0	0		7
N4P3	17	4	50-100	0		0
N4P4	30	1	500	0		0
N7P2	56	2	0-10	1.6		31
N7P4	75	1	0-10	1.7		57
N7P5	2	15	0	0		13
N13P1	1.5	9	0	0		0
N13P2	26	2	500	0.2	260	<0
N13P3	75	2	50-100	0.1	840	0
N13P5	232	5	0-10	0.1	700	1
N13P6	2	4	0	0.1	380	13
N13PW	2	9	0	0		22
N3Pond1	1.5	3	0	0.1	120	0
N3Pond2	14	1	250	0	60	0
N4Pond1	33	1	350	0.3	1620	0
N4Pond2	85	1	100	0	1920	0
N7Pond1	237	2	0	0	500	3
N7Pond2	124	2	100	0	600	0
N7Canal	21	1	500	0.2		0
N13Pond1	2	3	0	0	100	
N13Pond2	4		0	0	80	

Appendix A4 – On Site Comments

Nest	Piezometer	Depth (m)	Weather	Comments
S o u t h M a t l a b	1	17	Heavy Rain	Well heads of P 1, 2, 3, 4, 6 are at same height but P 5 is 1ft below from all others well heads
				Pond 1 --- 2 ft --- N 3 --- 25 ft --- Pond 2
	2	29	Heavy Rain	
	3	52	Cloudy	
	4	87	Cloudy	
	5 (Private Well)	240	Cloudy	
	6	95	Cloudy	
	Pond 1	2	Heavy Rain	
	Pond 2	1.2	Heavy Rain	
	1	17	Sunny	The nest is close to Pond 1
4				Cloudy water comes when pump starts
	2	30	Sunny	Cloudy water comes when pump starts
	3	56	Sunny	
	4	75	Sunny	
	Pond 1	2	Sunny	Pond 1 --- 15 ft --- N 4 --- 50 ft --- Pond 2
	Pond 2	1.5	Sunny	
	2	26	Sunny	When well mouth was opened up some gases were blowing out due to overpressure
				Water Level was fluctuating
				Initially sands were coming out from well when pump starts but it stopped after 2 min pumping
			Heavy Rain	Silt doesn't allow to store water for a long time because it has low hydraulic conductivity
N o r t h M a t l a b				First Exp. 1 min 1.8 L
				Second Exp. 1 min 0.8 L
	4	75	Sunny	Third Exp. 1 min 0.4 L
				P 3 filter is clogged
				Used peristaltic, submersible and suction pumps; Tried half an hour; Water flow is very slow by first then it stopped to flow
			Heavy Rain	Pond 1 --- 5 ft --- N 7 --- 10 ft --- Canal --- 50 ft --- Pond 2
				P 1 is abandoned (building); P 2 is close to Pond 1 and P 5 is close to Canal
	5	232	Sunny	
			Heavy Rain	
	Pond 1	2	Heavy Rain	
13	Pond 2	2	Heavy Rain	
	Canal	1.5	Heavy Rain	
	1	14	Drizzle + Heavy Rain	P 2 and 3 = Initially sands were coming out from well when pump starts; P 3 = Water flow is very slow
				Pond 1 --- 50 ft --- N 13 --- 60 ft --- Pond 2
	2	33	Drizzle + Heavy Rain	
	3	85	Drizzle + Heavy Rain	
	5 (Private Well)	237	Drizzle + Heavy Rain	
	6	124	Drizzle + Heavy Rain	
	Private Well	21	Drizzle + Heavy Rain	Private Well --- 50 ft --- Pond 2
				Water flow is very high
	Pond 1	2	Drizzle + Heavy Rain	
	Pond 2	4	Drizzle + Heavy Rain	

Appendix B – Water DOC Concentration

Sample ID	Depth (m)	DOC (mg/l)	Duplicate	STDEV
N3P1	17	4.8	4.8	0.0
N3P2	29	2.8	2.7	0.1
N3P3	52	2.1	1.9	0.1
N3P4	87	0.8	0.6	0.1
N3P5	240	2.0	2.0	0.1
N3P6	95	2.7	2.2	0.4
N3Pond1		3.0	2.9	0.1
N3Pond2		5.0	4.9	0.1
N4P1	17	12.2	11.9	0.2
N4P2	30	6.7	6.6	0.1
N4P3	56	0.8	0.7	0.0
N4P4	75	0.7	0.6	0.1
N4Pond1		7.4	7.2	0.2
N4Pond2		8.7	8.7	0.0
N7P2	26	4.5	5.4	0.6
N7P4	75	2.8	2.8	0.0
N7P5	232	1.1	1.7	0.4
N7Pond1		7.4	8.1	0.5
N7Pond2		5.1	5.3	0.1
N7Canal		5.9	6.3	0.3
N13P1	14	1.5	1.5	0.1
N13P2	33	5.0	4.9	0.1
N13P3	85	4.2	4.1	0.0
N13P5	237	2.5	2.1	0.3
N13P6	123	3.3	3.2	0.1
N13PW	21	2.6	2.5	0.1
N13Pond1		4.3	4.8	0.4
N13Pond2		2.9	2.7	0.1

Appendix B1 – Fluorescence Properties of DOC in Water

Integration Time = 0.25 sec, 1 sec				Fluorescence Index (FI)			Freshness Index (Frl)			Humification Index (HIX)			abs254	DOC (mg/L)	abs/DOC	SUVA (L/mg/m)	
Sample ID	Depth (m)	0.25 sec	0.25 sec	1 sec	STDEV	0.25 sec	0.25 sec	0.25 sec	1 sec	STDEV	0.25 sec	0.25 sec	1 sec	STDEV			
N3/P1	17	1.7	1.6		0.0	0.7	0.7	0.7	0.7	0.0	17.0	13.7	7.4	2.3	0.144	4.8	0.030
N3/P2	29	1.7	1.6	1.7	0.0	0.6	0.7	0.7	0.7	0.0	8.1	9.4	7.4	1.0	0.090	2.8	0.032
N3/P3	52	1.7	1.7	1.7	0.0	0.7	0.7	0.7	0.7	0.0	10.9	8.6	5.9	2.5	0.051	2.1	0.024
N3/P4	87	2.3	14.1	2.0	6.9	0.5	0.7	0.7	0.7	0.1	4.3	1.6	0.4	2.0	0.003	0.8	0.004
N3/P5	240	1.0	3.8	1.6	1.5	0.5	0.8	1.0	0.2	0.0	1.0	0.6	0.5	0.3	0.005	2.0	0.003
N3/P6	95	1.7	1.7	1.6	0.1	0.7	0.7	0.7	0.7	0.0	8.7	8.2	9.4	0.6	0.047	2.7	0.017
N3/POND1	2	1.5	1.5	1.5	0.0	0.6	0.6	0.6	0.6	0.0	11.1	9.7	9.5	0.8	0.110	3.0	0.036
N3/POND2	1	1.5	1.5	1.5	0.0	0.7	0.7	0.7	0.7	0.0	7.4	8.6	7.4	0.7	0.127	5.0	0.025
N4/P1	17	1.7	1.7		0.0	0.6	0.6			0.0	17.1	15.7		1.0	0.450	12.2	0.037
N4/P2	30	1.7	1.7		0.0	0.7	0.7			0.0	10.2	10.1		0.1	0.226	6.7	0.033
N4/P3	56	2.2	1.6	1.6	0.3	0.7	0.7	0.7	0.7	0.0	7.0	6.3	1.7	2.8	0.003	0.8	0.004
N4/P4	75	1.6	1.7	1.6	0.1	0.4	0.7	0.7	0.7	0.2	1.9	2.1	3.4	0.8	0.005	0.7	0.008
N4/POND1	2	1.5	1.6	1.6	0.1	0.7	0.7	0.7	0.8	0.0	7.0	6.7	6.9	0.2	0.151	7.4	0.020
N4/POND2	2	1.5	1.5	1.5	0.0	0.7	0.7	0.7	0.7	0.0	7.2	6.9	5.9	0.7	0.239	8.7	0.028
N7/P2	26	1.7	1.7		0.0	0.7	0.7	0.7	0.7	0.0	14.5	12.8		1.2	0.140	4.5	0.031
N7/P4	75	1.7	1.7	1.7	0.0	0.7	0.7	0.7	0.7	0.0	5.3	3.8	2.6	1.4	0.048	2.8	0.017
N7/P5	232	1.6	1.6	1.6	0.0	0.8	0.8	0.8	0.8	0.0	3.4	1.8	0.7	1.4	0.007	1.1	0.007
N7/POND1	2	1.6	1.6	1.6	0.0	0.7	0.7	0.7	0.7	0.0	6.3	5.8	6.2	0.2	0.205	7.4	0.028
N7/POND2	2	1.6	1.7	1.6	0.0	0.7	0.7	0.7	0.7	0.0	4.4	3.8	5.0	0.6	0.131	5.1	0.025
N7/CANAL	2	1.5	1.6	1.6	0.0	0.7	0.7	0.7	0.7	0.0	6.2	5.1	5.6	0.6	0.134	5.9	0.023
N13/P1	14	1.5	1.5	1.5	0.0	0.5	0.5	0.5	0.5	0.0	21.8	14.4	9.4	6.3	0.052	1.5	0.033
N13/P2	33	1.7	1.7		0.0	0.7	0.7			0.0	9.0	8.6		0.3	0.138	5.0	0.028
N13/P3	85	1.8	1.7		0.0	0.8	0.8			0.0	7.4	7.4		0.0	0.111	4.2	0.027
N13/P5	237	1.7	1.8	1.8	0.1	1.0	0.9	0.9	0.9	0.0	5.4	4.2	3.1	1.2	0.014	2.5	0.006
N13/P6	123	1.6	1.6	1.6	0.0	0.7	0.7	0.7	0.7	0.0	12.7	9.9	11.1	1.4	0.099	3.3	0.030
N13/PW (Private Well)	21	1.5	1.5	1.5	0.0	0.6	0.6	0.6	0.6	0.0	24.0	19.3	19.7	2.6	0.084	2.6	0.032
N13/POND1	2	1.7	1.7	1.7	0.0	0.6	0.6	0.6	0.6	0.0	6.3	4.6	3.4	1.5	0.092	4.3	0.022
N13/POND2	4	1.5	1.7	1.6	0.1	0.8	0.7	0.8	0.8	0.0	6.3	4.6	2.4	2.0	0.052	2.9	0.018

Appendix C - Fluorescence Spectroscopy (EEMs and Peaks)

Protocol for fluorescence spectroscopy

The quinine sulfate was scanned and recorded the emission at 450 nm (observed) in the Aqualog logbook.xls.

- Cuvette check-

Integration time = 0.25 sec

Gain = High

Increment = 3.28 nm

Excitation = 240 nm

- Raman scan check and calculate the area under Raman Peak-

Integration time = 0.25 sec

Gain = High

Increment = 3.28 nm

Excitation = 350 nm

- Quinine sulfate scan and record the emission at 450 nm-

Integration time = 0.25 sec

Gain = High

Increment = 0.41 nm

Excitation = 347.5 nm

- Acquisition 3D EEM-

Integration time = 0.25 and 1 second

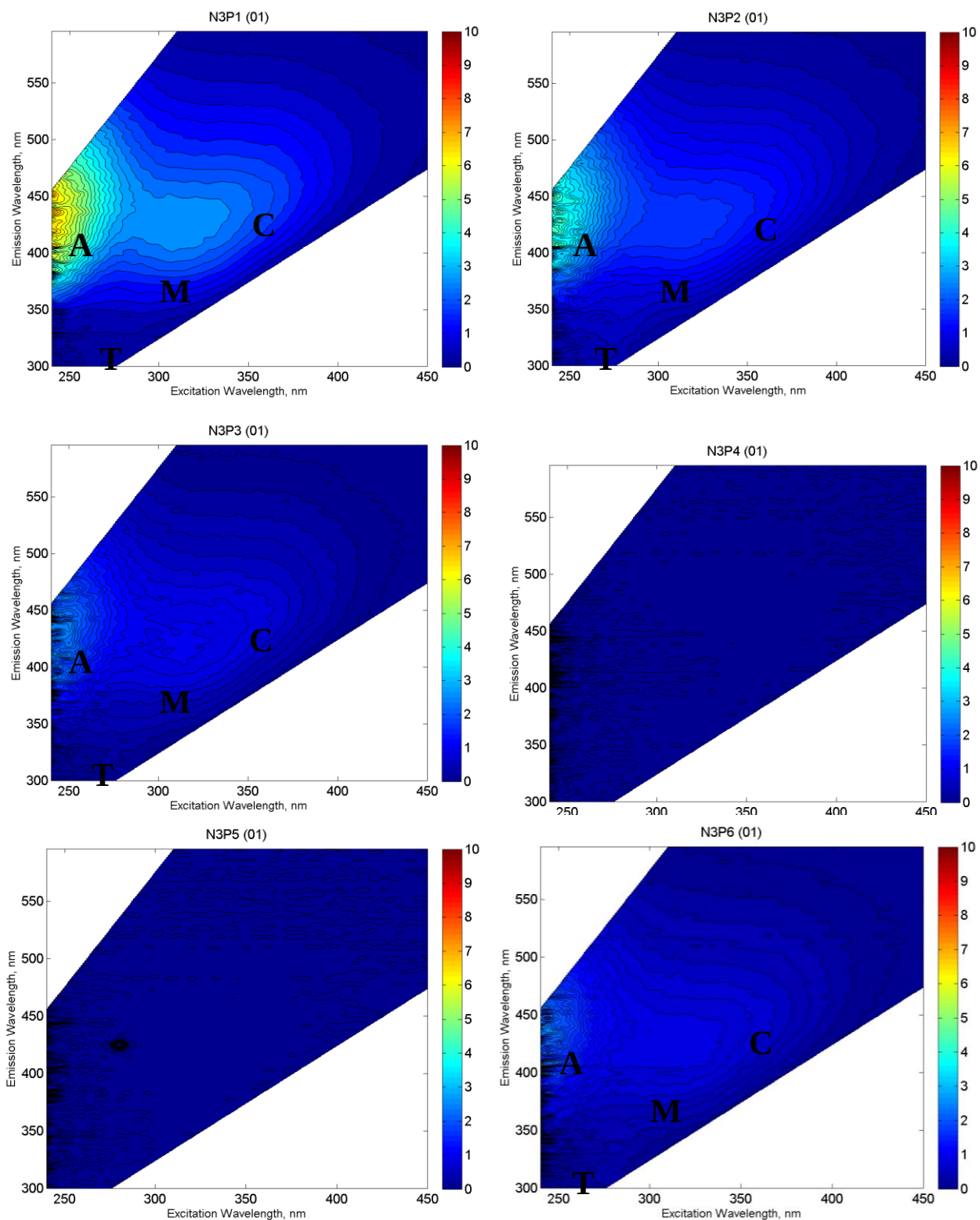
Increment = 3.28 nm

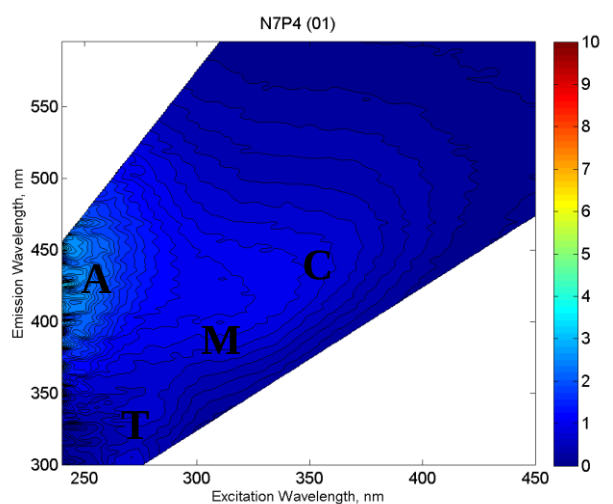
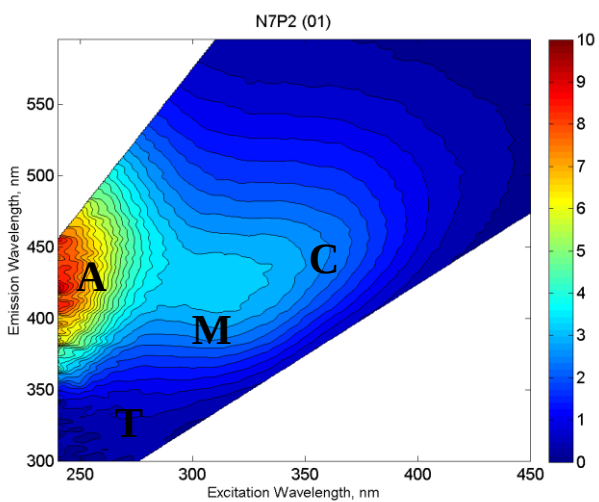
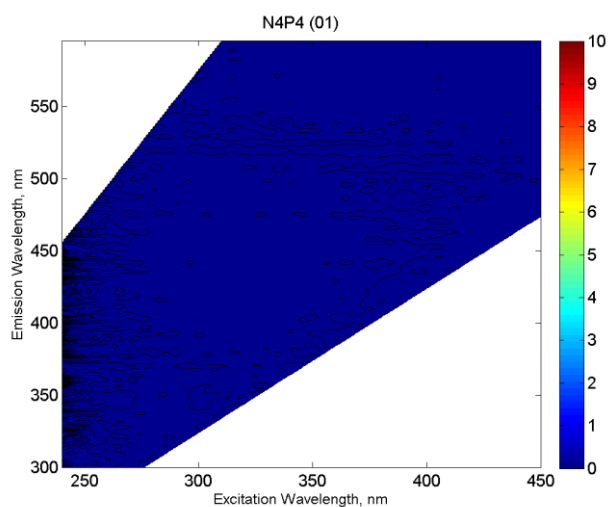
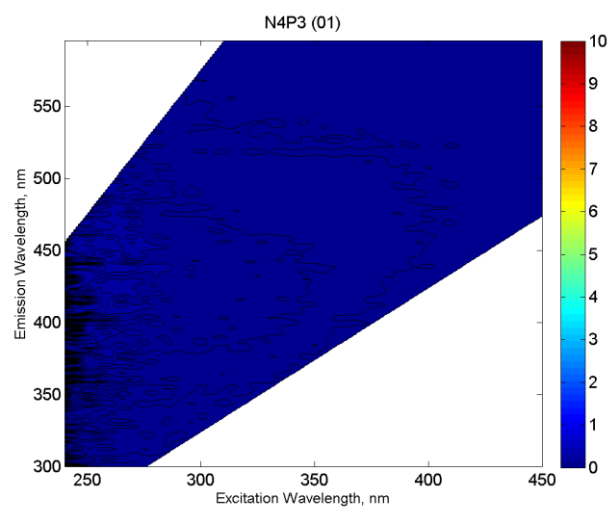
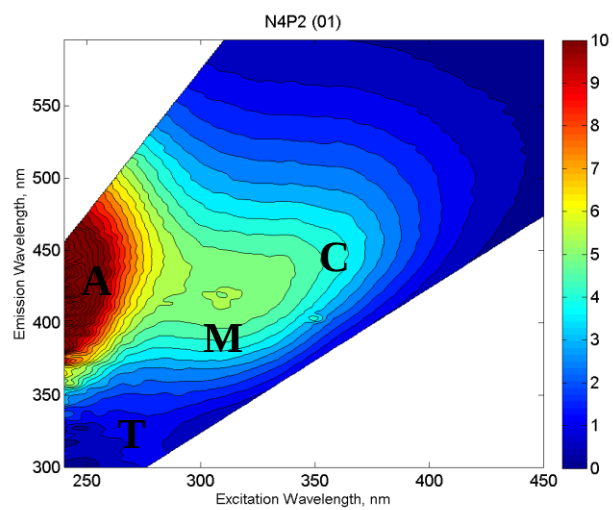
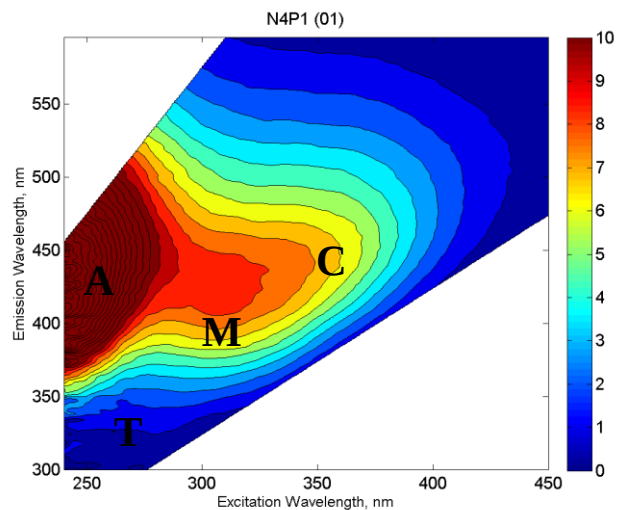
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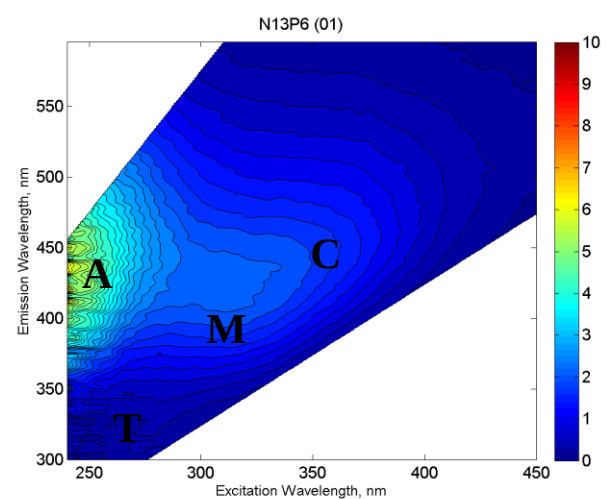
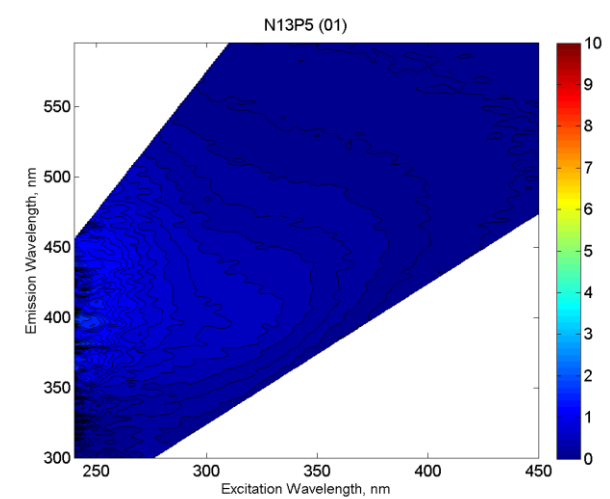
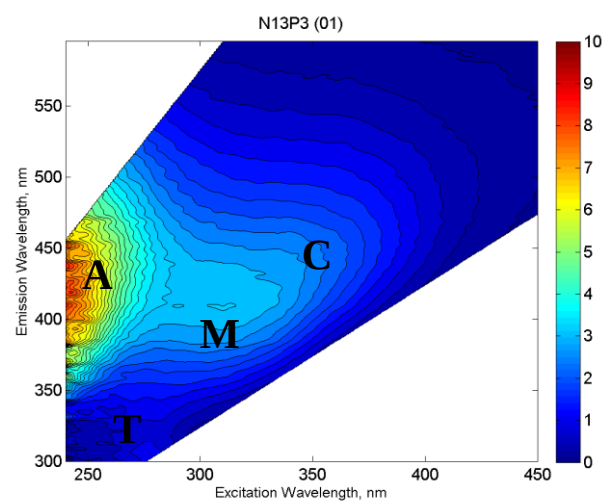
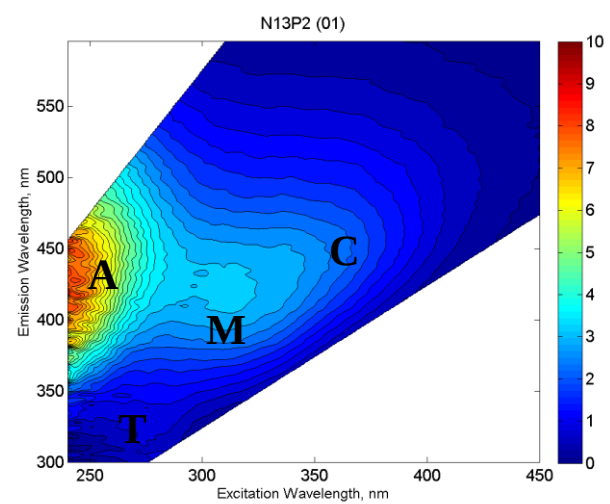
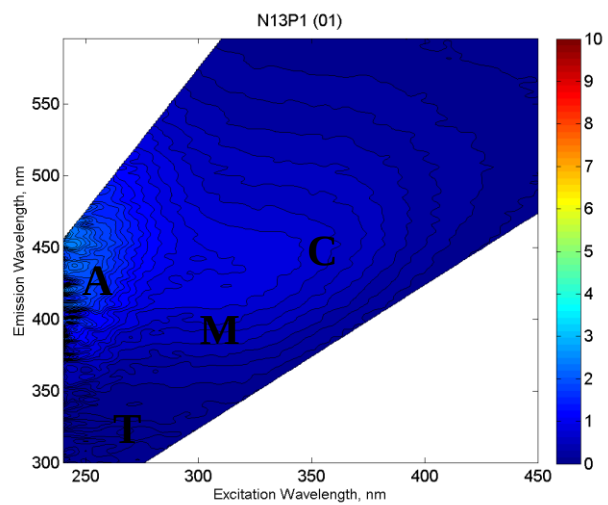
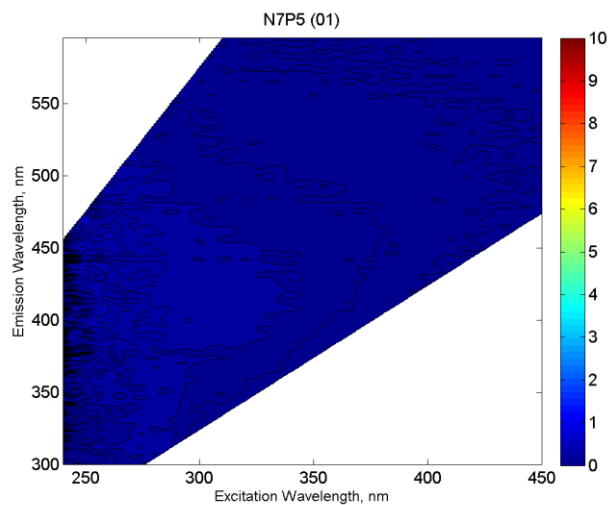
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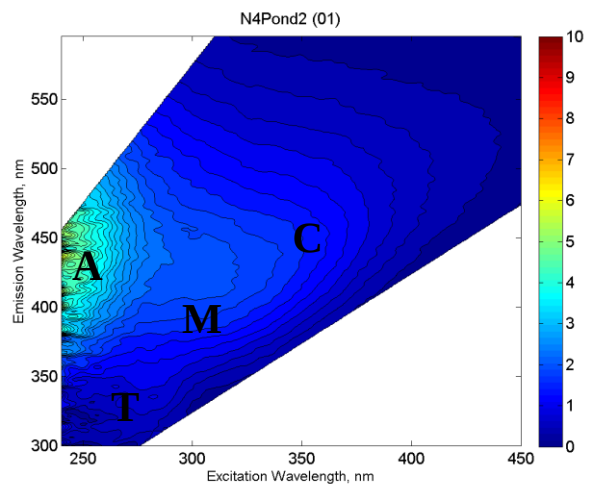
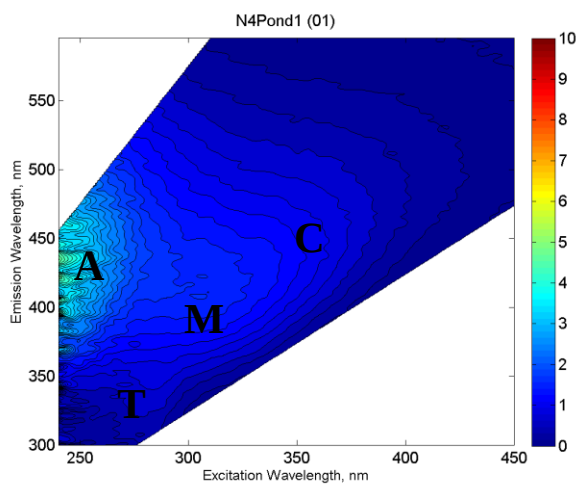
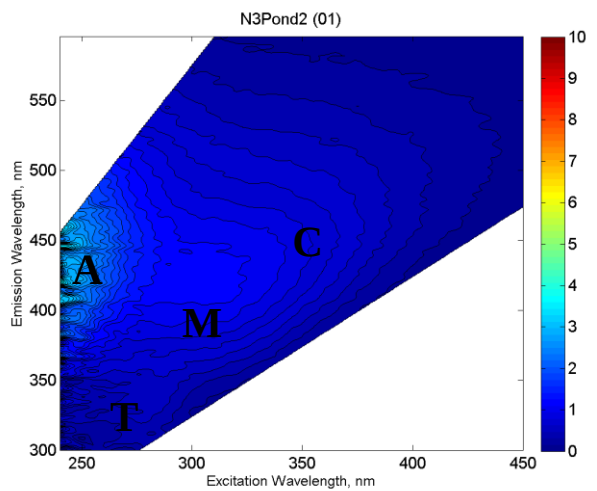
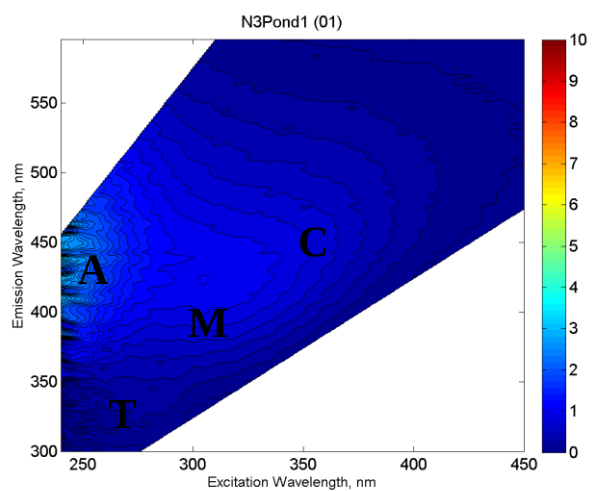
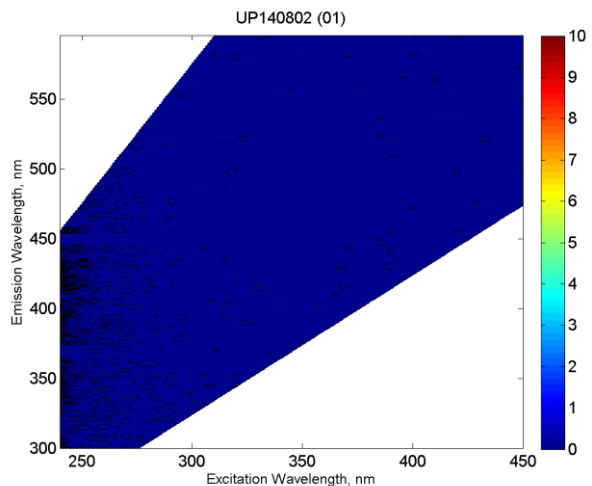
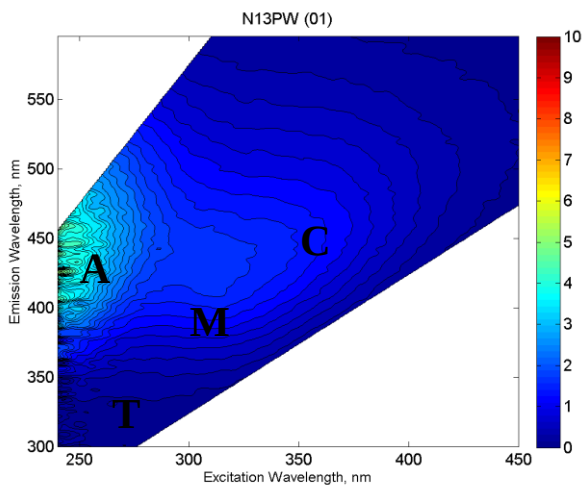
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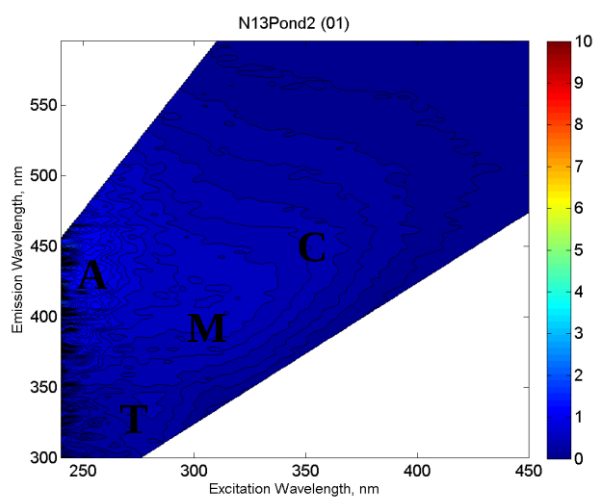
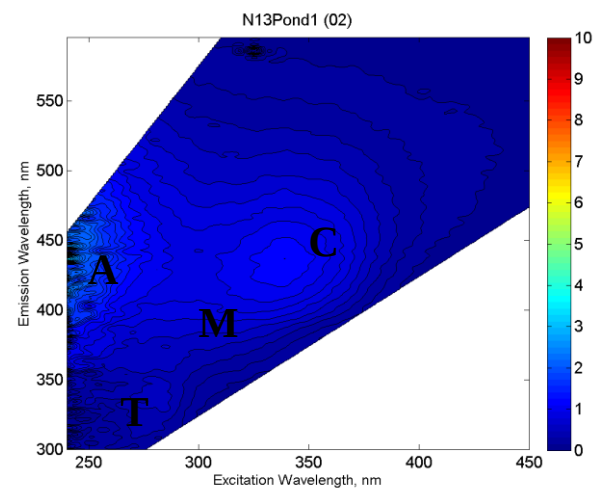
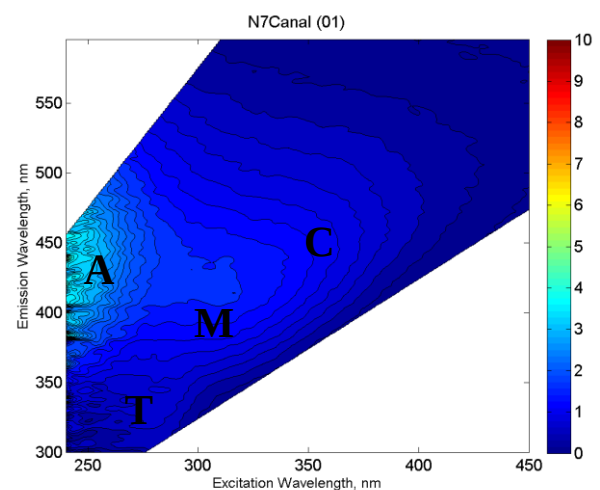
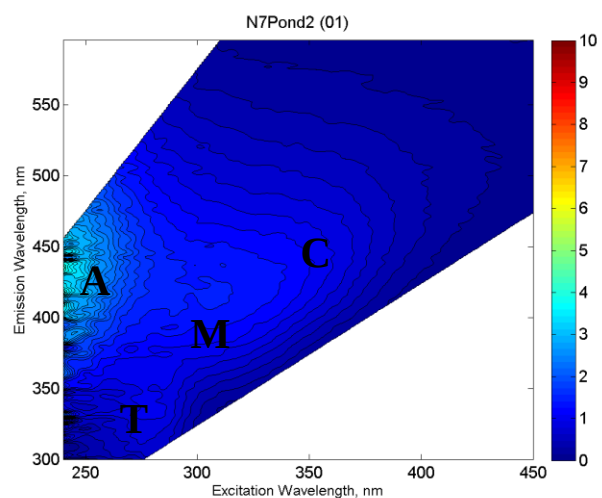
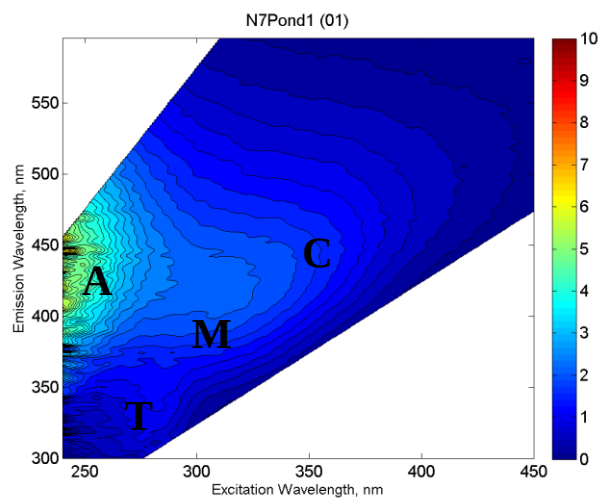
Appendix C1 – EEMs (First Experiment at 0.25 sec) (Not Label = Unknown Peak)







