GEOCHEMICAL SIGNIFICANCE OF ARSENIC AND MANGANESE TOXICITY IN GROUNDWATERS FROM MURSHIDABAD DISTRICT, WEST BENGAL, INDIA

by

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Abstract

Mass poisoning of arsenic (As) has affected roughly 60 million people in the Bengal Basin (Bangladesh and West Bengal, India) and 43 million people alone in West Bengal. Elevated levels of Manganese (Mn) is another alarming issue in the groundwaters of this region (MCLs: As<10µg/L and Mn< 0.4mg/L). Four locations in Murshidabad district (south-central part of Bengal Basin) were chosen for this current study. Among the 4 locations, two of them showed high concentration of As (>50 - 4622µg/L; 2009 survey) and they are Beldanga: 23° 56'N& 88°15'E and Hariharpara: 24°3.68'N & 88° 21.63'E. On the other hand: Nabagram (24°12.08'N & 88°13.29'E) and Kandi (23°58.6'N & 88°6.68'E) demonstrated less dissolved As (<10µg/L) in groundwaters. Study areas were located to the west (Nabagram, Kandi) and east (Beldanga, Hariharpara) of the river Bhagirathi, a tributary of the river Ganges, flowing N-S through the district of Murshidabad. Eastern side of the river is occupied by grey colored Holocene sediments and western side has more oxidized orangish-brown Pleistocene sediments. Comparative study of major water quality parameters between these sites revealed high As (10-1263µg/L) and low Mn (0.1-1.3mg/L) in the areas like Beldanga, Hariharpara while low As (0-15µg/L) and higher Mn (0.2-4.2mg/L) in Nabagram and Kandi. The pH range for high and low As areas were 4.5-7.8 and 5.1-8.2 respectively. Phosphates showed values <0.04-2.21mg/L in high As areas and <0.08-