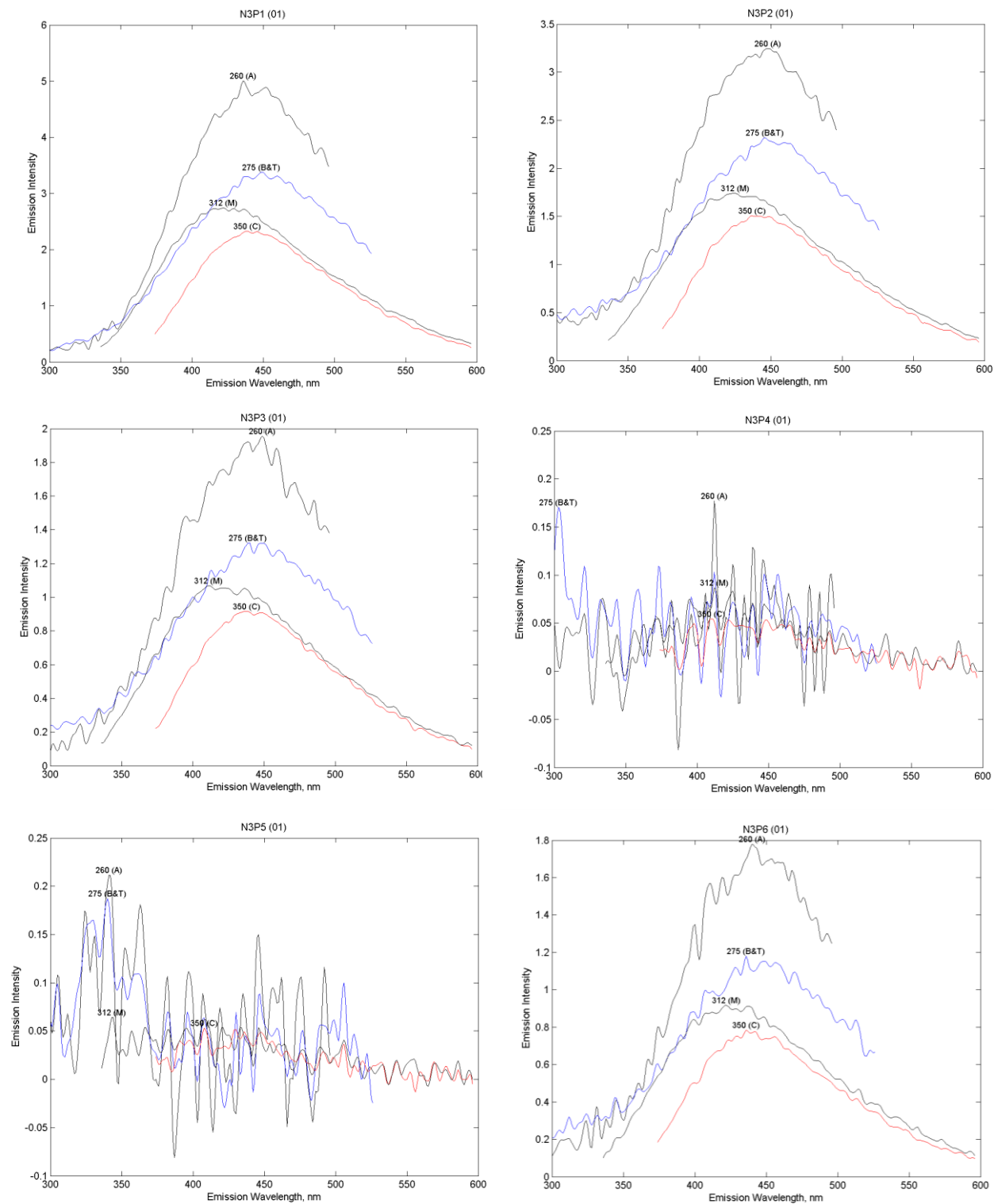


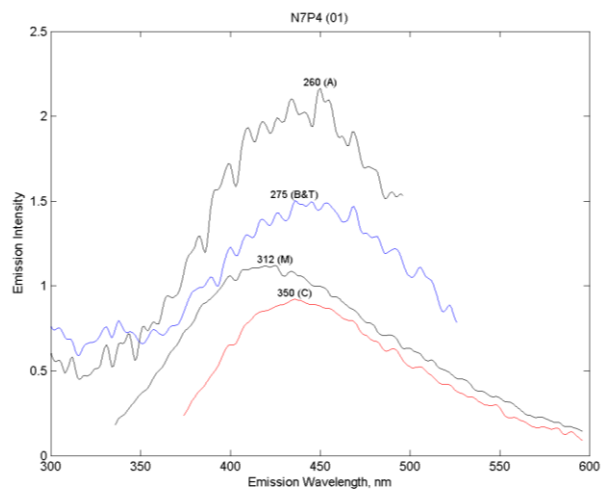
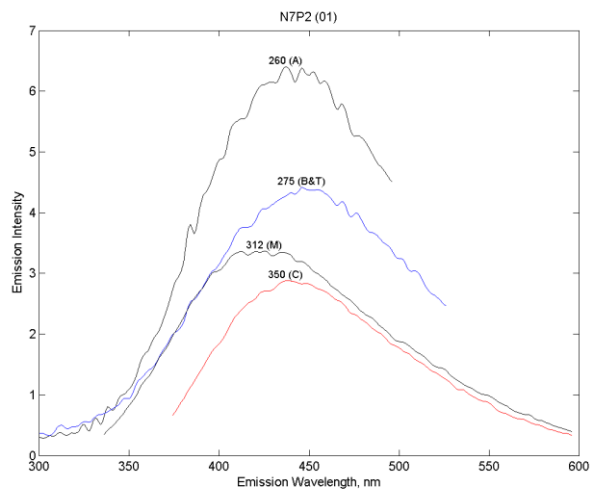
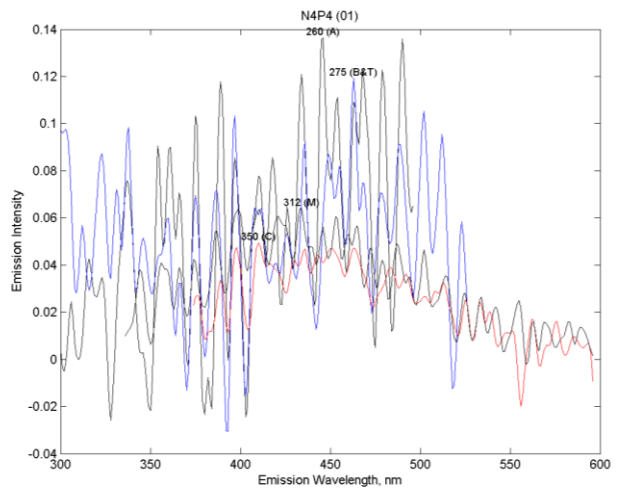
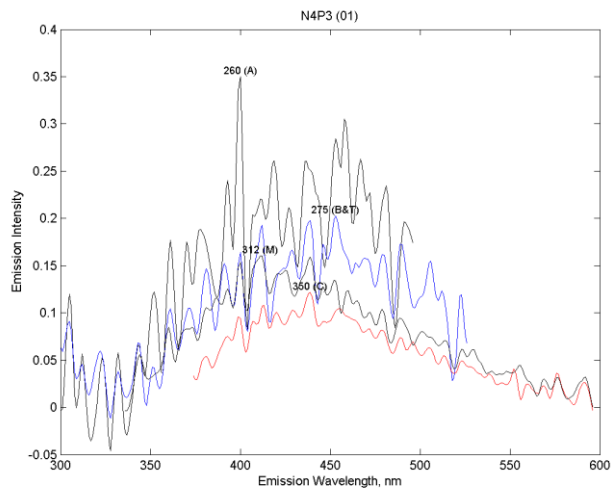
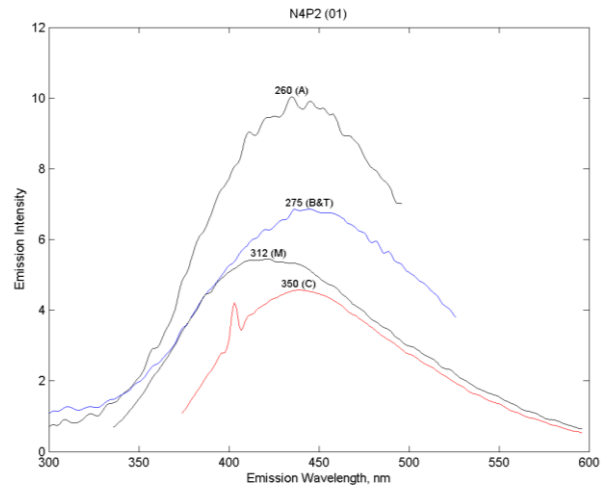
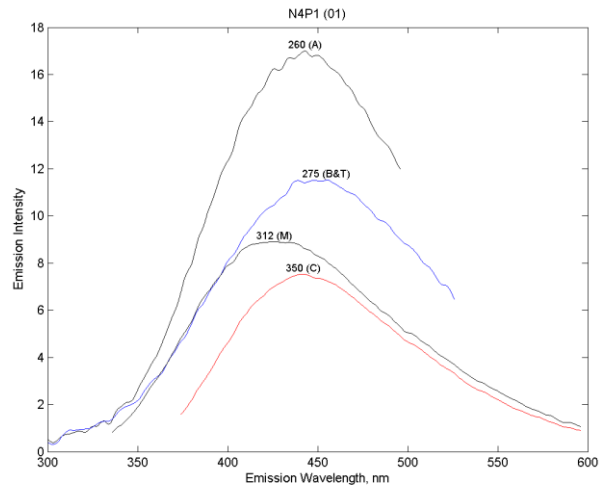


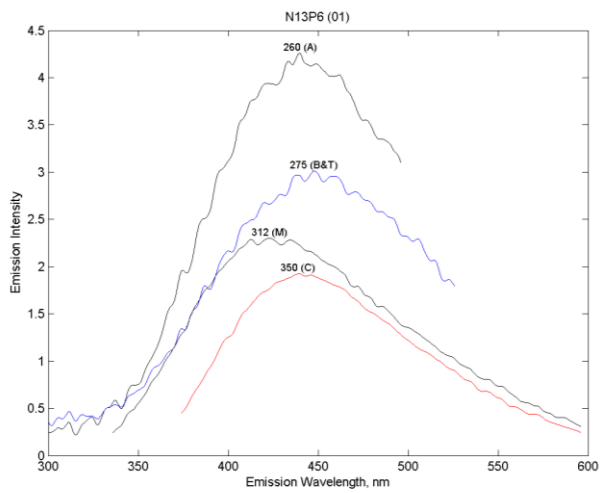
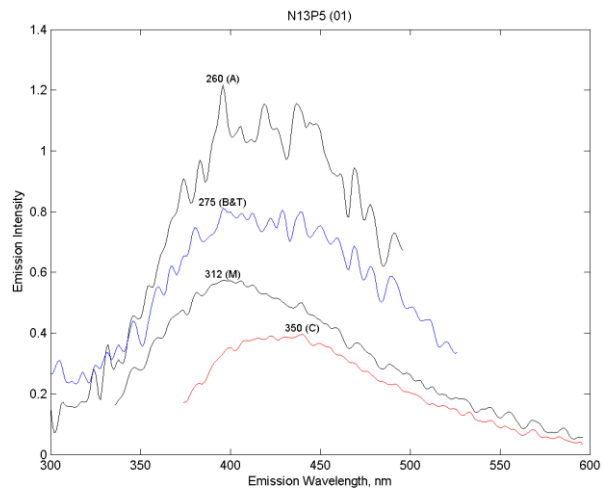
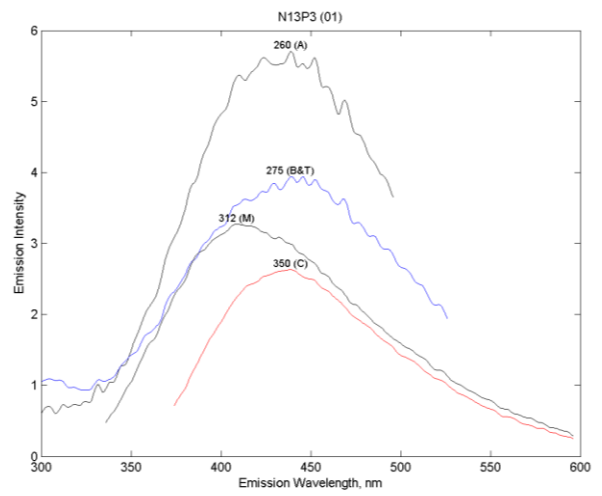
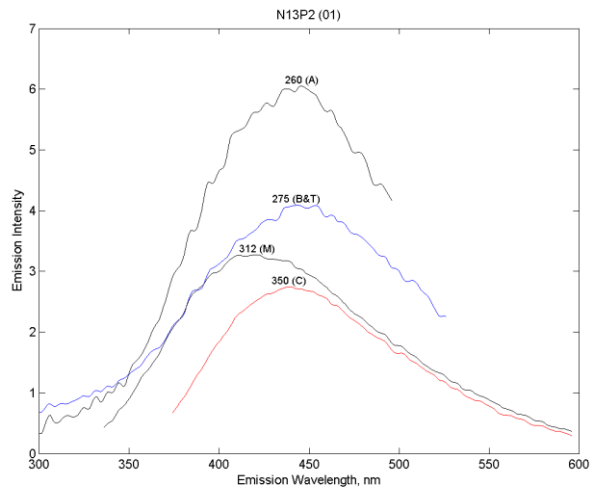
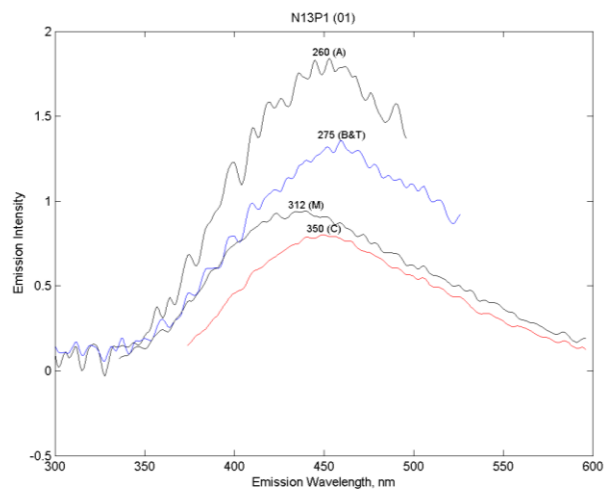
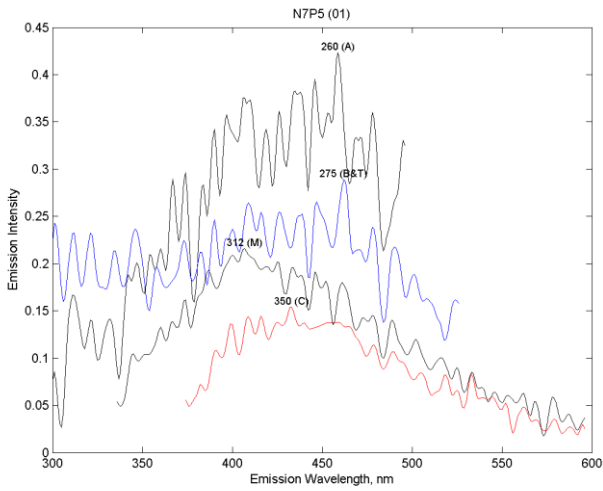
Appendix C2 – Peaks

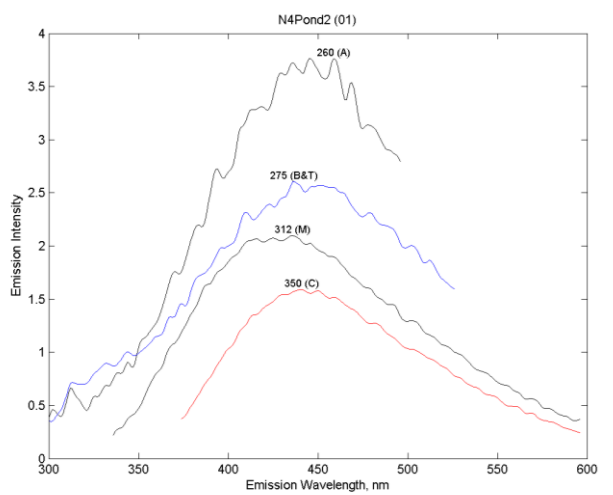
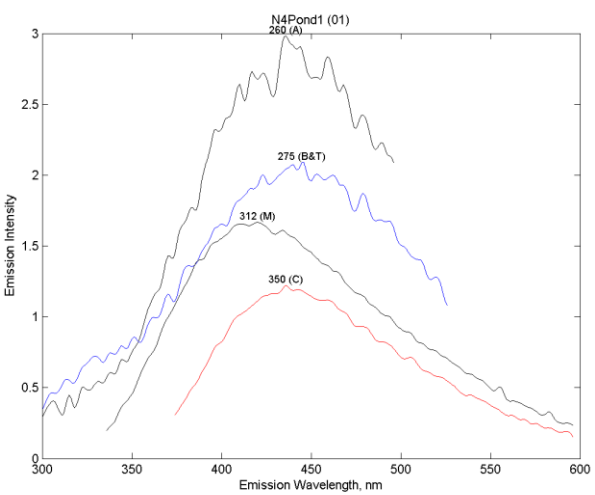
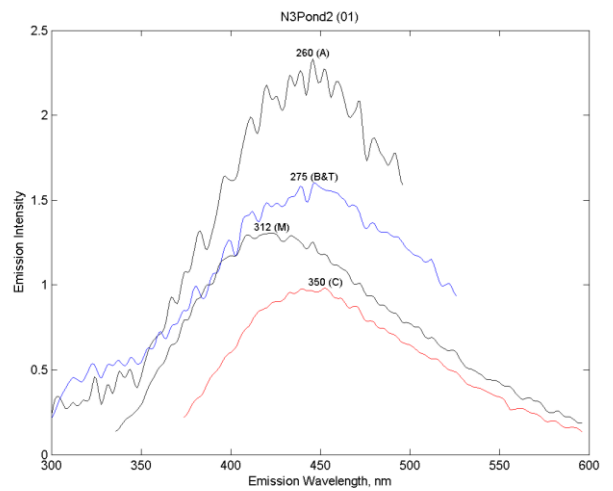
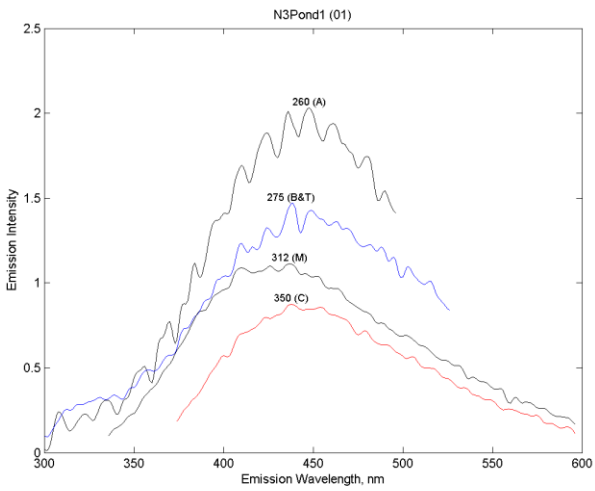
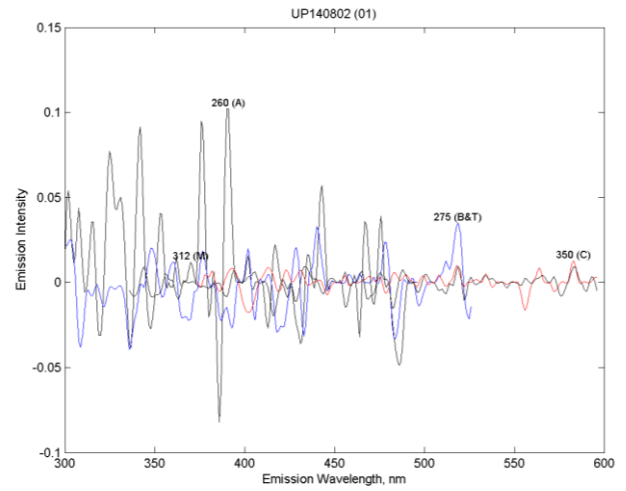
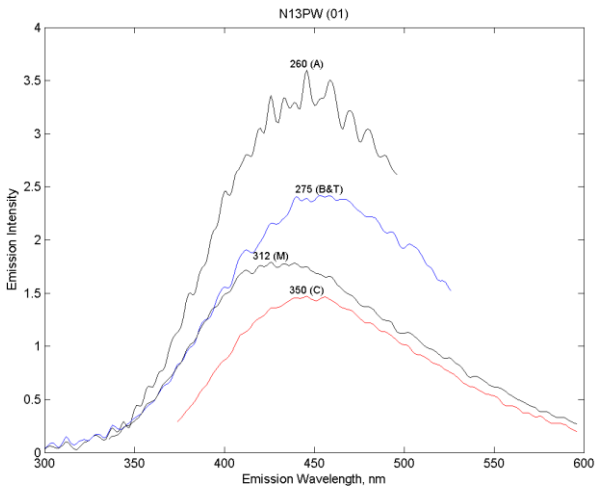
	Sample ID	Depth (m)	Peak A (ex 260, maxem (380-460)) 0.25 secs 0.25 secs 1 sec STDEV	Peak B (ex 275, em 310) 0.25 secs 0.25 secs 1 sec STDEV	Peak T (ex 275, em 340) 0.25 secs 0.25 secs 1 sec STDEV	Peak C (ex 350, maxem (420-480)) 0.25 secs 0.25 secs 1 sec STDEV	Peak M (ex 312, maxem (380-420)) 0.25 secs 0.25 secs 1 sec STDEV	Peak T:Peak A 0.25 secs 0.25 secs 1 sec	STDEV 0.25 secs	MaxEM@370 nm 0.25 secs 0.25 secs 1 sec STDEV			
	N3P1	17	5.0 3.8 0.9	0.3 0.2 0.1	0.6 0.5 0.4	2.3 1.8 0.4	2.7 2.1 0.5	0.1 0.1	0.0 448	458 7.1			
	N3P2	29	3.2 2.5 2.6	0.4 0.5 0.3	0.7 0.2 0.3	1.5 0.9 0.1	1.3 1.4 0.2	0.2 0.2	0.1 453	452 458 3.2			
	N3P3	52	2.0 1.5 1.5	0.3 0.2 0.6	0.2 0.3 0.3	0.9 0.7 0.1	1.1 0.8 0.8	0.1 0.2	0.4 0.1	455 449 456 3.8			
	N3P4	87	0.2 0.1 0.1	0.0 0.1 0.1	0.6 0.3 0.0	0.0 0.0 0.1	0.1 0.1 0.0	0.3 0.6	5.4 2.9	430 420 446 13.1			
	N3P5	240	0.1 0.1 0.1	0.0 0.0 0.2	0.1 0.2 0.1	0.1 0.0 0.0	0.1 0.0 0.0	1.3 0.8	2.4 0.8	445 421 14.2			
	N3P6	95	1.8 1.3 1.3	0.3 0.3 0.2	0.0 0.3 0.3	0.6 0.6 0.1	0.9 0.7 0.1	0.2 0.1	0.0 449	449 452 1.7			
	N3Pond1		2.0 1.4 1.5	0.3 0.2 0.2	0.0 0.3 0.3	0.0 0.9 0.6	0.7 0.1 1.1	0.8 0.8	0.2 0.2	0.1 0.0 462	456 453 4.6		
	N3Pond2		2.3 1.7 1.7	0.4 0.4 0.3	0.3 0.1 0.5	0.4 0.4 0.1	1.0 0.7 0.8	0.1 0.3	0.2 0.0	0.0 464	459 465 3.2		
	N4P1	17	17.0 11.9 3.6	0.8 0.5 0.2	1.7 1.2 1.2	4.4 7.5 5.4	1.5 8.9 6.3	4.0 1.8	0.1 0.1	0.0 459	453 4.2		
	N4P2	30	10.0 7.2 2.0	1.3 1.0 0.2	1.6 1.2 0.3	4.6 3.4 0.8	5.4 4.0 1.0	0.2 0.2	0.0 452	448 2.8			
	N4P3	56	0.4 0.2 0.2	0.1 0.0 0.3	0.2 0.0 0.1	0.0 0.1 0.1	0.0 0.2 0.1	0.1 0.1	1.6 0.9	438 422 446 12.2			
	N4P4	75	0.1 0.1 0.1	0.0 0.0 0.1	0.1 0.0 0.0	0.0 0.0 0.1	0.1 0.0 0.0	0.4 0.5	0.6 0.1	452 448 446 3.1			
	N4Pond1		3.0 2.1 2.2	0.5 0.5 0.4	0.4 0.1 0.7	0.6 0.6 0.1	1.2 0.9 0.9	0.2 1.7	1.2 1.3	0.2 0.1 459	458 7.8		
	N4Pond2		3.8 2.7 2.8	0.6 0.6 0.5	0.8 0.2 0.9	0.8 0.7 0.1	1.6 1.2 2.1	1.5 1.6	0.3 0.2	0.3 0.0 460	459 459 0.6		
	N7P2	26	6.4 4.7 1.2	0.5 0.4 0.0	0.8 0.6 0.1	2.9 2.1 0.5	3.4 2.5 0.6	0.1 0.1	0.0 454	453 0.7			
	N7P4	75	2.2 1.6 1.6	0.3 0.7 0.8	1.4 0.4 0.8	0.6 0.7 0.1	0.9 0.9 0.1	0.3 0.4	0.9 0.3	453 449 2.3			
	N7P5	232	0.4 0.3 0.3	0.1 0.2 0.4	1.3 0.6 0.2	0.3 0.1 0.2	0.2 0.2 0.0	0.4 0.7	4.3 2.1	460 463 465 2.5			
	N7Pond1		4.1 2.9 3.0	0.6 0.9 0.8	0.7 0.1 1.2	0.9 0.9 0.2	1.8 1.3 1.4	0.2 2.3	1.7 1.8	0.3 0.3 0.2	0.0 456	452 455 2.1	
	N7Pond2		2.6 1.9 1.9	0.4 0.8 0.9	0.6 0.2 1.1	0.8 0.7 0.2	1.2 0.9 0.9	0.2 1.5	1.1 1.2	0.2 0.4 0.3	0.1 445	449 447 2.0	
	N7Canal		2.8 2.0 2.1	0.5 0.6 0.7	0.5 0.1 0.8	0.6 0.6 0.1	1.3 0.9 1.0	0.2 1.6	1.2 1.2	0.3 0.3 0.3	0.0 458	450 457 4.4	
	N13P1	14	1.8 1.4 1.5	0.3 0.1 0.1	0.2 0.0 0.1	0.2 0.0 0.2	0.0 0.8 0.6	0.7 0.1	0.9 0.7	0.7 0.1 0.1	0.1 0.0 459	460 457 1.5	
	N13P2	33	6.1 4.3 1.2	0.8 0.7 0.0	1.1 0.8 0.2	0.0 1.1 0.8	0.2 0.0 0.5	3.3 2.4	0.6 0.2	0.2 0.0 445	448 2.1		
	N13P3	85	5.7 4.2 1.1	1.1 0.8 0.2	1.1 0.9 0.3	0.3 0.2 0.6	1.9 0.5 3.3	2.4 0.6	0.2 0.2	0.0 452	453 0.7		
	N13P5	237	1.2 0.9 0.8	0.2 0.3 0.5	0.1 0.3 0.3	0.3 0.0 0.4	0.3 0.3 0.1	0.6 0.4	0.4 0.1	0.3 0.3	0.6 0.2	439 441	446 3.6
	N13P6	123	4.3 3.1 3.1	0.7 0.4 0.6	0.4 0.1 0.5	0.5 0.4 0.0	1.9 1.4 1.5	0.3 2.3	1.7 1.7	0.3 0.1 0.1	0.1 0.0 446	456 458 6.4	
	N13Pw	21	3.6 2.5 2.6	0.6 0.1 0.2	0.2 0.0 0.2	0.0 1.5 1.1	0.2 1.8 1.3	1.3 0.3	0.1 0.1	0.0 458	458 462 2.3		
	N13Pond1		1.7 1.2 1.3	0.3 0.4 0.5	0.9 0.3 0.6	0.4 0.6 0.1	1.2 0.9 0.9	0.2 1.1	0.8 0.8	0.1 0.3 0.4	0.7 0.2 446	448 444 2.0	
	N13Pond2		1.1 0.7 0.8	0.2 0.3 0.3	0.7 0.2 0.3	0.3 0.0 0.4	0.3 0.3 0.1	0.6 0.4	0.5 0.1	0.3 0.4	0.9 0.3 449	460 452 5.7	
	U140802		0.1 0.0 0.0	0.0 0.0 0.0	0.0 0.0 0.0	0.0 0.0 0.0	0.0 0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.1 443	469 489 23.1		

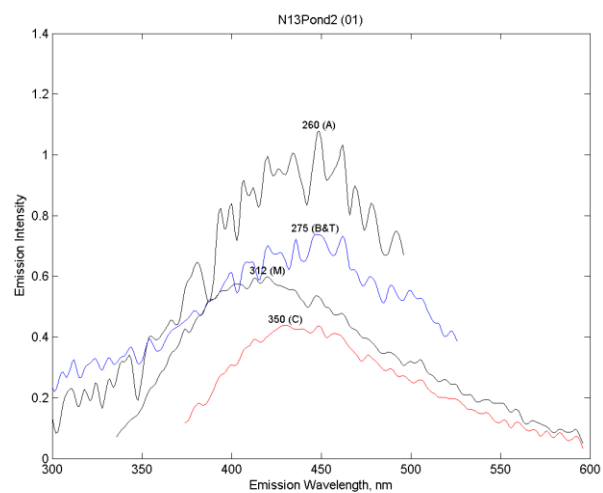
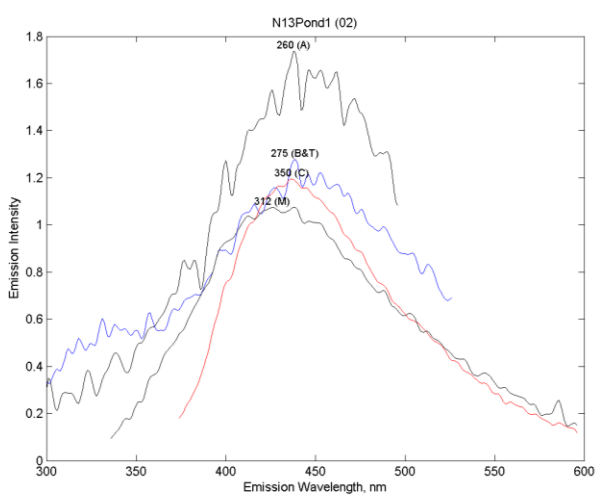
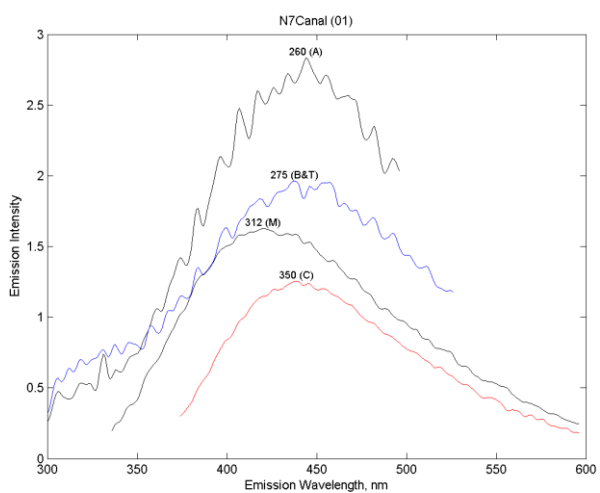
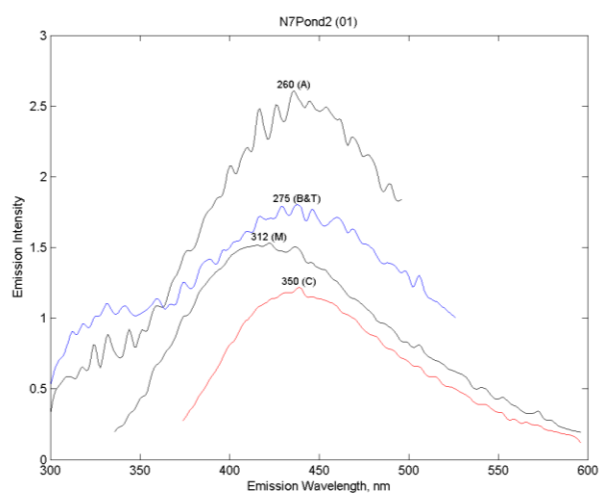
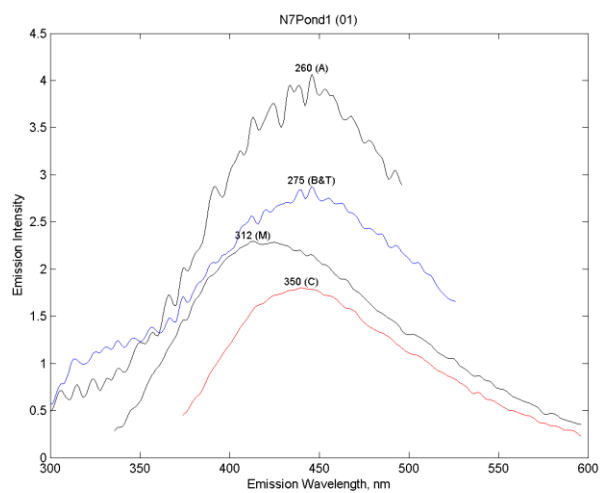
First Experiment at 0.25 sec



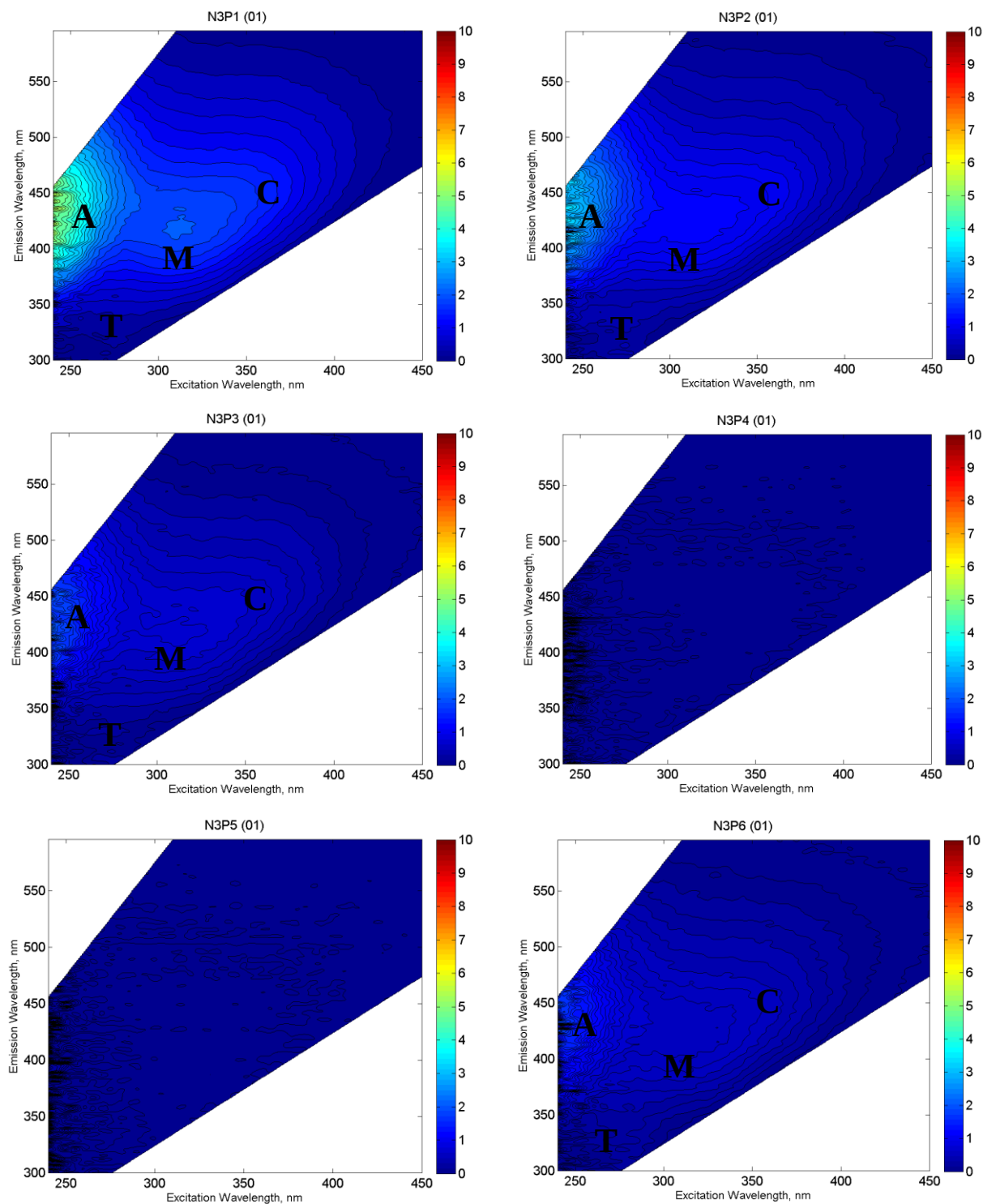


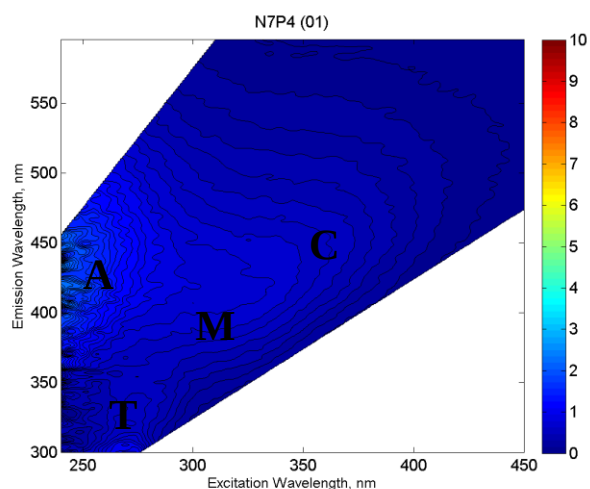
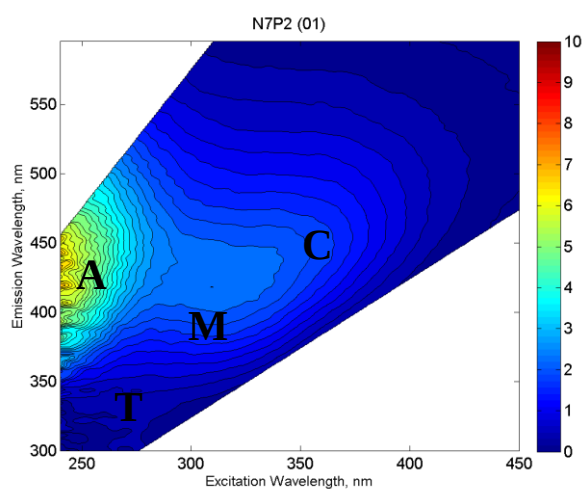
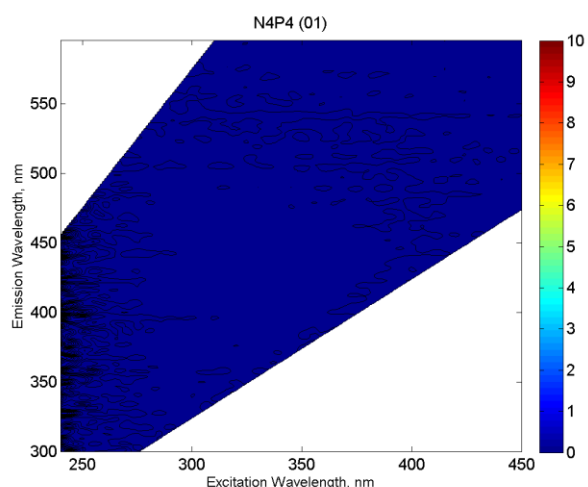
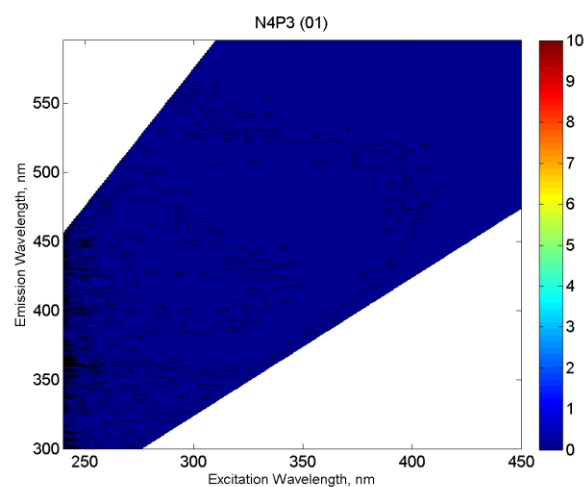
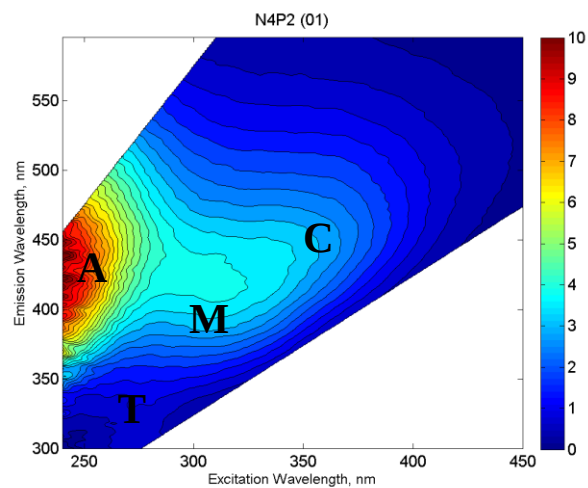
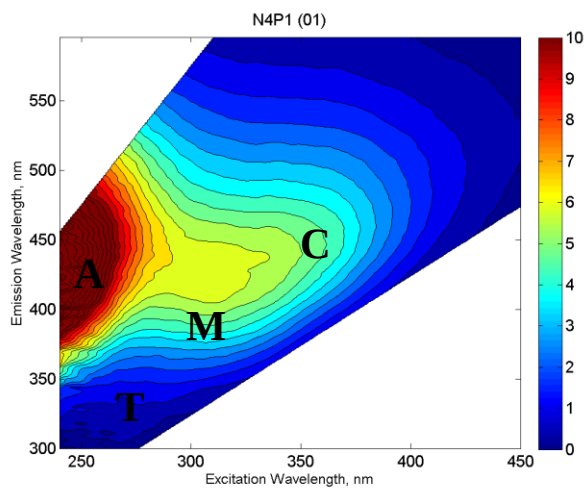


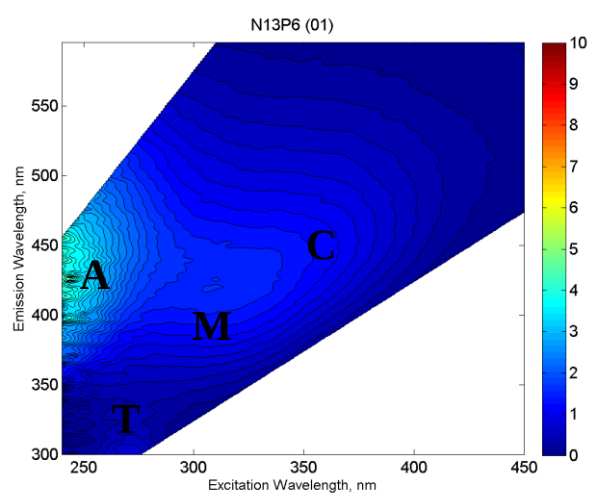
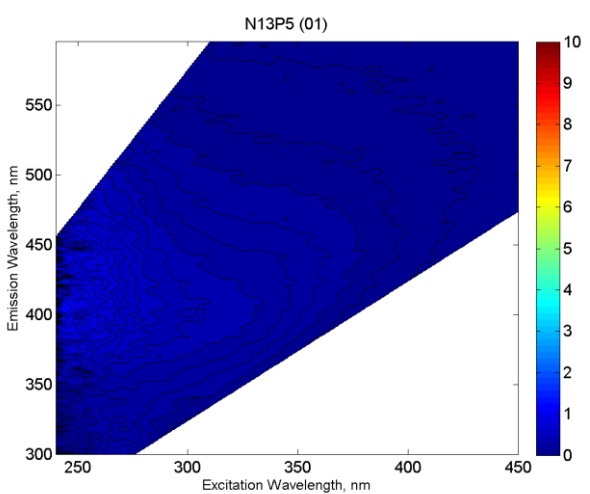
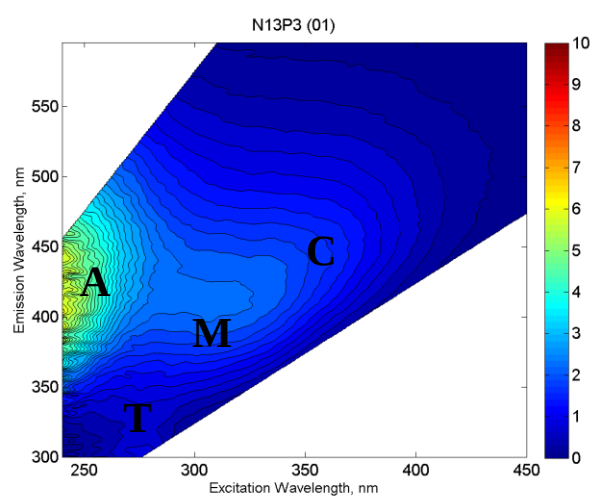
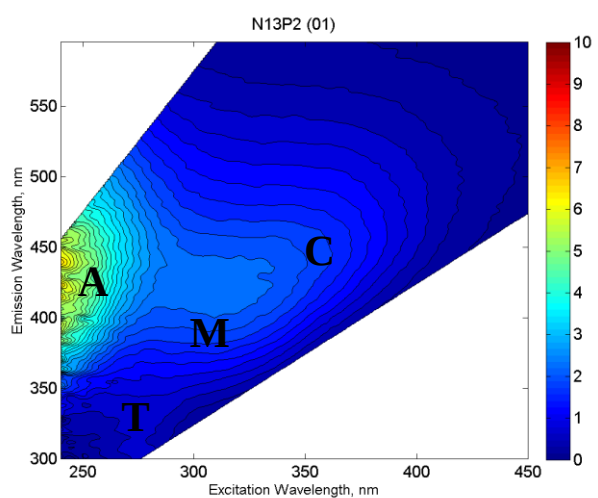
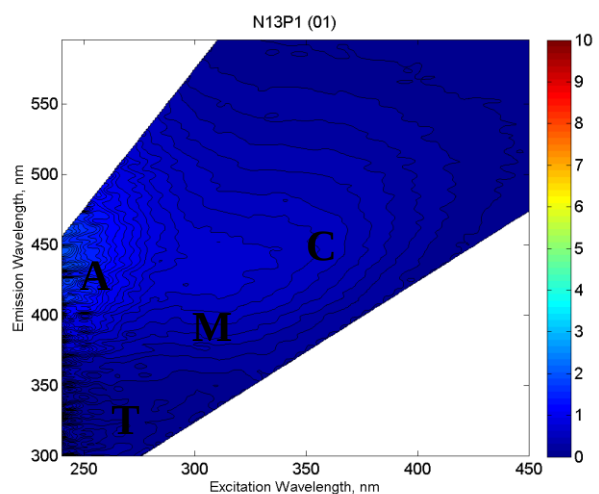
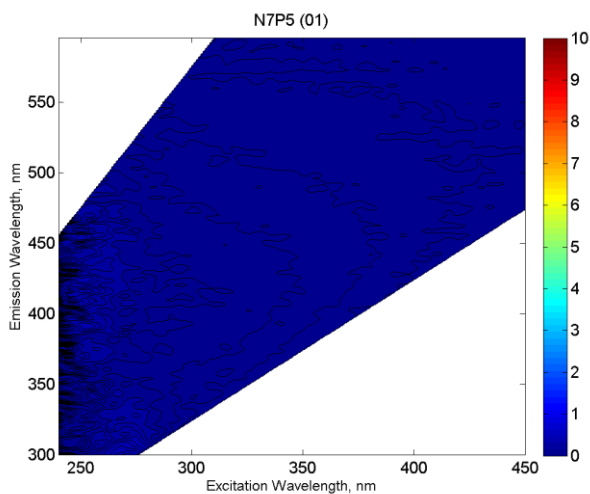


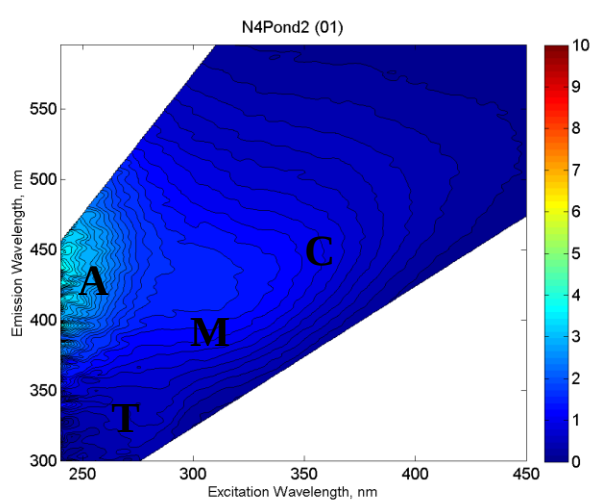
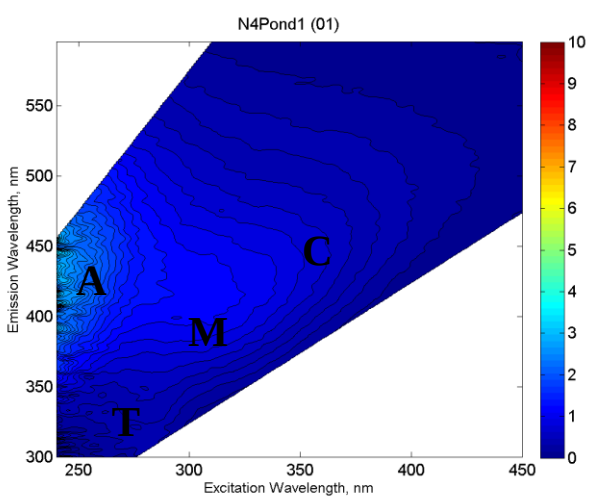
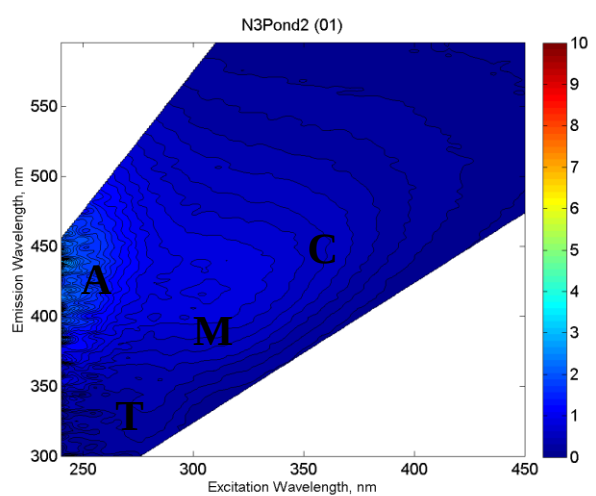
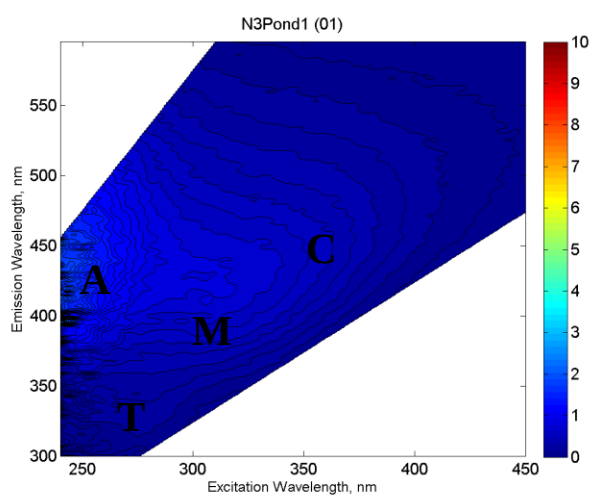
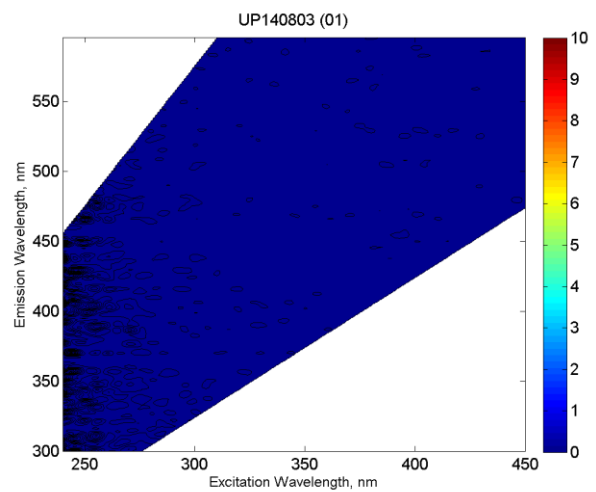
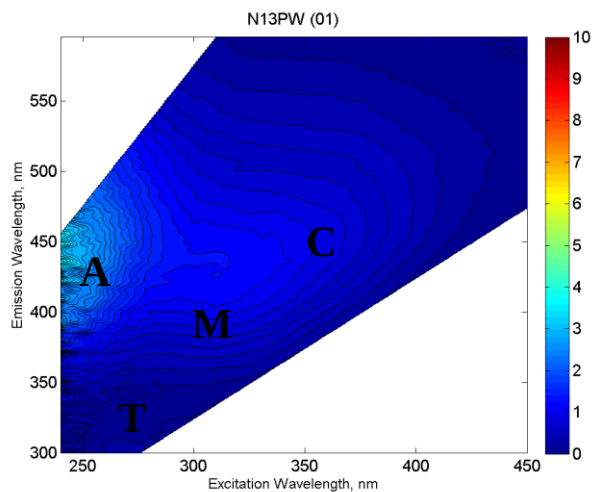


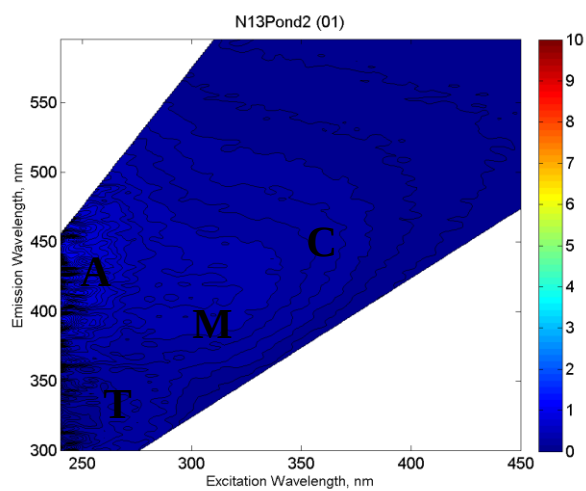
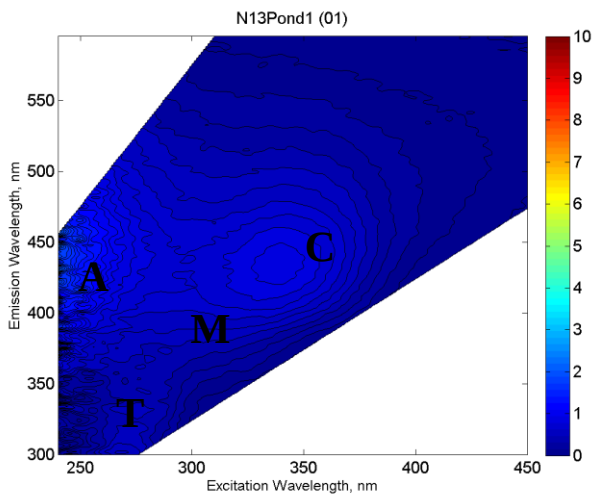
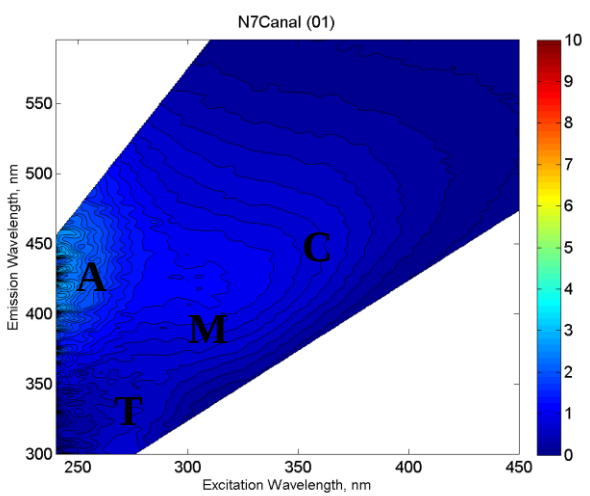
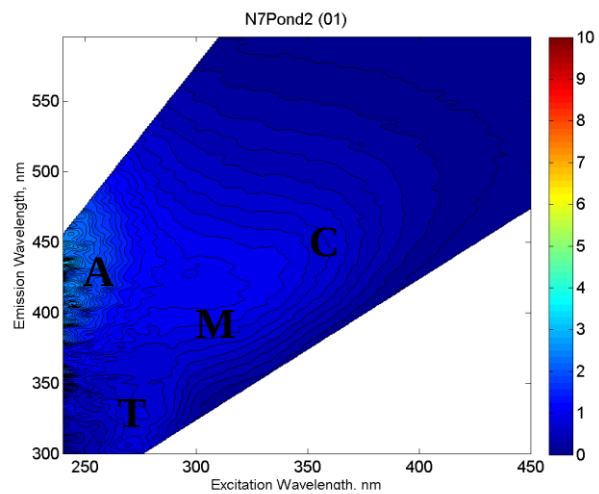
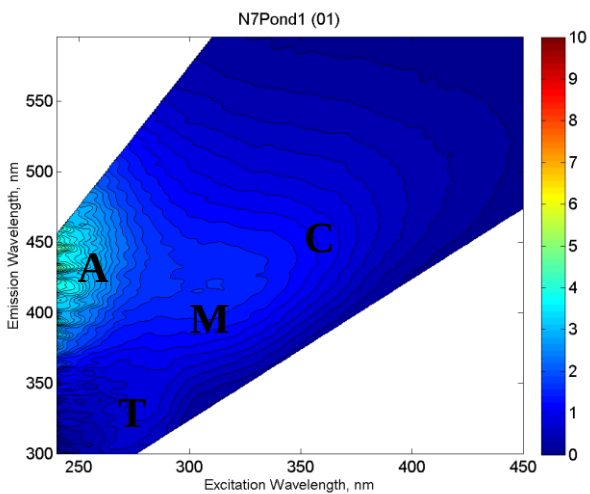
Appendix C3 – EEMs (Second Experiment at 0.25 sec) (Not Label = Unknown Peak)



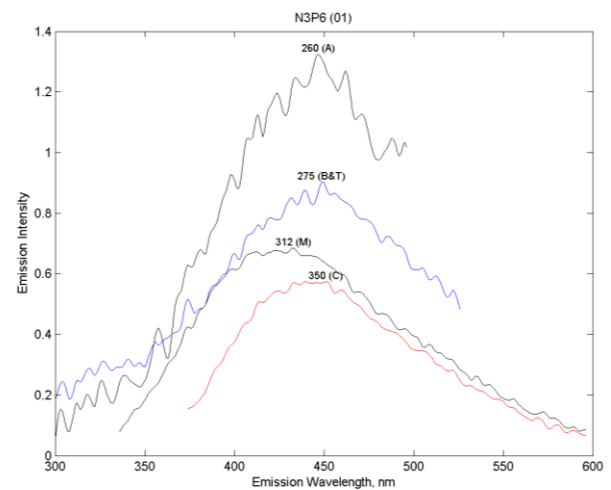
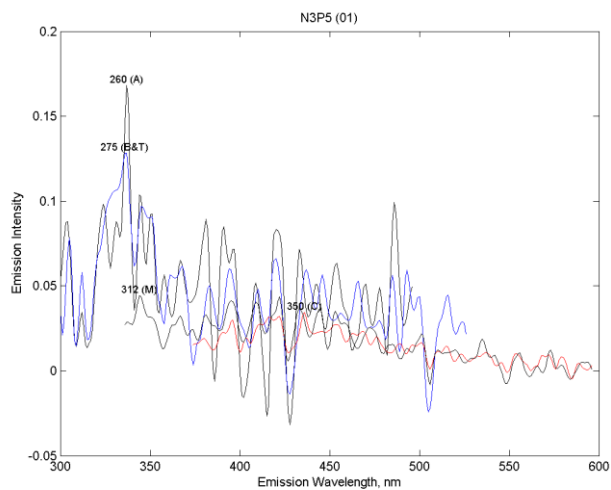
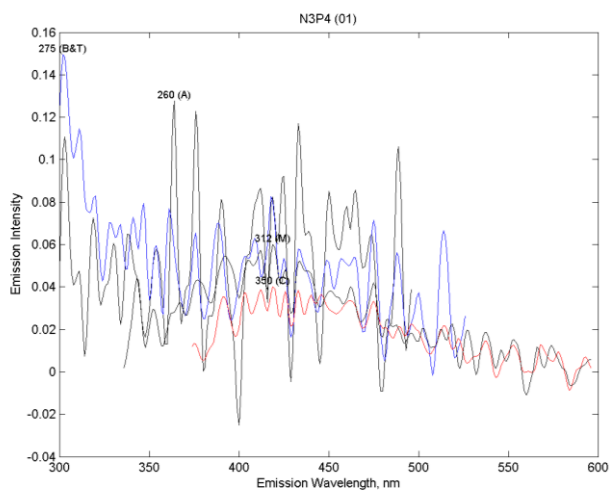
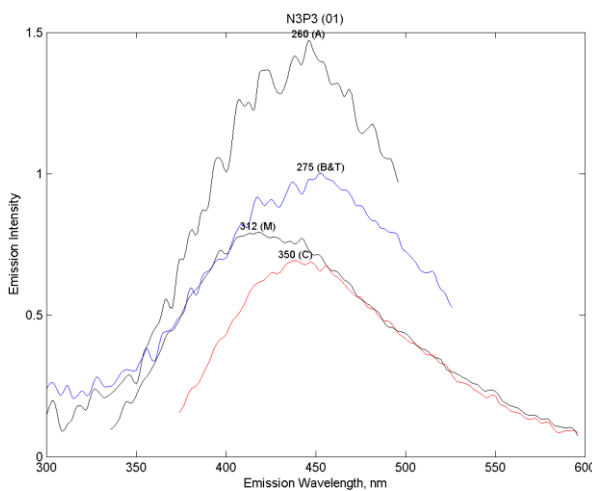
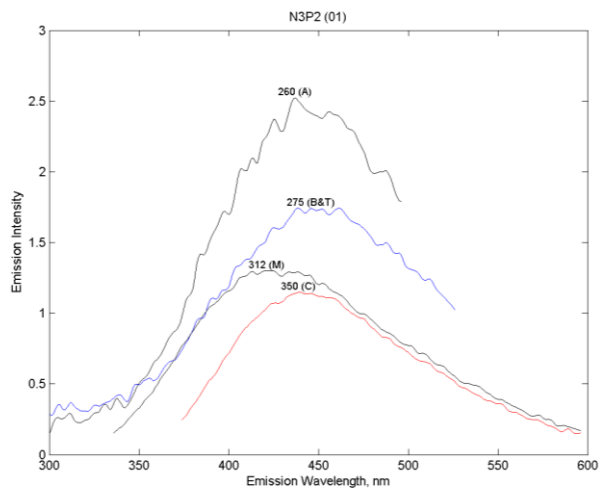
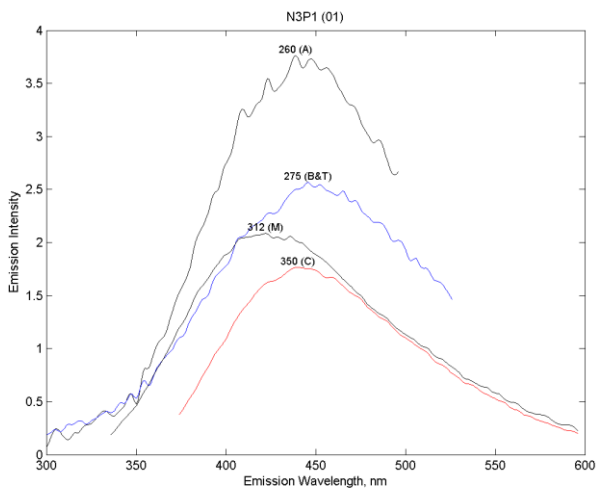


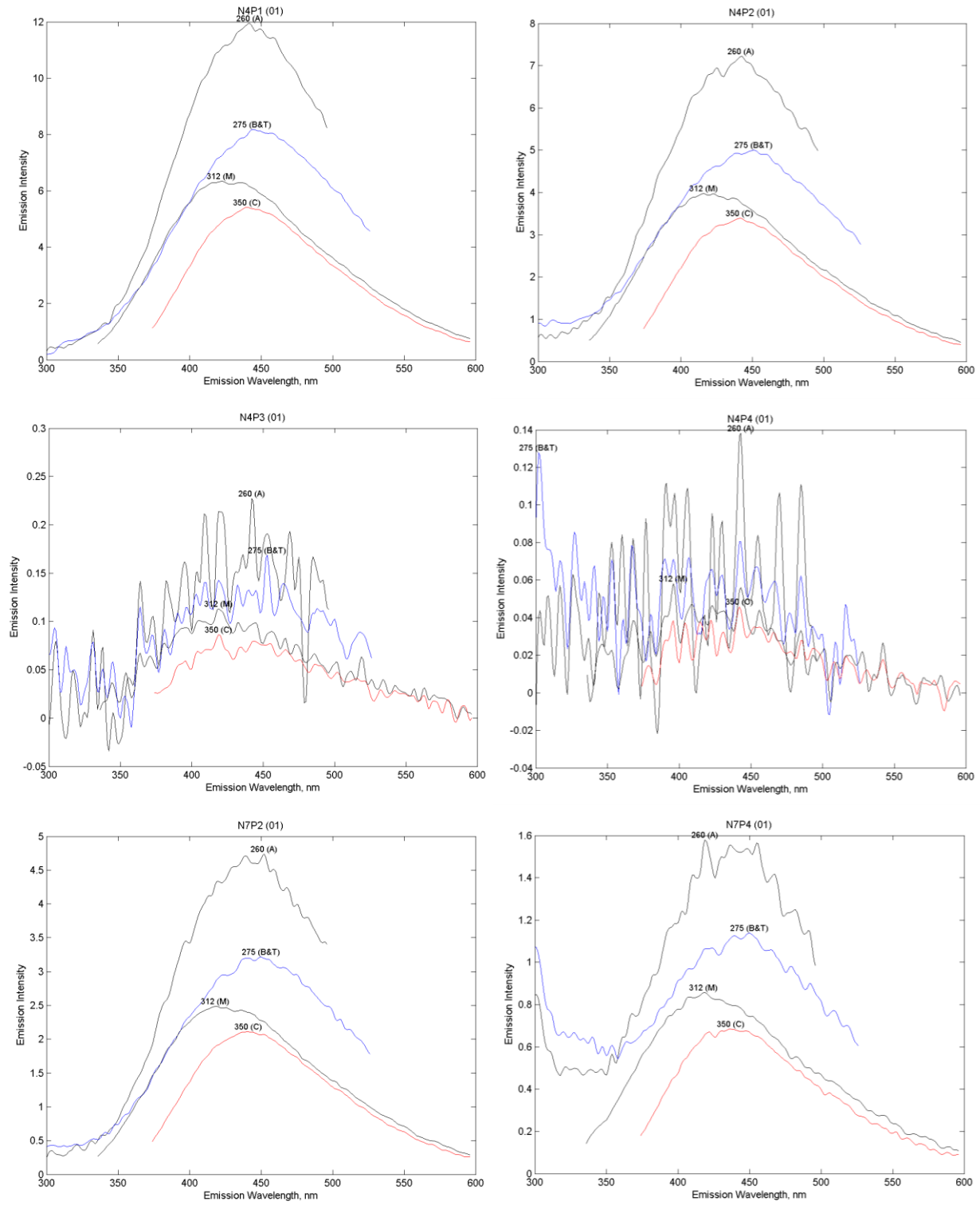


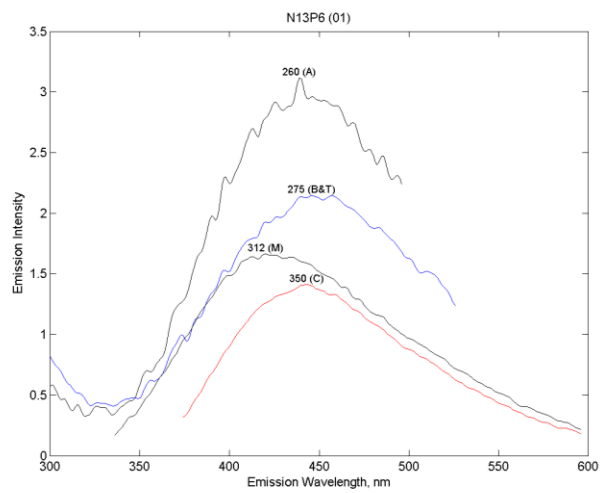
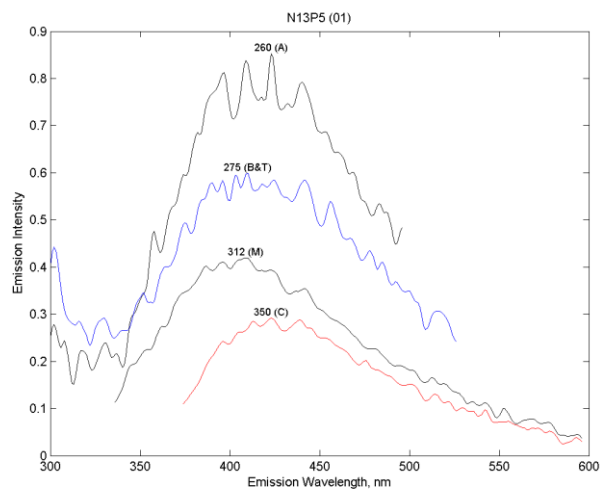
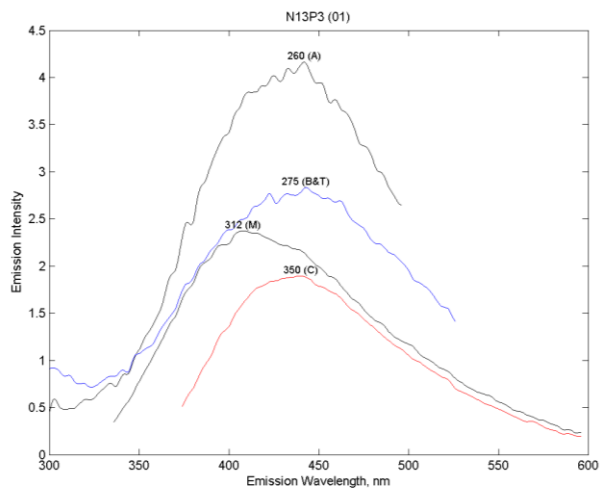
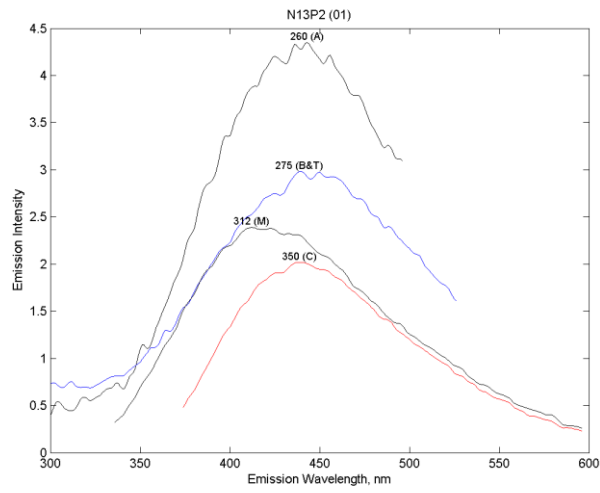
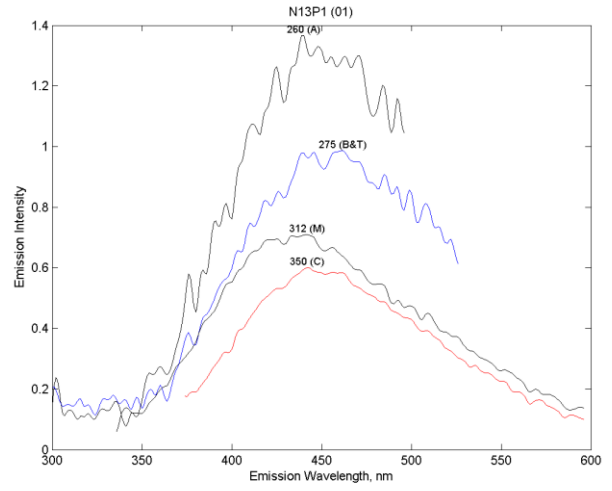
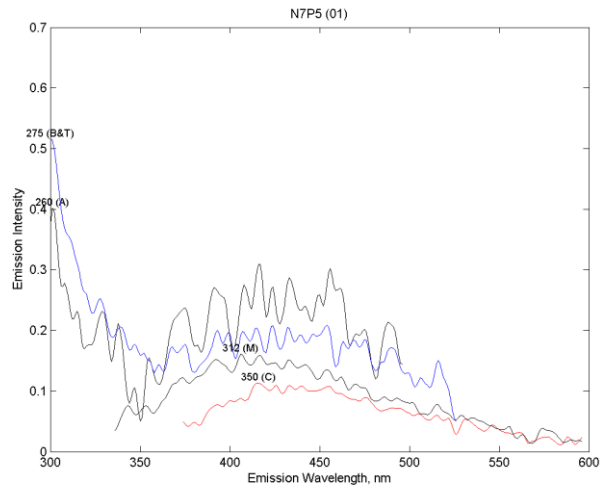


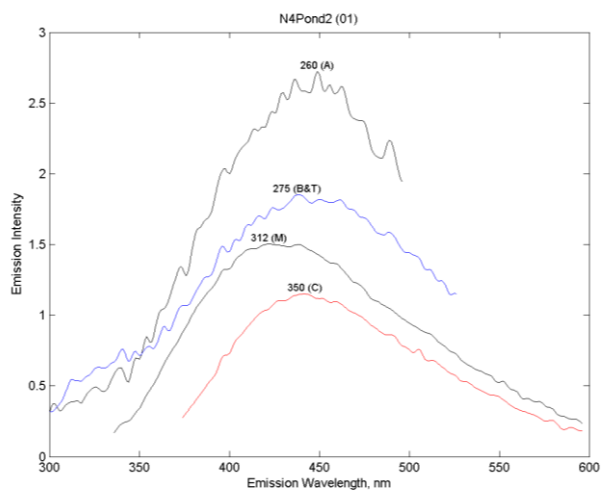
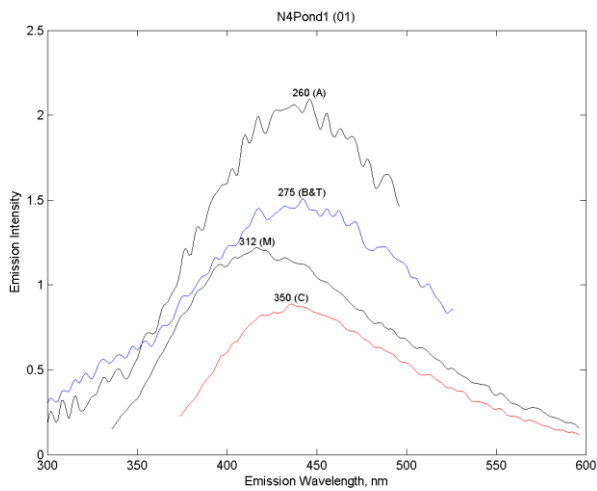
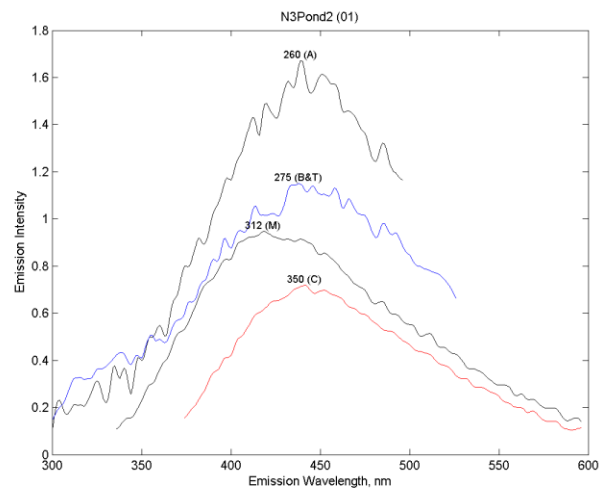
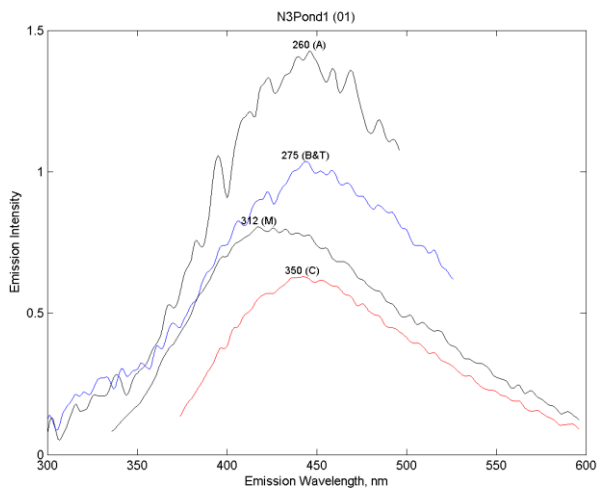
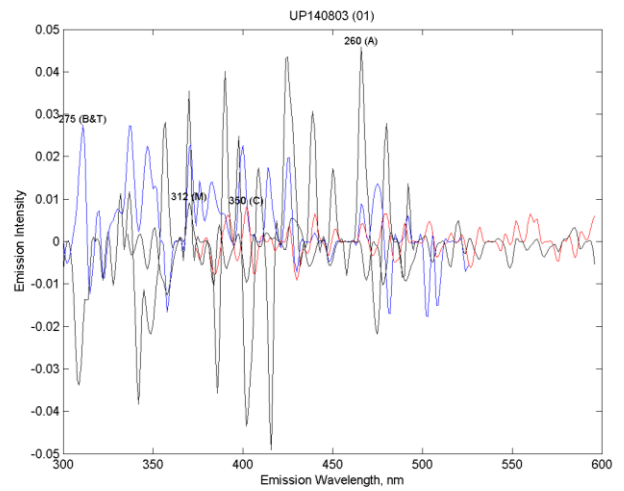
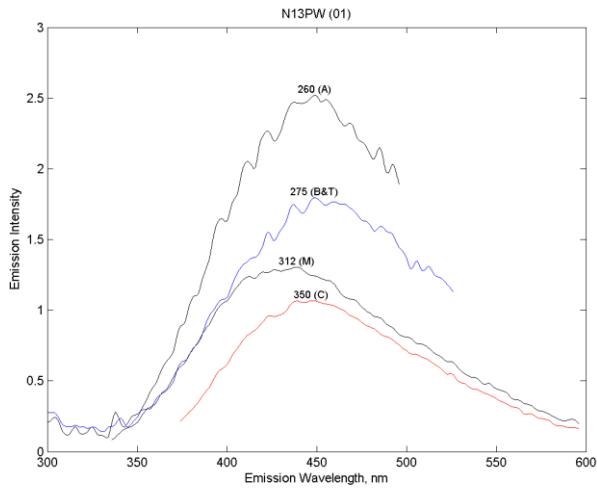


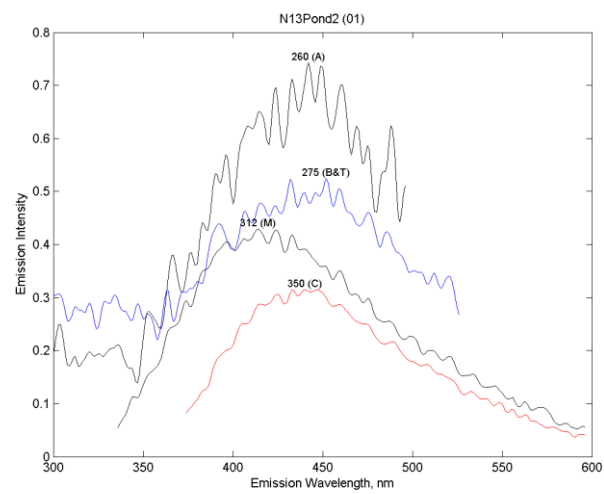
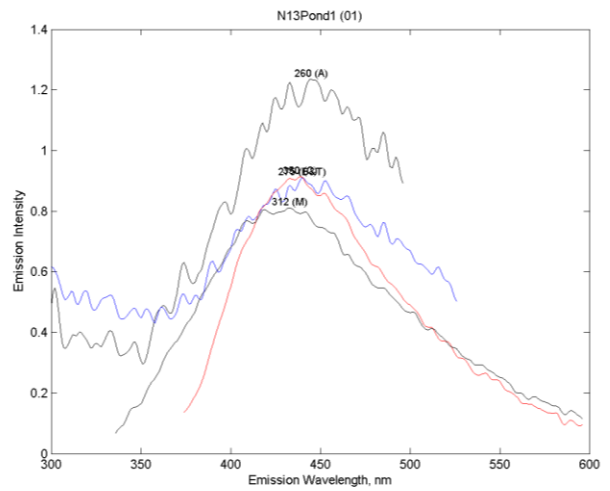
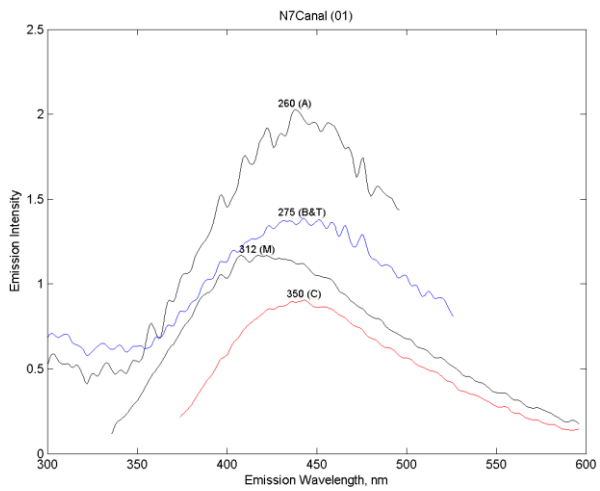
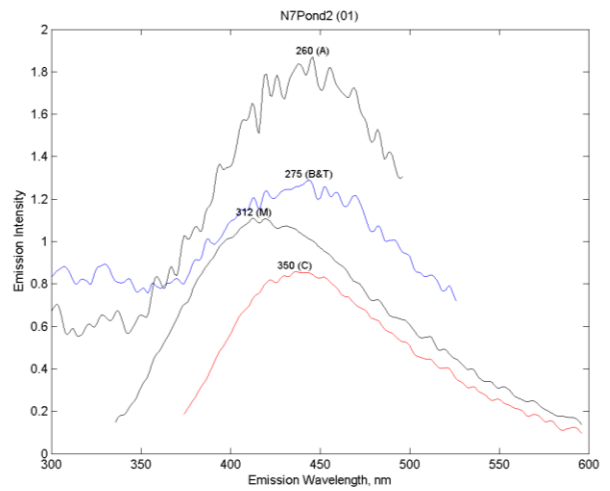
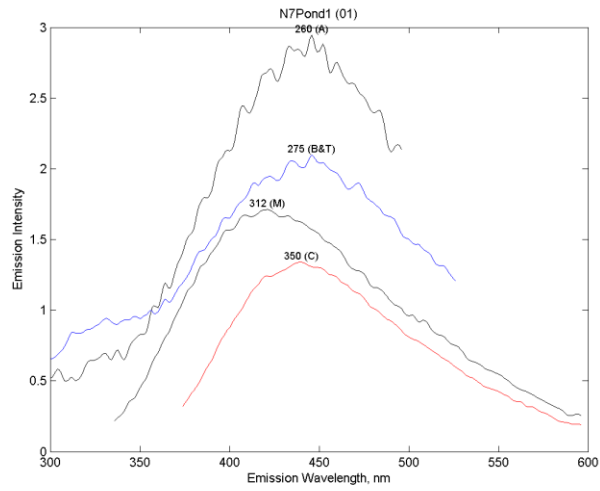
Appendix C4 – Peaks (Second Experiment at 0.25 sec)



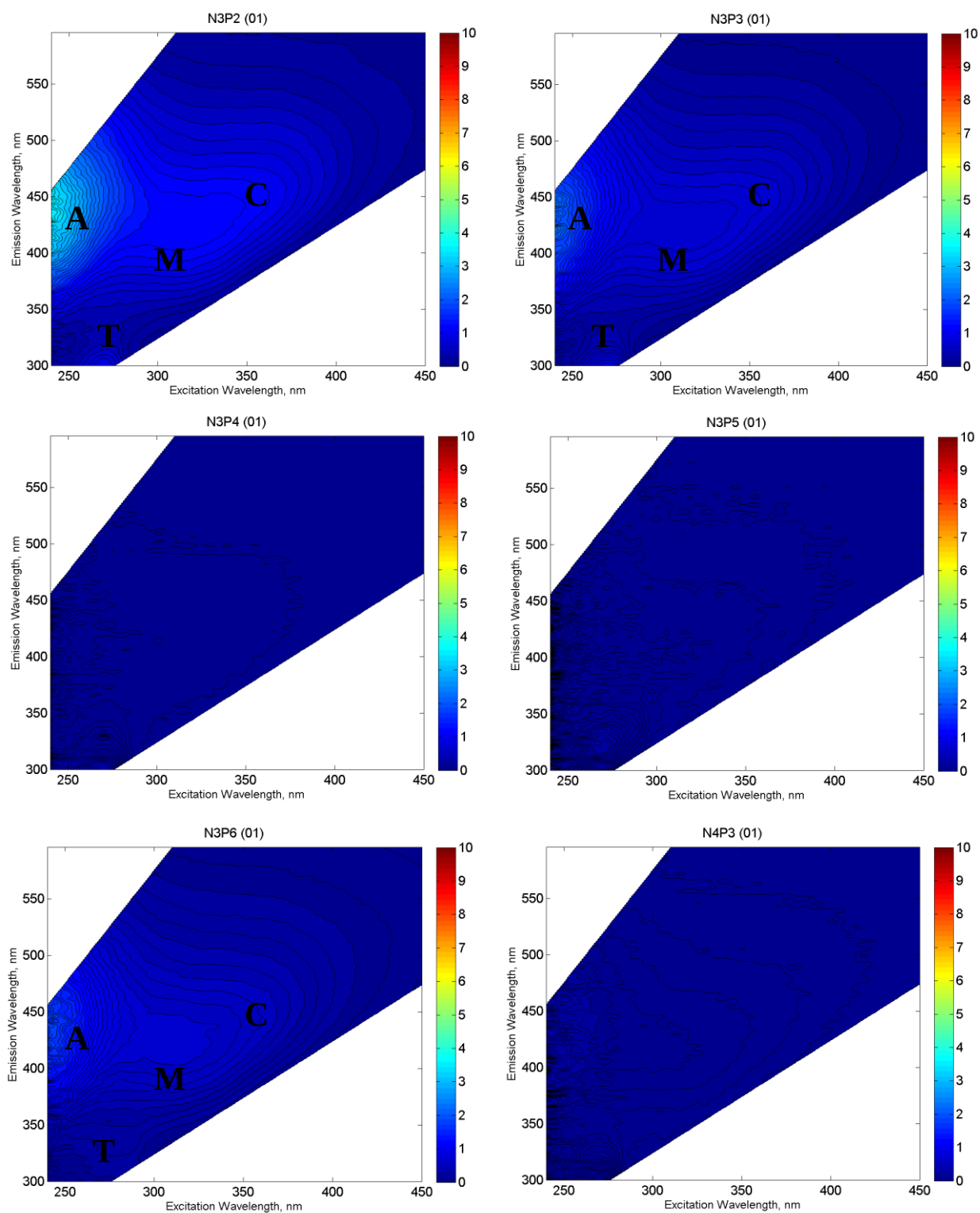


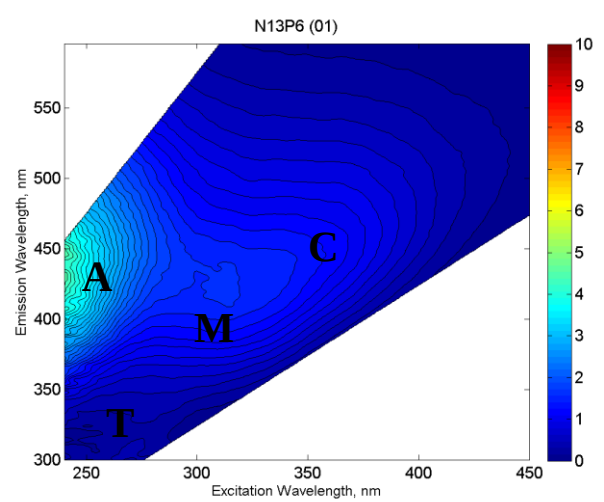
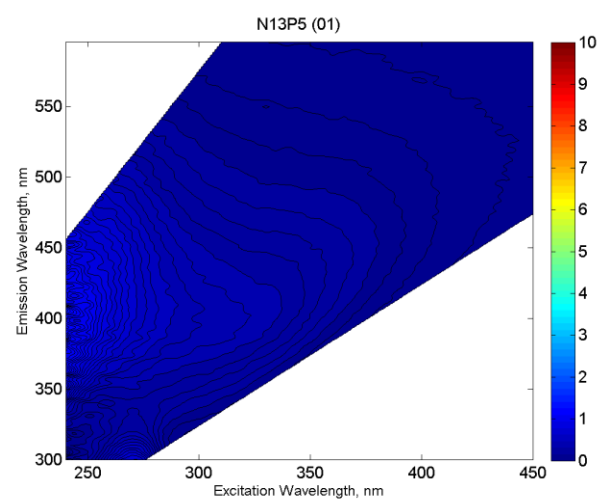
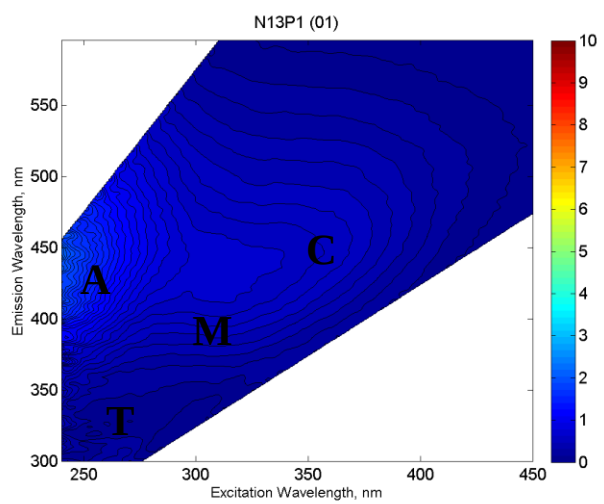
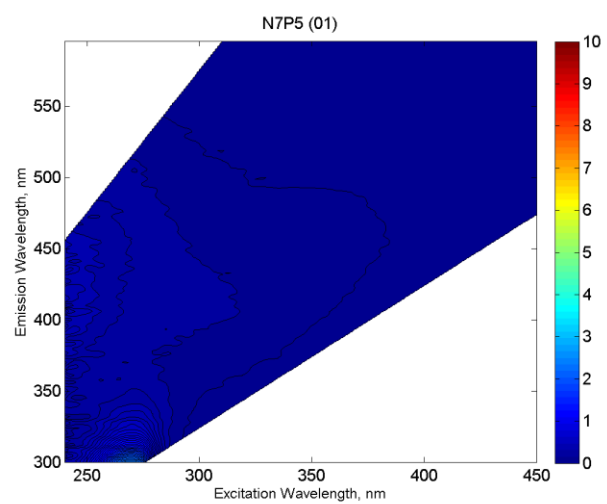
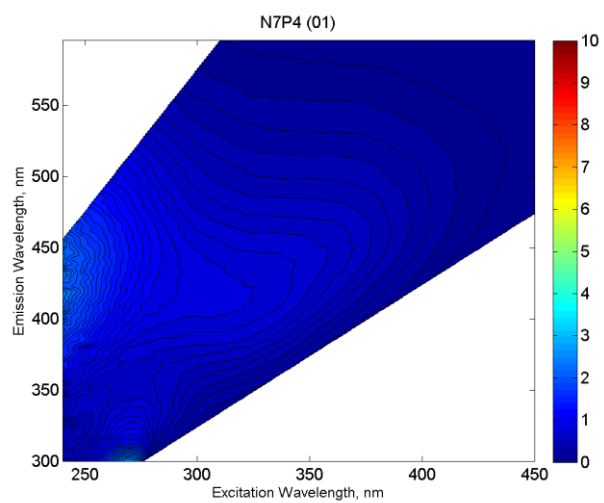
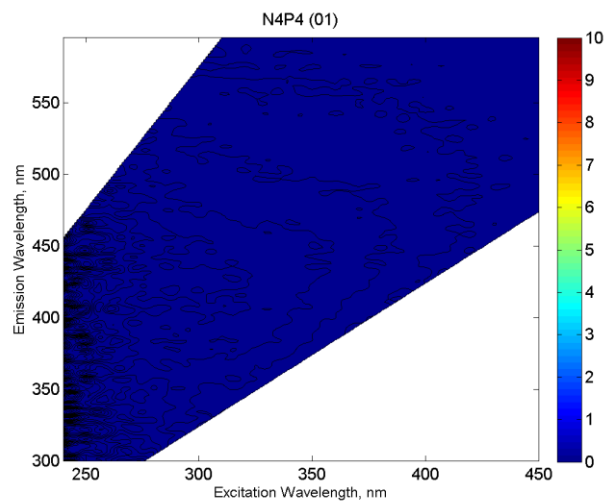


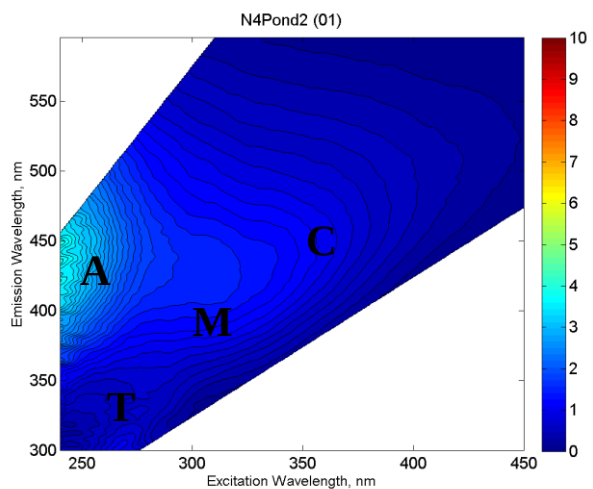
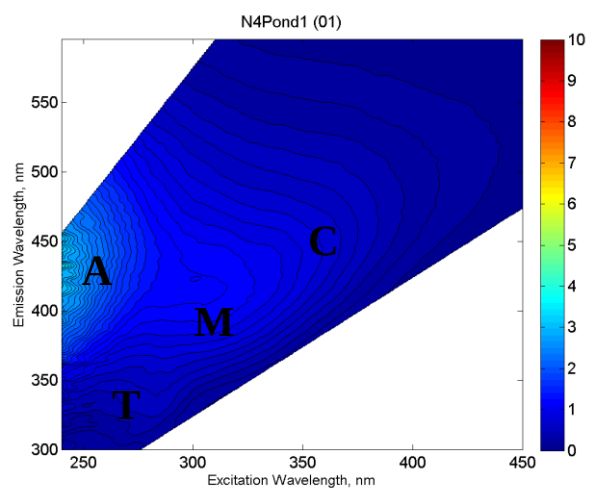
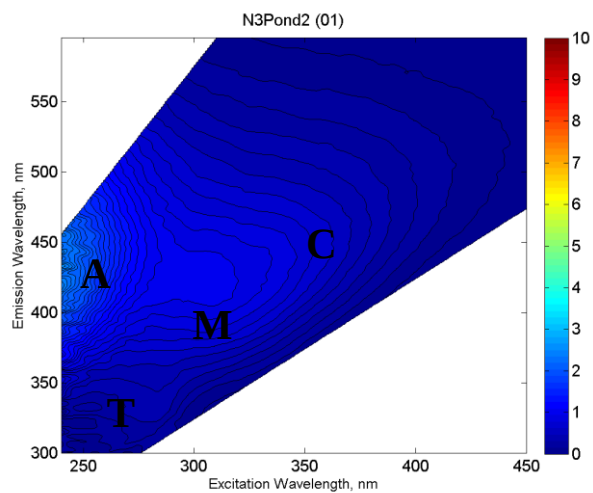
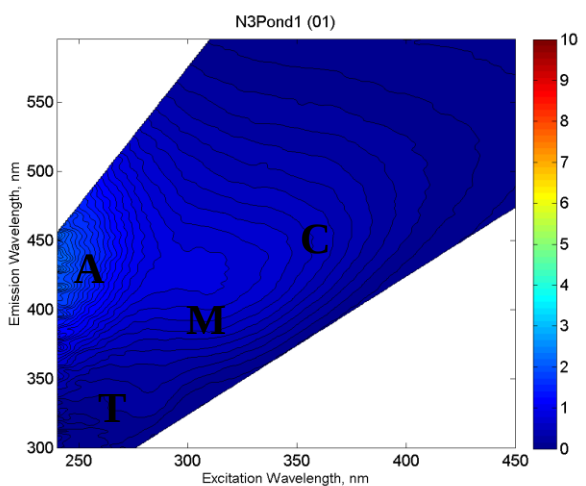
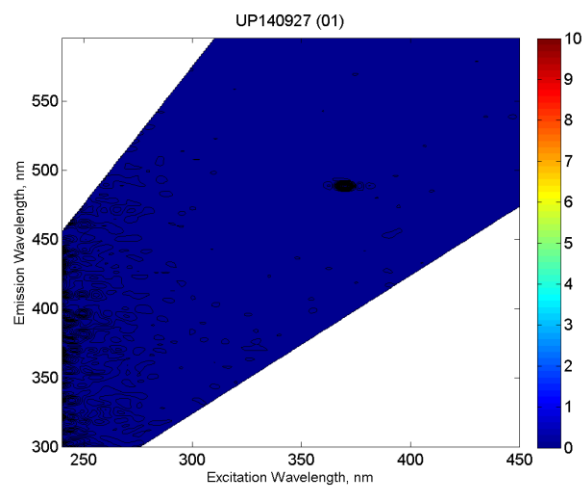
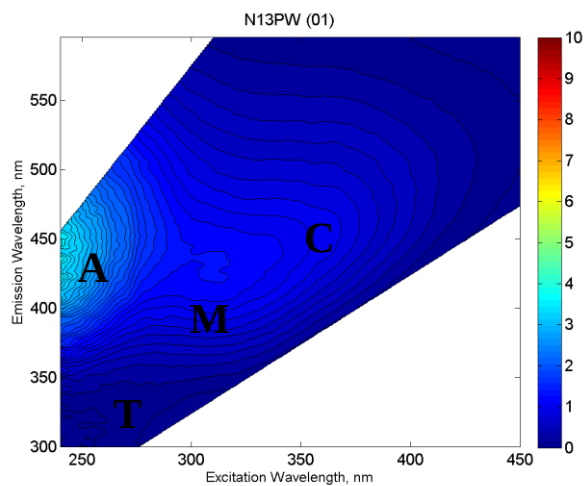


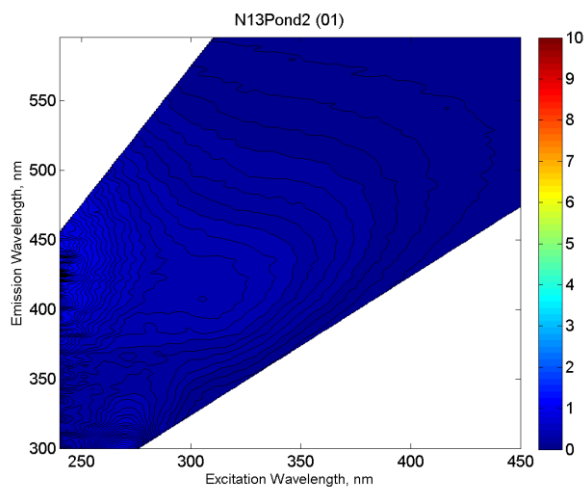
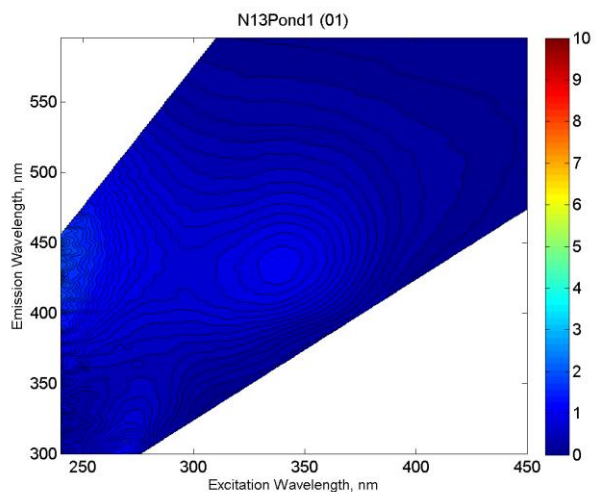
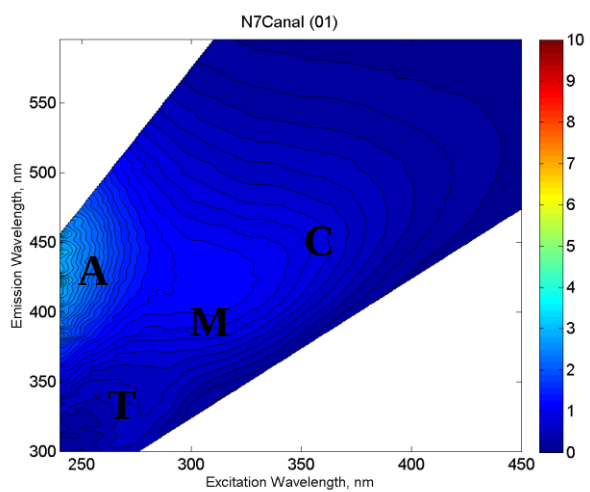
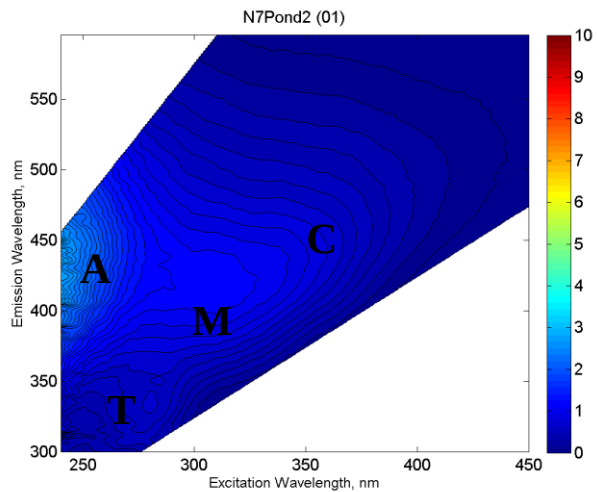
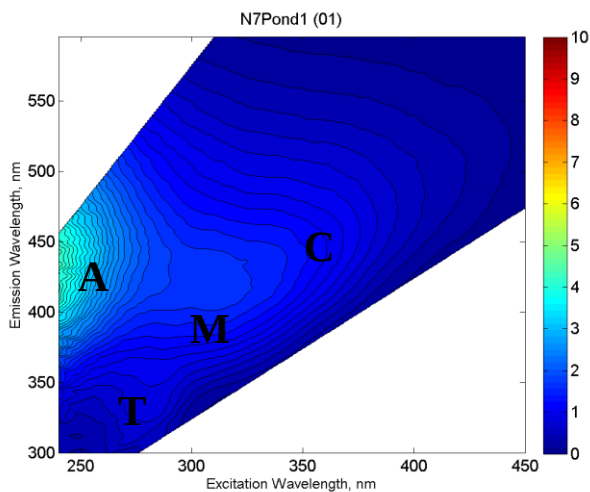


Appendix C5 – EEMs (Third Experiment at 1 sec) (Not Label = Unknown Peak)

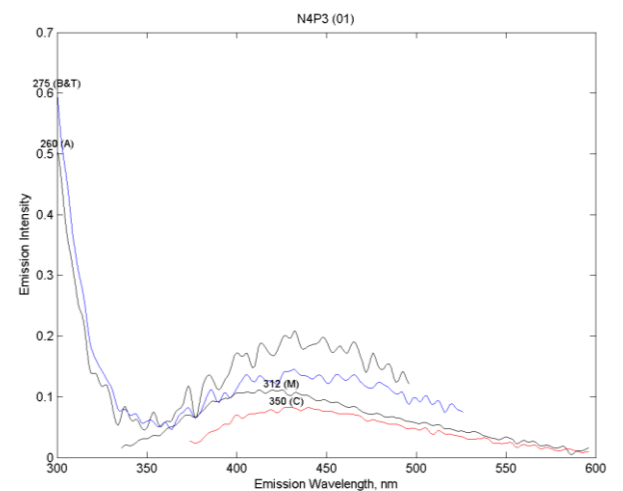
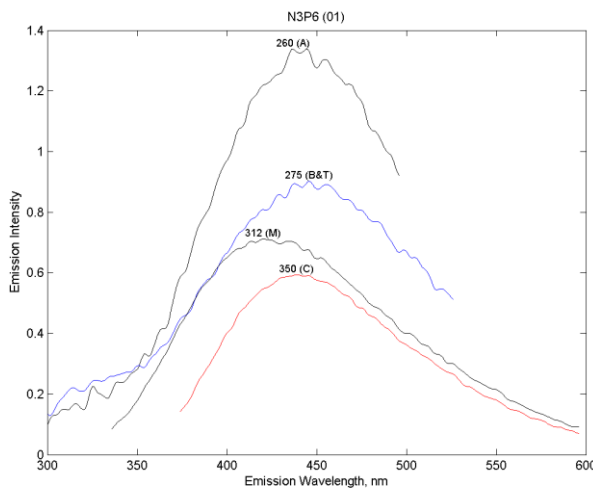
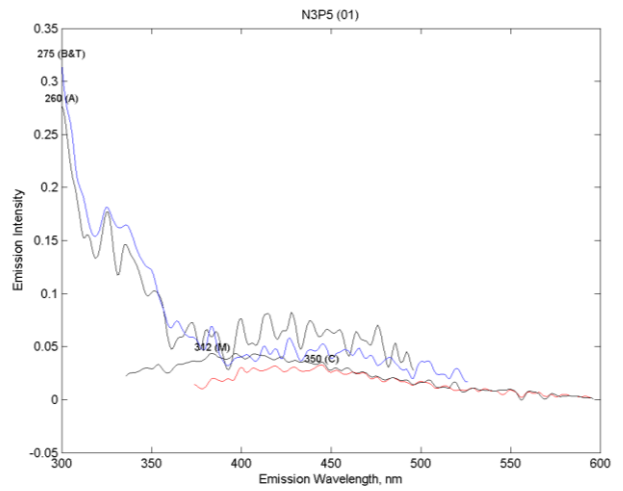
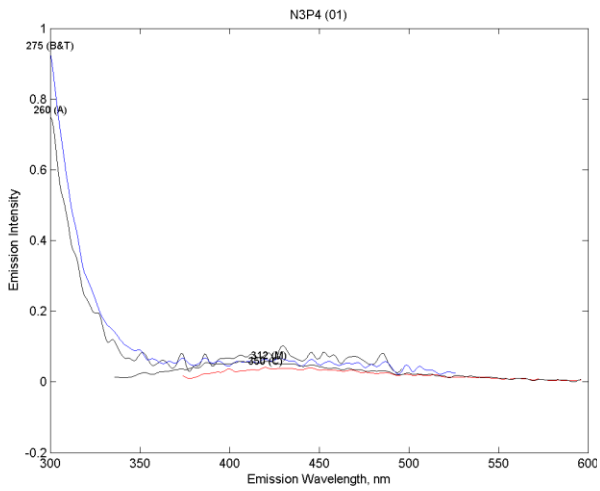
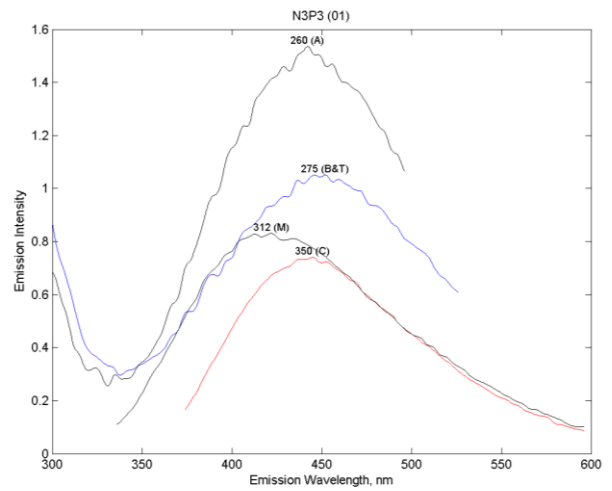
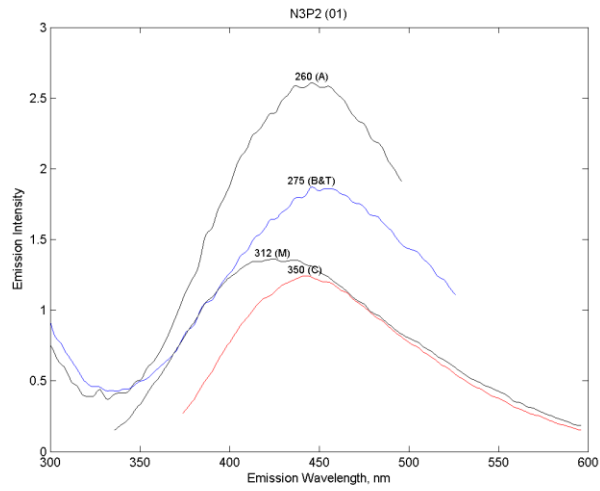


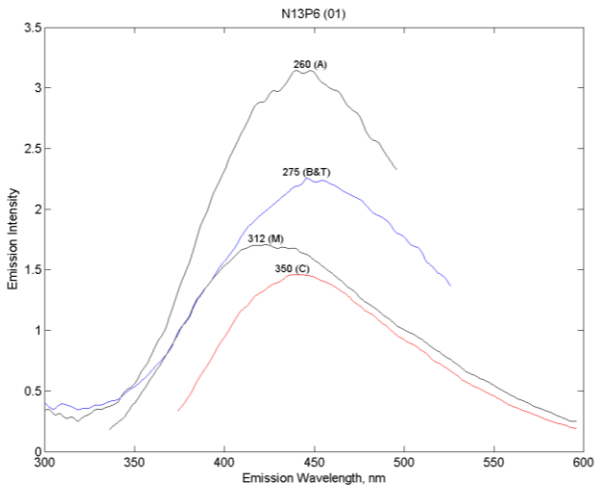
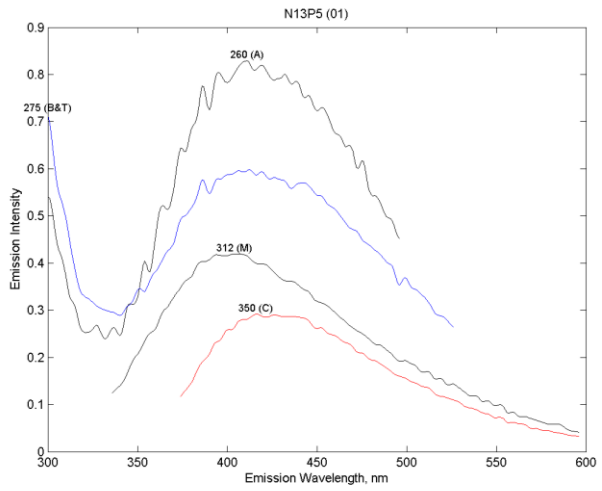
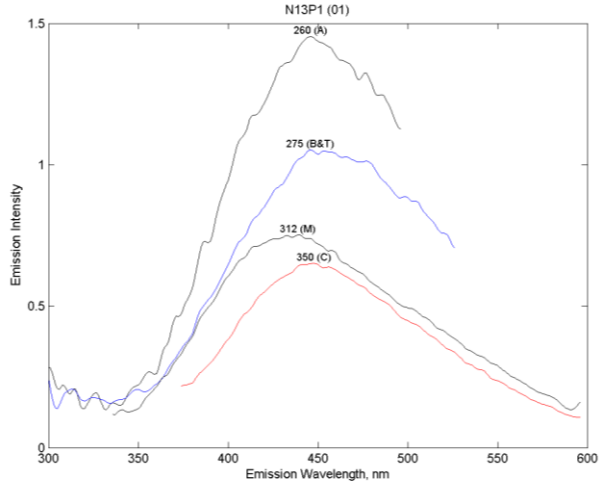
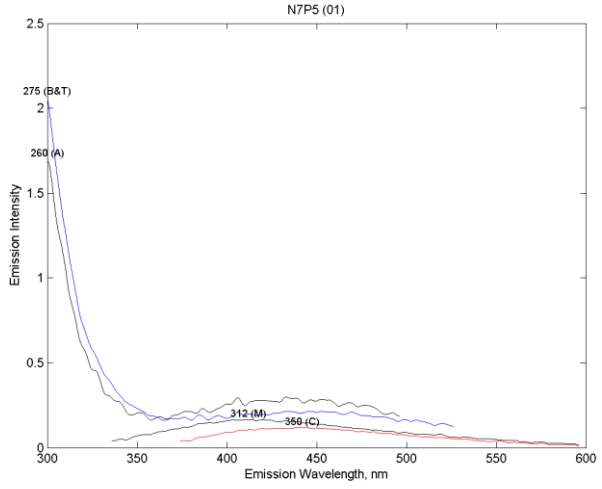
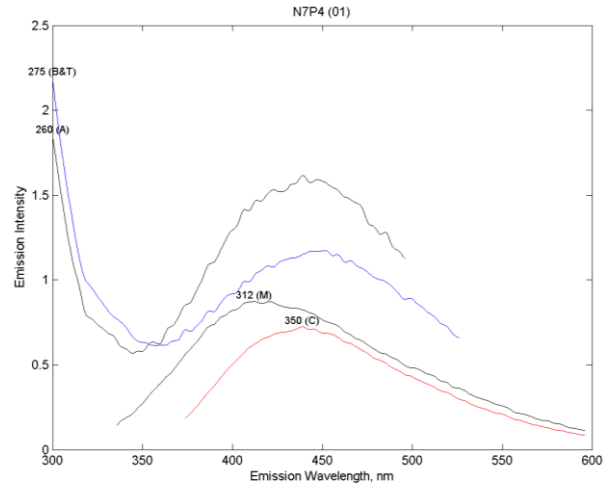
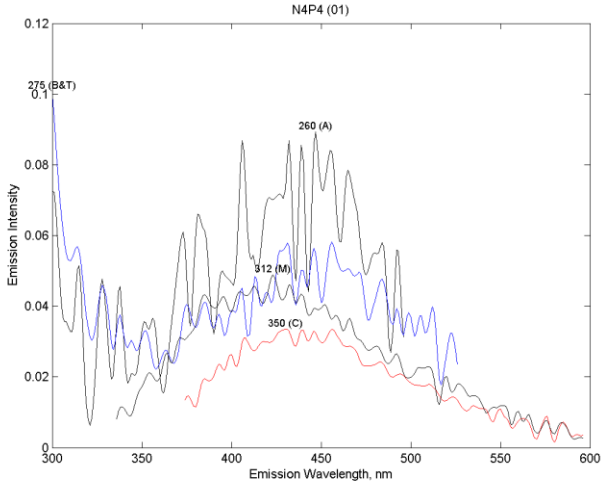


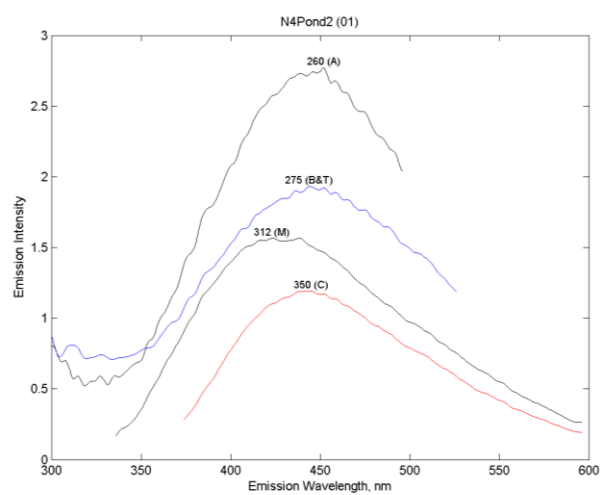
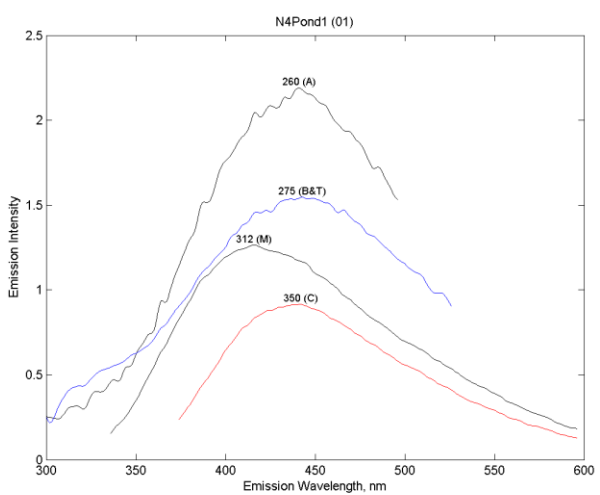
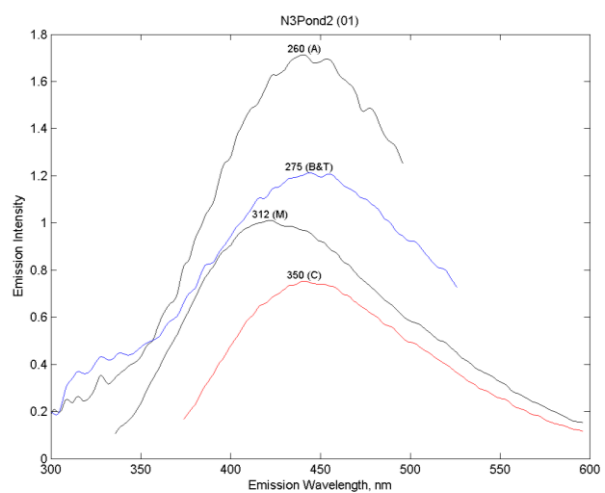
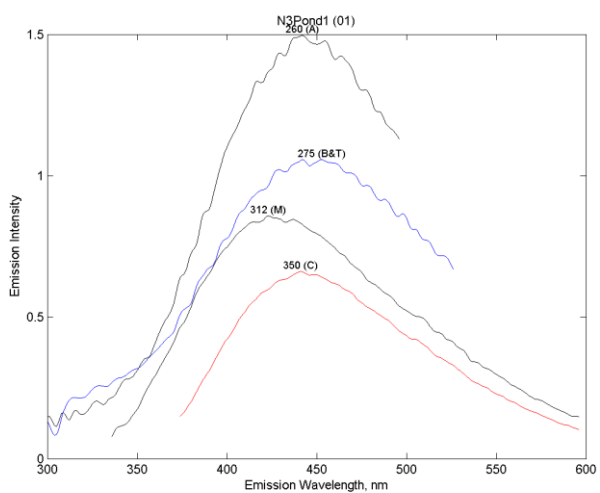
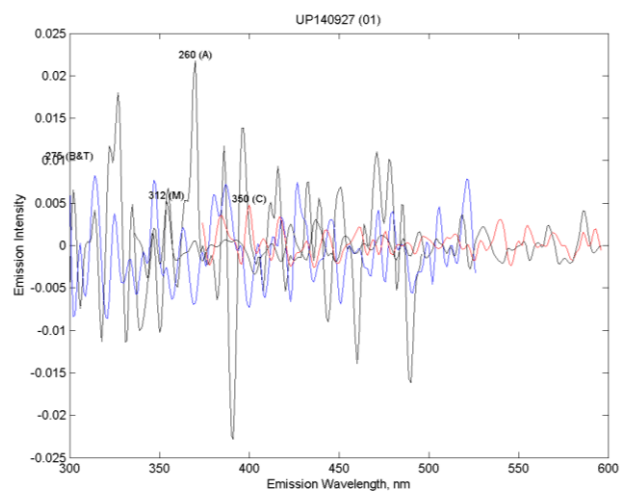
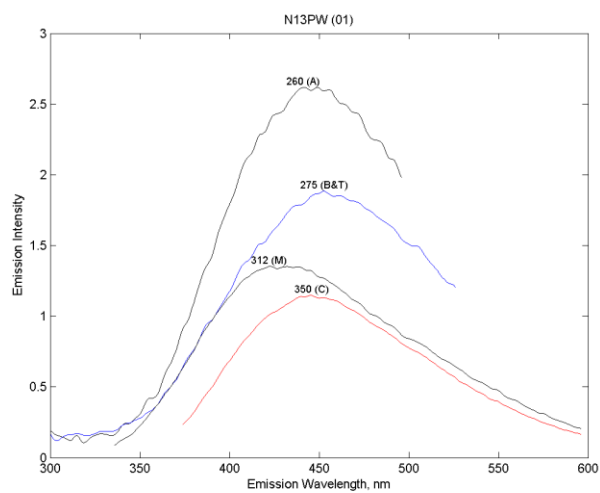


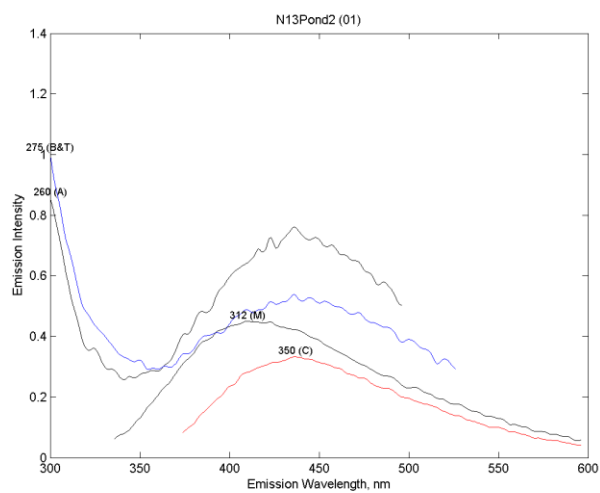
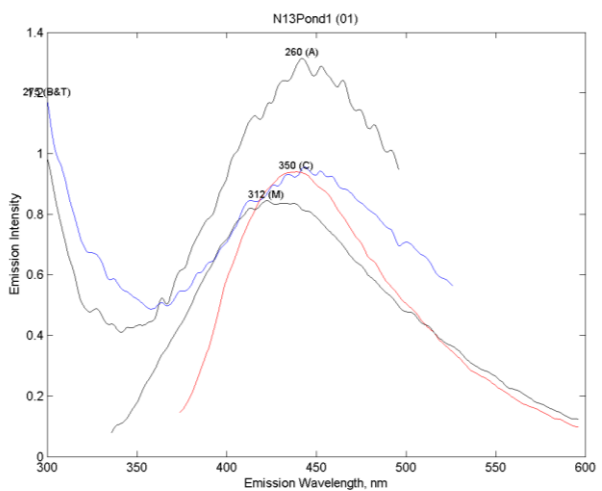
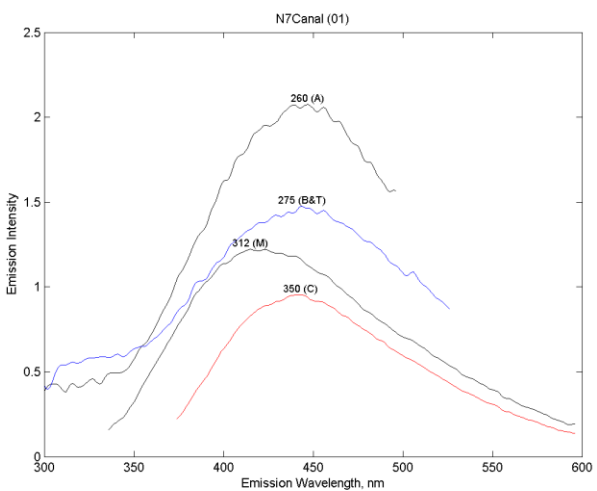
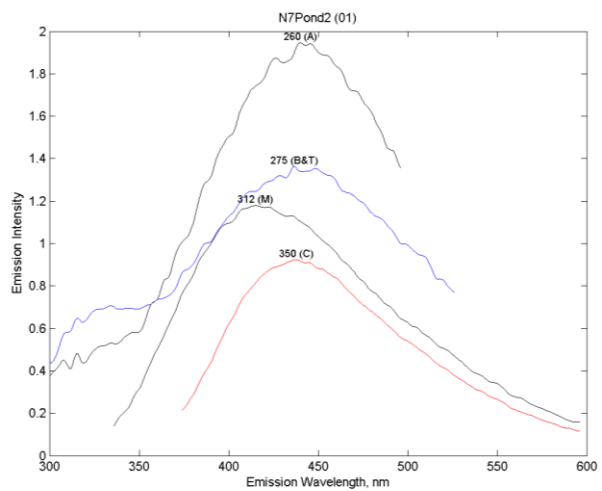
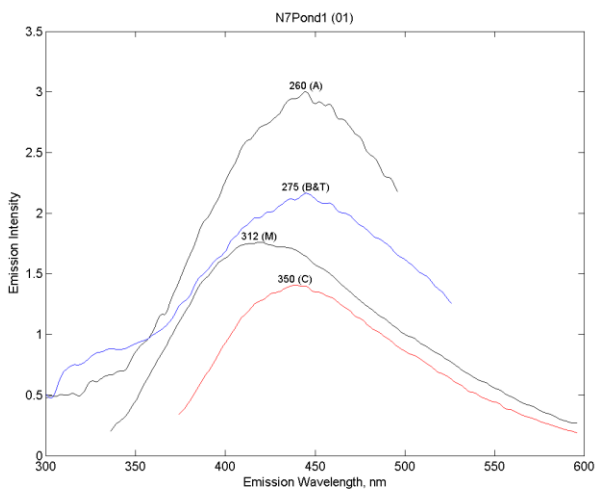


Appendix C6 – Peaks (Third Experiment at 1 sec)









Appendix D – Sample Lithology

Nest 3

Depth1 (m)	Depth2 (m)	Lithology	Screen Length (m)	Depth1 (m)	Depth2 (m)	Lithology	Screen Length (m)
0	6	Clayey sand		123	130	Med. Sand	
6	15	Fine to Med. Sand		130	134	Fine to Med. Sand	
15	18	Med. Sand	P1 (15-17)	134	146	Med. Sand	
18	26	Fine Sand		146	148	Fine to Med. Sand	
26	32	Med. Sand	P2 (27-29)	148	149	Fine Sand	
32	38	Fine to Med. Sand		149	151	Fine to Med. Sand	
38	40	Fine Sand		151	152	Med. to Coarse sand	
40	41	Fine to Med. Sand		152	155	Med. Sand	
41	46	Med. Sand		155	157	Fine to Med. Sand	
46	52	Fine Sand	P3 (50-52)	157	160	Med. Sand	
52	53	Fine to Med. Sand		160	174	Fine to Med. Sand	
53	56	Med. Sand		174	175	Clayey sand	
56	61	Fine to Med. Sand		175	178	Clay	
61	64	Clayey sand		178	180	Clayey sand	
66	67	Clay		180	188	Fine to Med. Sand	
67	70	Fine to Med. Sand		188	192	Med. Sand	
70	72	Med. Sand		192	194	Fine to Med. Sand	
72	81	Fine to Med. Sand		194	198	Med. Sand	
81	84	Med. Sand		198	200	Fine to Med. Sand	
84	85	Clayey sand		200	206	Clayey sand	
85	87	Fine Sand	P4 (85-87)	206	212	Med. Sand	
87	90	Clayey sand		212	215	Clayey sand	
90	99	Med. Sand	P6 (92-95)	215	218	Med. Sand	
99	101	Med. to Coarse sand		218	223	Clayey sand	
101	105	Fine to Med. Sand		223	226	Fine to Med. Sand	
105	108	Clayey sand		226	230	Clayey sand	
108	110	Fine to Med. Sand		230	232	Med. Sand	P5 (231-240)
110	122	Med. Sand		232	233	Med. to Coarse sand	
122	123	Med. to Coarse sand		233	242	Med. Sand	

Nest 4

Depth1 (m)	Depth2 (m)	Lithology	Screen Length (m)
0	9	Clay	
9	12	Clayey Fine Sand	
15	27	Fine Sand	P1 (15-18)
27	30	Fine Sand	P2 (27-30)
30	34	Fine Sand	
34	55	Clay	
55	64	Medium Sand	P3 (55-58)
64	73	Medium Sand to Fine Sand	
73	76	Medium Sand	P4 (73-76)

Nest 7

Depth1 (m)	Depth2 (m)	Lithology	Screen Length (m)	Depth1 (m)	Depth2 (m)	Lithology	Screen Length (m)
0	5	Silty Clay		165	169	Fine Sand	
5	6	Clayey Fine Sand		169	171	Med. To Fine Sand	
6	20	Fine Sand		171	175	Fine Sand	
20	27	Med. To Fine Sand	P2 (21-24)	175	177	Med. To Fine Sand	
27	29	Med. Sand		177	178	Med. Sand	
29	32	Med. To Fine Sand		178	180	Fine to Med. Sand	
32	34	Fine Sand		180	183	Med. Sand	
34	37	Med. To Fine Sand		183	188	Fine to Med. Sand	
37	55	Fine Sand		188	192	Med. Sand	
55	56	Clayey Fine Sand		192	200	Coarse to Med. Sand	
56	58	Very Fine Sand		200	201	Med. Sand	
58	61	Silty Clay		201	203	Med. To Fine Sand	
61	76	Very Fine Sand	P4 (70-73)	203	207	Med. Sand	
76	78	Clayey Very Fine Sand		207	209	Fine to Med. Sand	
78	87	Fine Sand		209	210	Med. Sand	
87	88	Very Fine Sand		210	212	Coarse to Med. Sand	
88	93	Fine Sand		212	213	Fine to Med. Sand	
93	101	Med. To Fine Sand		213	215	Med. To Fine Sand	
101	107	Fine Sand		215	221	Med. Sand	
107	108	Med. To Fine Sand		221	223	Med. To Fine Sand	
108	110	Fine Sand		223	224	Fine to Med. Sand	
110	114	Med. To Fine Sand		224	226	Med. To Fine Sand	P5 (223-232)
114	131	Med. Sand		226	229	Med. Sand	
131	136	Coarse to Med. Sand		229	230	Fine to Med. Sand	
136	152	Med. Sand		230	232	Med. To Fine Sand	
152	165	Med. To Fine Sand					

Nest 13

Depth1 (m)	Depth2 (m)	Lithology	Screen Length (m)	Depth1 (m)	Depth2 (m)	Lithology	Screen Length (m)
0	3	Fine Sand		101	102	Fine to Med. Sand	
3	17	Fine to Med. Sand	P1 (12-14)	102	110	Med. Sand	
17	18	Med. Sand		110	111	Fine to Med. Sand	
18	20	Fine to Med. Sand		111	117	Med. Sand	
20	26	Med. Sand		117	119	Fine to Med. Sand	
26	37	Fine to Med. Sand	P2 (31-33)	119	136	Med. Sand	P5 (122-123)
37	38	Silty Clay		136	139	Fine Sand	
38	40	Fine to Med. Sand		139	154	Med. Sand	
40	41	Silty Sand		154	162	Med. to Coarse Sand	
41	43	Fine Sand		162	163	Med. Sand	
43	46	Fine to Med. Sand		163	166	Med. to Coarse Sand	
46	49	Very fine Sand		166	168	Med. Sand	
49	50	Silty Sand		168	169	Fine to Med. Sand	
50	52	Very fine Sand		169	175	Med. Sand	
52	53	Fine Sand		175	177	Fine to Med. Sand	
53	56	Clayey Sand		177	181	Med. Sand	
56	58	Silty Sand		181	183	Fine to Med. Sand	
58	61	Fine Sand		183	184	Fine Sand	
61	63	Fine to Med. Sand		184	192	Med. Sand	
63	76	Med. Sand		192	194	Fine to Med. Sand	
76	79	Fine to Med. Sand		194	198	Med. Sand	
79	81	Fine Sand		198	203	Fine to Med. Sand	
81	84	Fine to Med. Sand	P3 (83-85)	203	204	Med. Sand	
84	88	Med. to Coarse Sand		204	206	Fine Sand	
88	90	Med. Sand		206	209	Fine to Med. Sand	
90	91	Med. to Coarse Sand		209	210	Med. Sand	
91	93	Med. Sand		210	230	Clayey Sand	P6 (228-237)
93	95	Fine to Med. Sand		230	242	Med. Sand	
95	101	Clayey Sand					

Appendix E – Mineral Saturation Indices (MSI)

Sample ID	Anhydrite Q/K	CaCl ₂ ^2H ₂ O Q/K	Epsomite Q/K	Gypsum Q/K	Halite Q/K	MgCl ₂ ^2H ₂ O Q/K	Mirabilite Q/K	SrCl ₂ (c) Q/K	SrCl ₂ ^2H ₂ O Q/K	Sylvite Q/K
N3P1	2.54E-04	2.56E-18	3.39E-07	3.82E-04	2.25E-08	1.54E-23	4.13E-10	3.08E-20	1.35E-15	7.14E-09
N3P2		3.72E-16			8.53E-07	4.27E-21		6.73E-18	2.95E-13	1.34E-07
N3P3		7.95E-16			2.16E-06	1.19E-20		2.42E-17	1.05E-12	1.52E-07
N3P4		3.64E-16			1.23E-06	4.68E-21		1.08E-17	4.68E-13	7.40E-08
N3P5	3.41E-04	8.14E-16	9.41E-07	5.14E-04	1.89E-06	1.02E-20	1.23E-08	2.35E-17	1.02E-12	1.09E-07
N3P6	3.27E-04	3.10E-16	7.01E-07	4.93E-04	8.28E-07	3.00E-21	5.94E-09	5.37E-18	2.34E-13	9.10E-08
N4P1	8.12E-05	7.34E-19	4.39E-07	1.22E-04	6.98E-09	1.79E-23	4.44E-11	1.66E-20	7.24E-16	6.75E-09
N4P2		7.26E-15			1.11E-05	1.49E-19		2.35E-16	1.02E-11	8.96E-07
N4P3	0.002184	5.07E-15	8.13E-06	0.003283	7.97E-06	8.58E-20	2.22E-07	1.31E-16	5.62E-12	3.39E-07
N4P4	0.005462	1.34E-14	2.05E-05	0.008202	1.53E-05	2.31E-19	7.62E-07	4.24E-16	1.82E-11	5.67E-07
N7P2	3.69E-04	3.47E-18	7.92E-07	5.56E-04	4.22E-08	3.36E-23	1.56E-09	4.79E-20	2.09E-15	1.23E-08
N7P4	2.17E-04	6.22E-17	6.46E-07	3.27E-04	3.71E-07	8.34E-22	3.96E-09	2.29E-18	1.00E-13	4.23E-08
N7P5	9.21E-05	6.78E-18	3.70E-07	1.39E-04	1.72E-07	1.23E-22	3.30E-09	3.34E-19	1.45E-14	2.21E-08
N13P1	9.71E-05	3.09E-20	1.65E-07	1.46E-04	7.98E-10	2.37E-25	1.65E-11	4.35E-22	1.91E-17	1.35E-09
N13P2	7.39E-05	1.16E-16	2.74E-07	1.11E-04	9.44E-07	1.94E-21	4.67E-09	2.37E-18	1.02E-13	1.14E-07
N13P3	6.82E-05	5.25E-16	2.13E-07	1.03E-04	2.62E-06	7.40E-21	7.32E-09	2.12E-17	9.12E-13	1.58E-07
N13P5	2.66E-05	9.07E-18	8.09E-08	4.00E-05	3.52E-07	1.25E-22	2.99E-09	5.99E-19	2.63E-14	1.84E-08
N13P6	8.82E-05	1.78E-17	1.88E-07	1.33E-04	1.32E-07	1.71E-22	7.06E-10	2.27E-19	9.77E-15	3.12E-08
N13PW	8.05E-05	3.62E-20	1.26E-07	1.21E-04	9.76E-10	2.55E-25	1.75E-11	4.07E-22	1.78E-17	1.13E-09
N3Pond1	1.14E-04	5.82E-20	2.92E-07	1.71E-04	2.20E-09	6.73E-25	7.79E-11	1.31E-21		3.10E-09
N3Pond2	2.67E-04	2.54E-19	4.92E-07	4.02E-04	4.51E-09	2.11E-24	1.76E-10	3.86E-21		5.72E-09
N4Pond1	5.40E-04	2.23E-18	1.30E-06	8.14E-04	1.70E-08	2.41E-23	5.76E-10	3.16E-20		3.07E-08
N4Pond2	9.75E-05	1.57E-18	3.65E-07	1.47E-04	1.91E-08	2.66E-23	1.86E-10	3.11E-20		4.53E-08
N7Pond1	6.01E-04	1.31E-17	1.52E-06	9.05E-04	9.55E-08	1.49E-22	3.45E-09	2.37E-19		1.03E-07
N7Pond2	0.001624	3.22E-18	1.68E-06	0.002447	2.59E-08	1.51E-23	2.79E-09	4.00E-20		1.91E-08
N7Canal	1.54E-04	4.39E-19	4.20E-07	2.32E-04	8.62E-09	5.40E-24	2.14E-10	7.87E-21		1.09E-08
N13Pond1	2.43E-05	3.61E-21	5.78E-08	3.66E-05	5.69E-10	3.87E-26	1.79E-11	5.69E-23		7.21E-10
N13Pond2	2.35E-04	2.84E-19	5.50E-07	3.53E-04	3.79E-09	3.01E-24	9.76E-11	3.59E-21		3.43E-09

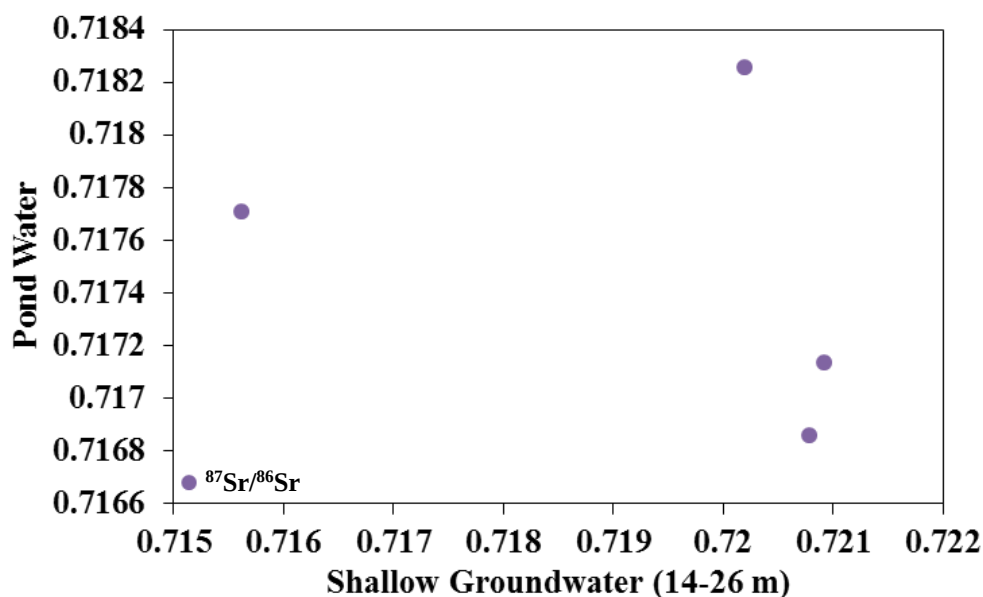
Appendix F - Water Isotopic Composition

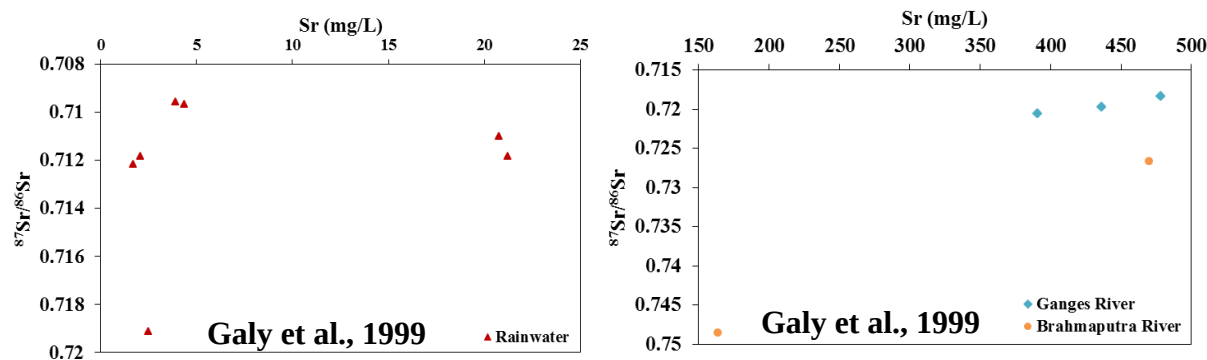
Appendix F1 - Stable Isotopes (δ^2H and $\delta^{18}O$)

Sample ID	Depth (m)	δ^2H (‰)	$\delta^{18}O$ (‰)	Local Meteoric Water Line (LMWL) Data				
				Sample ID	Location	Time	δ^2H (‰)	$\delta^{18}O$ (‰)
N3/P1	17	-16	-2.5	RW-1	Savar	Apr-06	5	-1.3
N3/P2	29	-21	-3.4	RW-2	Savar	May-06	-9	-3.3
N3/P3	52	-19	-3.2	RW-3	Savar	Jun-06	-15	-3.9
N3/P4	87	-18	-3	RW-4	Savar	Jul-06	-39	-6.5
N3/P5	240	-17	-2.7	RW-5	Savar	Aug-06	-57	-8.7
N3/P6	95	-17	-2.9	RW-6	Savar	Sep-06	-47	-7.5
N4/P1	17	-12	-1.3	RW-7	Savar	Feb-07	-3	-2.1
N4/P2	30	-21	-3.5	RW-8	Savar	Mar-07	21	1.4
N4/P3	56	-14	-2.7	RW-9	Savar	Apr-07	21	2.2
N4/P4	75	-16	-3.2	RW-10	Savar	May-07	-10	-2.5
N7/P2	26	-22	-3.4	RW-11	Savar	Jun-07	-25	-4.4
N7/P4	75	-15	-2.9	RW-12	Savar	Jul-07	-37	-6.2
N7/P5	232	-13	-2.6	RW-13	Savar	Aug-07	-47	-7.3
N13/P1	14	-10	-2.4	RW-14	Savar	Sep-07	-53	-7.6
N13/P2	33	-36	-5.5	LMWL data from Majumder et al., 2011, pg: 4588 Location: Savar station (NW Bangladesh) Time frame: April, 2006-September, 2007				
N13/P3	85	-19	-3.4					
N13/P5	237	-15	-3					
N13/P6	123	-11	-2.1					
N13/PW	21	-11	-2.4					
N3/Pond1		-8	-2.2					
N3/Pond2		-8	-1.2					
N4/Pond1		-1	0					
N4/Pond2		-1	0					
N7/Pond1		-6	-1					
N7/Pond2		-6	-1					
N7/Canal		-9	-1.3					
N13/Pond1		-12	-2.8					
N13/Pond2		-6	-1.3					

Appendix F2 - $\delta^{13}\text{C}$, C-14 and $\text{Sr}^{87}/\text{Sr}^{86}$

Sample ID	Depth (m)	$\delta^{13}\text{C}$ (‰)	Sample ID	Depth (m)	C-14 (BP)	Conventional Age
N3/P1	17	-16.7	N3/P1	17	1000	1000 +/- 40 BP
N3/P2	29	-13.1	N4/P1	17	300	300 +/- 40 BP
N3/P3	52	-13.1	N7/P2	26	1350	1350 +/- 40 BP
N3/P4	87	-17.5	N13/P1	14	65	Post 1950
N3/P5	240	-17.7				
N3/P6	95	-12.6	QC 1 Sample ID	IAEA C7	QC 2 Sample ID	IAEA C8
N4/P1	17	-6.4	QC Expected Value	49.35 +/- 0.50 pMC	QC Expected Value	15.05 +/- 0.20 pMC
N4/P2	30	-3.2	QC Measured Value	49.30 +/- 0.30 pMC	QC Measured Value	15.00 +/- 0.10 pMC
N4/P3	56	-9.3				
N4/P4	75	-9.3				
N7/P2	26	-12.0				
N7/P4	75	-11.9	Sample ID	Depth (m)	$^{87}\text{Sr}/^{86}\text{Sr}$	+/-2s
N7/P5	232	-7.6	N3/P1	17	0.720781	0.000003
N13/P1	14	-16.5	N4/P1	17	0.715618	0.000003
N13/P2	33	-2.3	N7/P2	26	0.720919	0.000003
N13/P3	85	-6.4	N13/P1	14	0.720195	0.000004
N13/P5	237	-7.9	N3/Pond1		0.71686	0.000005
N13/P6	123	-11.0	N4/Pond1		0.717708	0.000003
N13/PW	21	-15.0	N7/Pond1		0.717132	0.000003
N3/Pond2		-9	N13/Pond1		0.718255	0.000003
N4/Pond1		-8.3				
N7/Pond1		-9.5				
N13/Pond1		-12.2				





Appendix G – Fecal Indicator Bacteria (*E. coli*)

Appendix G1 – Single Test

Single				Total Coliform					<i>E. coli</i>				
Nest	Piezometer	Date	Dilution Factor	Big Wells (+)	Small Wells (+)	95L	MPN/100 mL	95H	Big Wells (+)	Small Wells (+)	95L	MPN/100 mL	95H
3	Pond 1	06/30/14	× 10	49	30	401.2	613.1	879.2	21	3	19.4	30.5	44.8
3	Pond 1	06/30/14	× 100	49	47	1630.4	2419.6	4716.1	47	12	119.5	172.3	242.2
3	Pond 1	06/30/14	Filtered	49	47	1630.4	2419.6	4716.1	48	14	145.5	209.8	301.1
3	Pond 2	06/30/14	× 10	49	48	1439.5	>2419.6	infinite	48	18	172.6	248.9	350.2
3	Pond 2	06/30/14	× 100	49	37	620.5	920.8	1282.0	24	2	23.3	34.5	50.1
3	Pond 2	06/30/14	Filtered	49	48	1439.5	>2419.6	infinite	15	3	12.6	21.1	32.6
7	2	06/25/14	Filtered	49	20	218.9	344.8	520.7	8	1	4.5	9.7	17.2
7	2	06/28/14	Filtered	49	16	185.7	275.5	416.8	10	2	7.1	13.2	22.0
7	Pond 1	06/24/14	× 10	49	48	1439.5	>2419.6	infinite	48	47	703.6	960.6	1245.4
7	Pond 1	06/24/14	× 100	48	32	341.2	478.6	652.5	48	17	165.2	238.2	340.8
7	Pond 1	06/25/14	Filtered	49	48	1439.5	>2419.6	infinite	35	7	50.1	70.3	94.6
7	Pond 1	06/28/14	× 10	49	48	1439.5	>2419.6	infinite	48	42	553.4	755.6	993.9
7	Pond 1	06/28/14	× 100	49	48	1439.5	>2419.6	infinite	40	9	70.2	95.9	128.9
7	Pond 2	06/28/14	× 10	49	48	1439.5	>2419.6	infinite	45	11	99.5	139.6	190.0
7	Pond 2	06/28/14	× 100	49	18	195.3	307.6	471.2	9	3	6.8	13.1	21.8
7	Pond 2	06/28/14	Filtered	47	48	546.6	691.0	886.5	45	23	151.3	201.2	260.5
7	Canal	06/24/14	× 10	49	48	1439.5	>2419.6	infinite	48	18	172.6	248.9	350.2
7	Canal	06/24/14	× 100	49	19	206.6	325.5	498.1	28	3	30.6	44.1	62.5
7	Canal	06/24/14	Filtered	49	48	1439.5	>2419.6	infinite	28	1	27.7	41.0	58.8
13	1	06/21/14	Filtered	25	0	22.0	33.6	48.9	1	0	0.1	1.0	5.5
13	Pond 1	06/24/14	Filtered	49	48	1439.5	>2419.6	infinite	48	31	334.6	456.9	618.9
13	Pond 1	06/26/14	× 10	49	43	924.9	1413.6	2101.6	48	42	553.4	755.6	993.9
13	Pond 1	06/26/14	× 100	49	32	449.3	686.7	974.4	46	11	108.0	151.5	207.8
13	Pond 2	06/26/14	× 10	49	22	245.9	387.3	567.0	9	3	6.8	13.1	21.8
13	Pond 2	06/26/14	× 100	45	14	112.0	152.9	206.2	5	2	2.9	7.3	13.9
13	Pond 2	06/24/14	Filtered	49	48	1439.5	>2419.6	infinite	48	31	334.6	456.9	618.9

Appendix G2 – Duplicate Test

Duplicate				Total Coliform							E. coli						
Nest	Piezometer	Date	Dilution Factor	LARGE1	SMALL1	LARGE2	SMALL2	MPN/100 mL	LB	UB	LARGE1	SMALL1	LARGE2	SMALL2	MPN/100 mL	LB	UB
3	1	06/30/14	× 1	49	29	46	12	238.4	183.9	309.0	6	1	0	0	3.6	1.7	7.6
3	2	06/30/14	× 1	44	7	49	16	155.7	123.6	196.2	4	1	3	8	8.3	5.1	13.7
7	2	06/25/14	× 1	25	1	28	3	39.5	30.3	51.4	1	0	1	0	1.0	0.3	4.0
7	2	06/28/14	× 1	47	26	47	7	193.2	151.4	246.6	10	6	3	0	10.2	6.5	16.0
7	4	06/24/14	× 1	1	1	8	3	6.8	3.9	11.8	0	0	0	0	<0.5	<0.07	<3.564
7	5	06/24/14	× 1	46	12	49	13	176.9	139.4	224.5	3	1	4	0	4.1	2.1	8.3
13	1	06/19/14	× 1	27	1	3	0	18.2	12.8	25.9	0	0	0	0	<0.5	<0.07	<3.564
13	1	06/21/14	× 1	31	3	48	10	86.4	69.2	107.9	1	0	7	0	4.2	2.1	8.3
13	2	06/24/14	× 1	49	24	33	27	153.3	121.8	193.0	30	9	33	21	74.1	59.1	92.9
13	3	06/24/14	× 1	16	2	3	1	12.1	8.0	18.4	3	0	2	0	2.6	1.1	6.1
13	5	06/29/14	× 1	49	15	47	16	209.6	163.2	269.1	8	1	7	0	8.6	5.3	14.1
13	6	06/26/14	× 1	49	25	46	16	238.4	183.9	309.0	16	3	10	1	17.2	12.0	24.7
13	Private Well	06/26/14	× 1	45	12	47	17	164.1	129.9	207.3	4	0	26	0	17.6	12.3	25.1
13	Pond 1	06/20/14	× 100	49	30	49	12	320.9	243.8	422.5	20	12	15	16	39.1	30.1	51.0
13	Pond 2	06/24/14	× 100	47	3	47	2	120.9	96.8	151.0	33	3	27	4	49.6	38.8	63.4

Appendix G3 – Summary of Fecal Indicator Bacteria (*E. coli*) Results

Sample ID	Depth (m)	Total Coliform	<i>E. coli</i> (MPN/100 mL)	<i>E. coli</i> DNA (Copies/100 mL)
N3P1 (×1)	17	238	4	No Sample
N3P2 (×1)	29	156	8	No Sample
N7P2 (×1)	26	193	10	<11
N7P5 (×1)	232	177	4	<11
N13P1 (×1)	14	86	4	<11
N13P3 (×1)	85	12	3	<11
N13P5 (×1)	237	210	9	<11
N13P6 (×1)	123	238	17	<11
N13PW (×1)	21	164	18	<11
N3Pond1 (×100)		241,957	17,233	No Sample
N3Pond2 (×100)		92,084	3,451	No Sample
N7Pond1 (×100)		47,860	23,822	116,138
N7Pond2 (×100)		308	1,310	16,981
N7Canal (×100)		32,554	4,412	13,538
N13Pond1 (×100)		68,667	15,152	27,521
N13Pond2 (×100)		15,286	731	No Sample

Appendix G4 – qPCR Results

Analysis Parameters:

Type of Application: Quantification

Dye(s):FAM

Inverted Data: OFF

Threshold setting: Noiseband

Threshold level: 289

Baseline setting: Automatic

Drift Correction: OFF

Standard Curve Parameters:

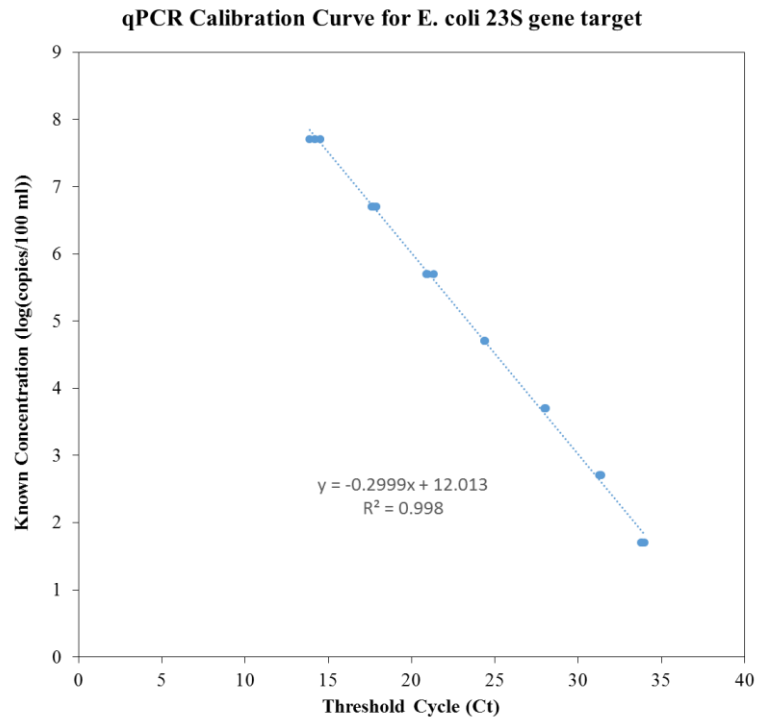
Slope: -3.328

Y-Intercept: 37.70

Efficiency: 1.00

R²: 0.998

*BDL = Below Detection Limit



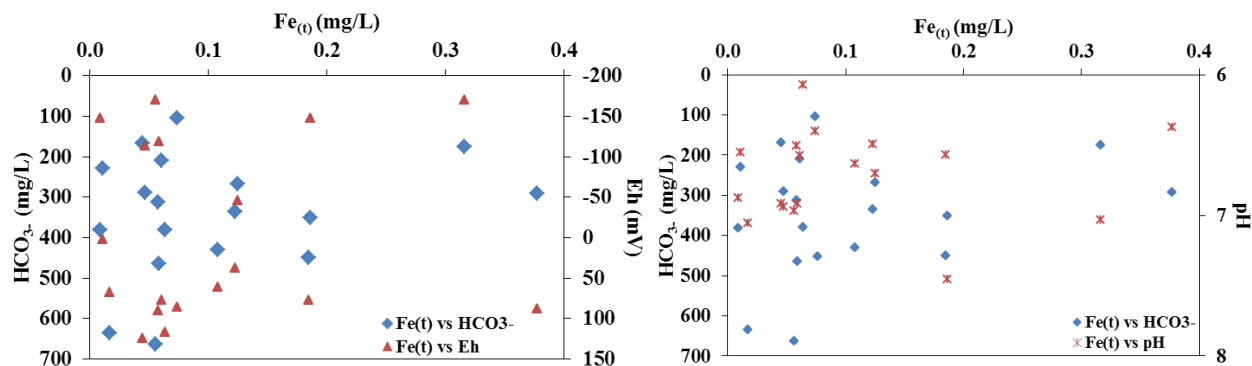
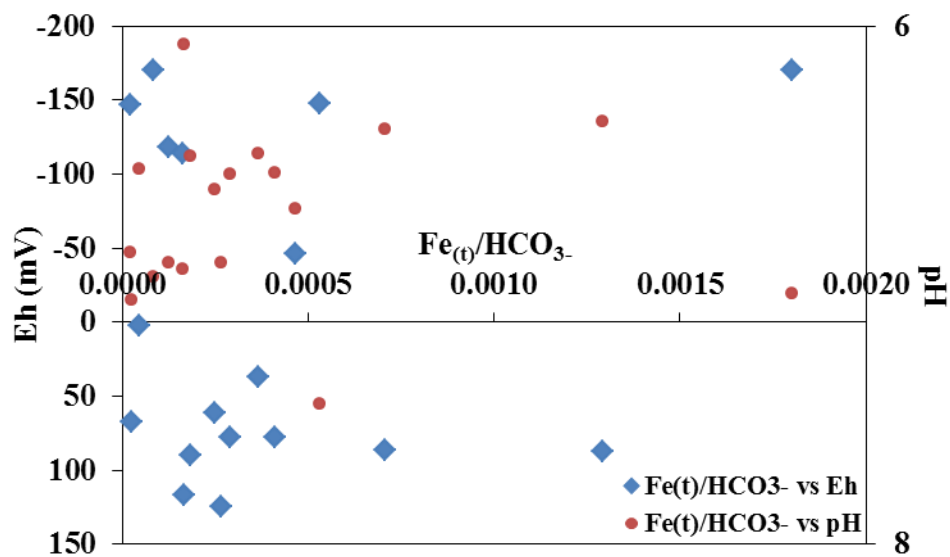
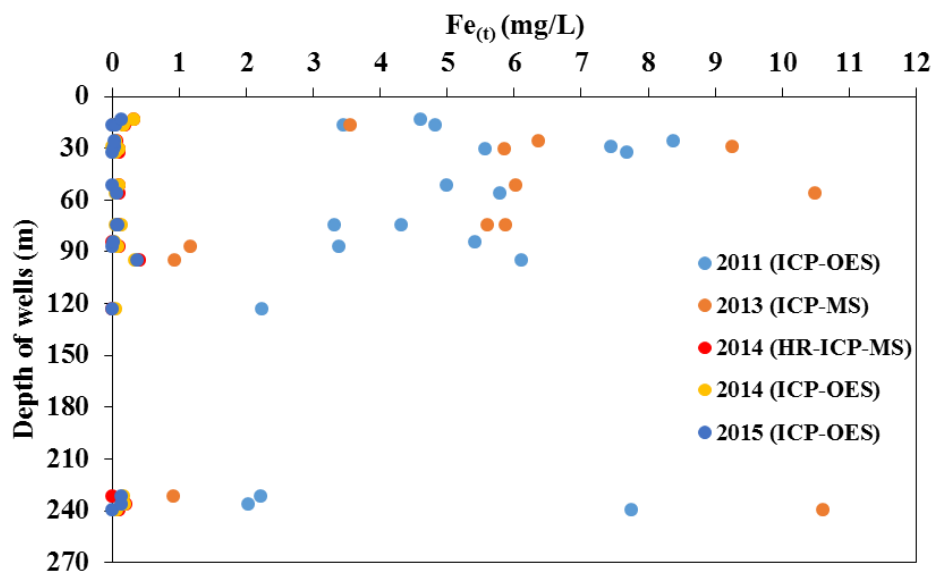
Position in 96-well qPCR plate										Important Numbers for Calculating Concentration									
Sample ID	Sample Date	Ct (cycles)	Ct Mean	FAM	Ct Dev	FAM	Standard copies/ml	Log ₁₀ transformed copies/ml	Detected Concentrations (copies/ml)	Detected Concentrations (copies/ml)	Copies/sample	Volume Filtered (ml)	Concentration (copies/100 ml)	Direction Limit (copies/100 ml)	Imported Numbers for Calculating Concentration	Value			
A1	10-7	13.9					5000000	7.698570004	5000000						Sample Volume in Box (ul)	5			
A2	10-7	14.2					5000000	7.698570004	5000000						Total Sample Volume (ul)	50			
A3	10-7	14.2					5000000	7.698570004	5000000						Blank	50			
A4	10-6	17.73	17.74				5000000	6.698570004	5000000						Blank	50			
A5	10-6	17.61	17.74	0.14			5000000	6.698570004	5000000						Blank	50			
A6	10-6	17.89	17.74	0.14			5000000	6.698570004	5000000						Blank	50			
A7	10-6	17.89	17.74	0.14			5000000	6.698570004	5000000						Blank	50			
A8	10-5	20.9	21.08	0.23			500000	5.698570004	500000						Blank	50			
A9	10-5	21	21.08	0.23			500000	5.698570004	500000						Blank	50			
A10	10-4	24.48	24.39	0.03			50000	4.698570004	50000						Blank	50			
A11	10-4	24.42	24.39	0.03			50000	4.698570004	50000						Blank	50			
B1	10-3	28.01	28.04	0.02			5000	3.698570004	5000						Blank	50			
B2	10-3	28.06	28.04	0.02			5000	3.698570004	5000						Blank	50			
B3	10-3	28.05	28.04	0.02			5000	3.698570004	5000						Blank	50			
B4	10-2	31.29	31.35	0.06			500	2.698570004	500						Blank	50			
B5	10-2	31.29	31.35	0.06			500	2.698570004	500						Blank	50			
B6	10-2	31.4	31.35	0.06			500	2.698570004	500						Blank	50			
B7	10-1	34					50	1.698570004	50						Blank	50			
B8	10-1	33.63					50	1.698570004	50						Blank	50			
B9	10-1	33.63					50	1.698570004	50						Blank	50			
B10	NTC	35.62						1.30662							Blank				
B11	NTC	35.62						1.30662							Blank				
B12	NTC	34.63						1.567483							Blank				
C7	N7P2	41814	35					1.3165							Blank				
C8	N7P2	41814	35					1.3165							Blank				
C9	N7P2	41814	35.31					1.42531							Blank				
C10	N7P2	41814	35.31					1.42531							Blank				
C1	N7P5	41813	36.85					1.261565							Blank				
C2	N7P5	41813	36.85					1.021665							Blank				
C3	N7P5	41813	35.54					3.35554							Blank				
C4	N7P5	41813	35.54					3.35554							Blank				
C5	N7P5	41813	35.54					3.35554							Blank				
F1	N7Pend1	41813	29.22					3.249622							Blank				
F2	N7Pend1	41813	28.99					3.318899							Blank				
F3	N7Pend1	41813	31.98					2.421198							Blank				
F4	N7Pend1	41813	31.98					2.421198							Blank				
F5	N7Pend1	41813	31.98					2.421198							Blank				
F6	N7Pend1	41813	32.32					2.329232							Blank				
F7	N7Pend1	41813	32.32					2.329232							Blank				
F8	N7Pend1	41813	32.32					2.329232							Blank				
F9	N7Pend1	41813	31.88					2.452188							Blank				
F10	N7Pend1	41813	31.88					2.452188							Blank				
F11	N7Pend1	41813	31.88					2.452188							Blank				
F12	N7Pend1	41813	31.88					2.452188							Blank				
F13	N7Pend1	41813	31.88					2.452188							Blank				
F14	N7Pend1	41813	31.88					2.452188							Blank				
F15	N7Pend1	41813	31.88					2.452188							Blank				
F16	N7Pend1	41813	31.88					2.452188							Blank				
F17	N7Pend1	41813	31.88					2.452188							Blank				
F18	N7Pend1	41813	31.88					2.452188							Blank				
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F24	N7Pend1	41813	31.88					2.452188							Blank				
F25	N7Pend1	41813	31.88					2.452188							Blank				
F26	N7Pend1	41813	31.88					2.452188							Blank				
F27	N7Pend1	41813	31.88					2.452188							Blank				
F28	N7Pend1	41813	31.88					2.452188							Blank				
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F62	N7Pend1	41813	31.88					2.452188							Blank				
F63	N7Pend1	41813	31.88					2.452188							Blank				
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F65	N7Pend1	41813	31.88					2.452188							Blank				
F66	N7Pend1	41813	31.88					2.452188							Blank				
F67	N7Pend1	41813	31.88					2.452188							Blank				
F68	N7Pend1	41813	31.88					2.452188		</									

Appendix H - Water Chemistry

Appendix H1 - Cation

Analyte Symbol	Ag	Al	As	B	Ba	Be	Bi	Ca	Ce	Co	Cd	Cr	Cs	Cu	Dy	Er	Eu	Ga	Gd	Ge	Hf	Hg	Ho	In	K	La	Li	Lu	Mg	
Unit Symbol	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	
Detection Limit	0.002	0.5	0.02	0.1	0.01	0.001	0.001	5	0.001	0.001	0.001	0.01	0.001	0.05	0.0005	0.00005	0.00005	0.001	0.00005	0.001	0.00005	0.05	0.00001	0.0001	0.0001	1	0.001	0.05	0.00005	0.2
N3P1	0.082	22.8	407	119	44.7	0.001	<0.001	130000	0.006	0.688	0.017	0.84	0.01	1.33	0.009	0.00083	0.00083	0.00083	0.00083	0.00083	0.00083	0.00083	0.00083	0.00083	0.00083	0.00083	0.00083	0.00083	0.00083	0.00083
N3P2	0.27	2.7	82.5	137	104	<0.001	<0.001	87800	0.009	0.282	0.006	1.32	0.084	0.69	0.0008	0.00096	0.00096	0.00096	0.00096	0.00096	0.00096	0.00096	0.00096	0.00096	0.00096	0.00096	0.00096	0.00096	0.00096	0.00096
N3P3	0.364	3.8	16	167	93	<0.001	<0.001	65800	0.01	0.226	0.006	0.97	0.045	0.6	0.0011	0.0007	0.00769	<0.001	0.00407	0.029	0.00056	0.36	0.00046	0.0003	5940	4.11	5.85	0.00016	35100	
N3P4	0.462	4.3	0.25	81.5	33.1	0.01	<0.001	54200	0.011	3.63	0.073	1.34	0.026	0.74	0.0026	0.00083	0.00492	<0.001	0.00168	0.039	0.00093	0.64	0.00067	<0.0001	4110	2.32	17.6	0.00064	25200	
N3P5	0.367	1.7	0.23	78.8	28.6	0.009	<0.001	55900	0.004	4.18	0.037	0.95	<0.001	0.37	0.0008	0.00067	0.0011	<0.001	0.00044	0.034	<0.00005	0.54	0.0001	0.0002	3800	1.4	17.5	0.00066	25100	
N3P6	0.5	19.9	7.07	100	75.5	0.002	<0.001	69200	0.002	0.224	0.004	1.32	0.049	0.57	0.0098	0.00046	0.00707	0.024	0.00756	0.08	<0.00005	0.41	0.00178	<0.0001	6280	10.9	6.91	0.00091	23700	
N3Pond1	0.733	12.9	4.97	48.5	17.4	0.004	0.001	6860	0.06	0.045	0.013	1.49	0.005	2.27	0.0095	0.00621	0.00539	0.055	0.0124	0.02	<0.00005	0.24	0.00187	0.0001	4660	2.32	0.63	0.00067	2970	
N3Pond2	1.3	17.4	5.97	52	11.6	<0.001	<0.001	13100	0.041	0.07	0.005	1.44	0.017	1.33	0.0035	0.00126	0.00131	0.00747	0.023	<0.00005	0.32	0.0008	<0.0001	5720	2.07	0.87	0.00035	3910		
N4P1	0.288	8.6	75.4	78.2	24.2	0.003	0.002	52000	0.016	1.09	0.003	1.66	0.017	1.33	0.0016	0.00081	0.00185	0.007	0.00296	0.071	<0.00005	0.26	0.00034	0.0003	8880	0.144	2.6	0.00024	46100	
N4P2	1.18	6.9	22.3	25.1	81.7	<0.001	<0.001	78200	0.018	0.448	0.008	1.57	0.071	0.88	0.0024	<0.00005	0.00571	0.004	0.00383	0.04	0.00051	0.14	0.00052	<0.0001	12300	0.416	5.82	0.00024	52500	
N4P3	1.79	21.7	2.69	135	154	<0.001	<0.001	65200	0.029	0.699	0.012	1.59	0.007	0.77	0.0023	0.00296	0.0104	<0.001	0.00356	0.04	0.00047	11.6	0.00073	0.0009	4930	0.12	10	0.00114	36800	
N4P4	2.24	2.5	2.28	165	76.2	0.002	<0.001	95000	0.006	4.31	0.012	1.31	0.002	0.74	0.00014	0.00011	0.00512	<0.001	0.00021	0.054	0.00047	1.64	0.00017	<0.0001	5820	0.122	25.7	0.00011	53300	
N4Pond1	1.03	12.8	6.71	56.9	27.1	<0.001	0.002	25100	0.007	0.132	0.007	1.6	0.005	2.46	0.0043	0.0049	0.00154	0.053	0.00482	0.021	0.00038	0.49	0.00116	0.0001	15200	0.234	0.53	0.00086	9620	
N4Pond2	2.03	11.1	4.66	51.5	17.1	0.009	0.001	7870	0.067	0.062	0.002	1.59	0.004	2.21	0.0134	0.0053	0.0047	0.029	0.0146	0.021	0.00094	0.94	0.00258	0.0003	15100	1.12	1.1	0.00138	4810	
N7P2	0.378	1.4	285	96.4	41.8	<0.001	<0.001	57300	0.005	0.32	0.007	1.05	0.18	0.44	<0.0005	0.00027	0.0042	0.007	0.00177	0.035	<0.00005	0.19	0.00041	0.0003	6790	0.112	2.27	0.00018	20000	
N7P4	0.693	2.3	159	116	95.7	<0.001	<0.001	43300	0.018	0.142	0.013	1.41	0.02	2.35	0.014	0.00078	0.00084	0.00324	0.005	0.00196	0.093	<0.00005	1.09	0.00032	0.0005	5320	0.376	7.56	0.00028	21300
N7P5	1.64	2	0.76	273	44.4	0.002	0.002	24400	0.003	0.117	2.81	0.005	0.015	0.41	0.0009	0.00179	0.00341	0.00165	0.063	0.00065	1.73	0.00007	0.0002	3880	0.003	14.4	0.00013	16400		
N7Pond1	1.59	67.4	8.2	91.6	85.2	0.006	0.003	24400	0.093	0.144	0.006	1.34	0.017	2.01	0.0202	0.0117	0.00949	0.043	0.0199	0.03	<0.00005	0.44	0.00375	0.0002	19600	0.304	2.56	0.00185	9720	
N7Pond2	1.74	7.5	7.23	51	40.6	0.001	0.002	34600	0.058	0.092	0.007	1.19	0.011	1.61	0.0069	0.00746	0.00448	0.032	0.0111	0.031	<0.00005	0.36	0.0019	0.0001	8900	0.139	3.34	0.0008	6300	
N7Pond3	1.82	66.9	11.4	44.5	21	0.007	0.006	11200	0.006	0.105	0.013	1.41	0.02	2.35	0.014	0.00758	0.00517	0.036	0.0181	0.021	0.00798	0.25	0.00255	0.0002	7740	0.176	1.3	0.00126	4640	
N13P1	0.319	6.1	222	37.3	16.1	<0.001	0.003	27600	0.015	1.1	0.055	147	1.93	4.97	0.0011	0.00094	0.00366	0.023	0.00663	0.022	0.00089	1.94	0.00025	<0.0001	5590	0.017	1.25	0.00021	7560	
N13P2	1.12	0.7	97.4	202	46.9	<0.001	0.001	38800	0.003	0.478	0.004	0.94	0.043	0.42	0.0011	0.00129	0.00405	0.003	0.0017	0.042	<0.00005	1.97	0.00017	<0.0001	9080	0.179	2.31	0.00036	23000	
N13P3	1.67	3	29.6	177	243	<0.001	<0.001	39500	0.007	0.281	<0.001	0.86	0.12	0.56	0.0008	0.00073	0.0166	0.003	0.00305	0.075	0.00008	1.33	0.00021	0.0003	5950	0.069	1.65	0.00036	20100	
N13P5	0.653	4.2	2.21	346	40.3	0.015	<0.001	12100	0.014	0.052	0.008	0.81	0.106	1.4	<0.0005	0.00071	0.00271	0.013	0.00125	0.093	<0.00005	1.8	0.00033	<0.0001	3370	0.359	8.48	0.00032	5940	
N13P6	0.362	3	263	78.2	20.3	0.001	0.002	31400	0.011	0.221	0.015	0.55	0.012	1.46	0.0009	0.00069	0.00127	<0.001	0.00143	0.028	<0.00005	0.41	0.00026	<0.0001	5710	0.046	1.59	0.00025	11400	
N13PW	0.39	3.1	296	42.5	22.4	0.001	<0.001	35000	0.008	0.17	0.01	0.82	0.04	0.58	0.0018	0.00055	0.00214	<0.001	0.00123	0.018	<0.00005	0.25	0.00041	<0.0001	4670	0.089	1.31	0.00021	8980	
N13Pond1	1.34	54	1.86	27.7	18.3	0.005	0.004	5260	0.094	0.12	0.005	1.28	0.015	2.66	0.0122	0.0092	0.0052	0.038	0.00165	0.023	<0.00005	0.45	0.00309	0.0002	4260	8.44	0.53	0.00081	2040	
N13Pond2	0.18	6.2	3.12	29.9	35.9	<0.001	<0.001	27800	0.016	0.535	0.053	52.5	0.008	5.78	0.0055	0.00033	0.00599	0.028	0.00581	0.043	<0.00002	0.40	0.00207	<0.0001	4600	0.025	0.38	0.00082	10600	
Analyte Symbol	Mn	Mo	Na	Nb	Nd	Ni	Ni	Ph	Pr	Rb	Re	Sb	Se	Sm	Sr	Ta	Tb	Te	Th	Ti	Tl	Tm	U	V	W	Y	Yb	Zn	Zr	
Unit Symbol	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	
Detection Limit	0.05	0.005	5	0.0001	0.0001	0.05	0.005	0.0005	0.0005	0.0005	0.0001	0.001	0.01	5	0.0005	0.01	0.01	0.0005	0.00002	0.001	0.00002	0.01	0.0001	0.0001	0.0001	0.001	0.0005	0.5	0.001	
N3P1	1330	7.55	56100	0.0015	0.0054	0.9	0.054	0.00093	1.11	0.0013	0.431	0.05	<5	0.0017	0.04	313	<0.0005	0.00119	0.006	0.00058	0.73	0.0007	0.0009	0.00194	1.1	0.107	0.0562	0.00304	28.6	0.002
N3P2	704	4.14	145000	0.0001	0.0069	0.19	0.115	0.00092	6.08	0.0004	0.399	0.04	<5	0.0028	0.08	499	<0.0005	0.00058	0.008	0.00087	1.4	0.0022	0.0003	0.0404	0.654	1.4	0.0056	<0.00005	41.6	0.005
N3P3	764	0.733	216000	<0.0001	0.0028	0.16	0.108	0.00135	5.01	0.0002	0.213	0.03	<5	0.0032	0.1	475	<0.0005	0.00045	0.02	0.00005	0.01	0.0008	<0.0001	0.0108	1.09	0.159	0.0077	0.00238	44.9	0.003
N3P4	4410	0.202	169000	<0.0001	0.0043	1.55	0.168	0.00084	0.371	0.0006	0.284	0.09	<5	<0.0005	0.07	417	<0.0005	0.00032	0.011	0.00024	0.25	<0.0001	0.0004	0.249	1.13	0.061	0.0264	<0.00005	46	0.008
N3P5	4270	0.183	175000	<0.0001	0.0031	1.92	0.093	0.00063	0.29	0.0003	0.163	0.08	<5	0.0011	0.05	408	<0.0005	0.00004	0.003	0.00027	0.05	<0.0001	0.0003	0.254	0.714	0.042	0.0094	0.00077	31.8	0.001
N3P6	572	0.316	138000	0.0007	0.0344	0.24	0.217	0.0063	4.58	0.0005	0.211	0.09	<5	0.0057	0.04	313	<0.0005	0.00119	0.006	0.00058	0.73	0.0007	0.0009	0.00194	1.1	0.107	0.0562	0.00304	28.6	0.002
N3Pond1	2.05	0.512	8960	0.0004	0.0426	0.92	0.264	0.0102	3.88	0.0003	0.496	0.02	<5	0.0143																

Appendix H2 – Dissolved Total Fe Concentration



Fe_(t) (mg/L)					
Sample ID	Depth (m)	HR ICP MS	ICP OES	ICP OES	STDEV
N3P1	17	0.02	0.01	0	0.01
N3P2	29	0.01	0	0.04	0.02
N3P3	52	0.1	0.10	0	0.06
N3P4	87	0.1	0.08	0	0.05
N3P5	240	0.1	0.06	0	0.05
N3P6	95	0.4	0.34	0.37	0.03
N4P1	17	0.19	0.17	0.04	0.08
N4P2	30	0.11	0.11	0.01	0.06
N4P3	56	0.1	0.05	0.07	0.03
N4P4	75	0.1	0.04	0.07	0.03
N7P2	26	0.06	0.05	0.04	0.01
N7P4	75	0.1	0.13	0.08	0.02
N7P5	232	0	0.17	0.14	0.09
N13P1	14	0.32	0.32	0.13	0.11
N13P2	33	0.1	0.05	0	0.05
N13P3	85	0	0.04	0.02	0.02
N13P5	237	0.2	0.19	0.13	0.04
N13P6	123	0	0.04	0	0.02
N13PW	21	0.08	0.08	0	0.04
N3Pond1		0.11	0.12		0
N3Pond2		0.03	0.04		0
N4Pond1		0.06	0.06		0
N4Pond2		0.18	0.17		0
N7Pond1		0.18	0.18		0
N7Pond2		0.13	0.13		0
N7Canal		0.21	0.23		0.01
N13Pond1		0.08	0.07		0.01
N13Pond2		0.21	0.21		0

First Experiment: HR ICP MS

Second Experiment: ICP OES – University of Kansas

Third Experiment: ICP OES – Department of Agronomy, Kansas State University

Appendix H3 – Total As and As Speciation

Procedure for preparation of 6 M HCl from 36.5-38 % laboratory grade HCl

Molarity = moles/L; 37 % HCl indicates that there are 37 g of HCl (37 % mass to volume) in 100 mL of solution. The number of moles of HCl in 37 g can be worked out by Moles = mass /molecular weight. Therefore, moles = 37 g / 36.5 g/mol = 1.02 moles. So there are 1.02 moles of HCl in 100 mL of 37 % HCl. The molarity of the solution is $M = \text{moles/L} = 1.02/0.1 = 10.2 \text{ M}$

C_1 = original concentration

V_1 = required volume of original solution

C_2 = desired concentration

V_2 = desired volume of 6 M HCl

$$C_1 V_1 = C_2 V_2 \Rightarrow V_1 = C_2 V_2 / C_1 = (6 \times 100)/10.2 = 58.82 \text{ mL}$$

Hence, the solution dilutes 58.8 mL of 37 % HCl up to a total volume of 100 mL with water.

Sample ID	Depth (m)	As (III) (µg/L)	As (V) (µg/L)	As _(t) (µg/L)
N3P1	17	13	386	407
N3P2	29	<5	79	82.5
N3P3	52	<5	15	16
N3P4	87	<5	<5	0.25
N3P5	240	<5	<5	0.23
N3P6	95	<5	8	7.07
N4P1	17	<5	73	75.4
N4P2	30	<5	221	223
N4P3	56	<5	<5	2.69
N4P4	75	<5	<5	2.28
N7P2	26	<5	278	285
N7P4	75	<5	157	159
N7P5	232	<5	<5	0.76
N13P1	14	12	209	222
N13P2	33	<5	81	97.4
N13P3	85	<5	23	29.6
N13P5	237	<5	<5	0.21
N13P6	123	<5	262	263
N13PW	21	23	273	296
N3Pond1				5.0
N3Pond2				6.0
N4Pond1				6.7
N4Pond2				4.7
N7Pond1				8.2
N7Pond2				7.2
N7Canal				11.4
N13Pond1				1.9
N13Pond2				3.1

Appendix H4 – Anion

Sample ID	F ⁻	F ⁻	CH ₃ COO ⁻	CH ₃ COO ⁻	Cl ⁻	Cl ⁻	NO ₂ ⁻	NO ₂ ⁻	Br ⁻	Br ⁻	NO ₃ ⁻	NO ₃ ⁻	PO ₄ ³⁻	PO ₄ ³⁻	SO ₄ ²⁻	SO ₄ ²⁻
	mg/L	effective	mg/L	effective	mg/L	effective	mg/L	effective	mg/L	effective	mg/L	effective	mg/L	effective	mg/L	effective
N3P1	bdl	0.5	bdl	1	17.1442	2.25	bdl	0.25	bdl	0.25	bdl	0.25	0.2653	0.25	1.568	1
N3P2	bdl	0.5	bdl	1	252.957	22.5	bdl	0.25	0.8322	0.25	bdl	0.25	bdl	0.25	bdl	1
N3P3	bdl	2	bdl	4	437.16	67.5	bdl	1	1.2888	1	bdl	1	33.892	1	bdl	4
N3P4	bdl	1.5	9.882	3	308.336	45	bdl	0.75	1.3167	0.75	bdl	0.75	1.0146	0.75	bdl	3
N3P5	bdl	2	bdl	4	459.471	67.5	bdl	1	1.3236	1	bdl	1	1.9696	1	4.3996	4
N3P6	bdl	1	bdl	2	252.734	45	bdl	0.5	0.992	0.5	bdl	0.5	0.7096	0.5	3.3554	2
N3Pond1	bdl	0.5	bdl	1	9.1299	2.25	bdl	0.25	bdl	0.25	bdl	0.25	2.1315	0.25	6.2371	1
N3Pond2	bdl	0.5	bdl	1	14.1225	2.25	bdl	0.25	bdl	0.25	0.7123	0.25	1.6675	0.25	8.1901	1
N4P1	bdl	0.5	bdl	1	13.6175	2.25	bdl	0.25	bdl	0.25	bdl	0.25	1.4297	0.25	1.0224	1
N4P2	bdl	5	bdl	10	1420.236	135	bdl	2.5	2.628	2.5	bdl	2.5	bdl	2.5	bdl	10
N4P3	bdl	5	bdl	10	1256.226	135	bdl	2.5	bdl	2.5	bdl	2.5	bdl	2.5	36.223	10
N4P4	bdl	7.5	bdl	15	1856.628	135	bdl	3.75	bdl	3.75	bdl	3.75	bdl	3.75	80.121	15
N4Pond1	0.5658	0.5	2.4906	1	31.0312	2.25	bdl	0.25	bdl	0.25	bdl	0.25	2.0563	0.25	9.8073	1
N4Pond2	bdl	0.5	bdl	1	44.8702	2.25	bdl	0.25	bdl	0.25	3.5336	0.25	1.319	0.25	4.937	1
N7P2	bdl	0.5	bdl	1	28.1543	2.25	bdl	0.25	bdl	0.25	0.312	0.25	6.5773	0.25	3.984	1
N7P4	bdl	0.5	1.2818	1	136.2825	11.25	bdl	0.25	0.7652	0.25	0.3037	0.25	0.4182	0.25	3.0379	1
N7P5	bdl	0.5	bdl	1	57.7386	2.25	bdl	0.25	0.3411	0.25	0.2508	0.25	bdl	0.25	1.9992	1
N7Pond1	bdl	0.5	bdl	1	79.7786	4.5	0.2618	0.25	0.2774	0.25	3.6613	0.25	1.3156	0.25	12.4657	1
N7Pond2	bdl	0.5	bdl	1	32.6004	2.25	bdl	0.25	bdl	0.25	1.8897	0.25	bdl	0.25	22.8696	1
N7Canal	bdl	0.5	bdl	1	20.2982	2.25	bdl	0.25	bdl	0.25	0.2972	0.25	bdl	0.25	5.7383	1
N13P1	bdl	0.5	bdl	1	3.3363	2.25	bdl	0.25	bdl	0.25	0.2743	0.25	5.8225	0.25	1.4517	1
N13P2	bdl	0.5	2.0914	1	213.988	22.5	bdl	0.25	0.972	0.25	bdl	0.25	18.3233	0.25	1.4	1
N13P3	bdl	0.5	bdl	1	447.492	45	bdl	0.25	2.5019	0.25	0.4903	0.25	0.3204	0.25	1.2597	1
N13P5	0.5294	0.5	bdl	1	96.392	11.25	bdl	0.25	0.4787	0.25	0.2538	0.25	0.3657	0.25	1.1474	1
N13P6	bdl	0.5	bdl	1	80.2516	4.5	bdl	0.25	0.5025	0.25	0.3	0.25	3.8724	0.25	1.3853	1
N13PW	bdl	0.5	bdl	1	3.48	2.25	bdl	0.25	bdl	0.25	0.2524	0.25	0.5541	0.25	1.1622	1
N13Pond1	bdl	0.5	bdl	1	2.6289	2.25	bdl	0.25	bdl	0.25	0.3649	0.25	bdl	0.25	1.7408	1
N13Pond2	bdl	0.5	bdl	1	10.2975	2.25	bdl	0.25	bdl	0.25	6.8034	0.25	3.8634	0.25	3.6513	1

bdl = below detection limit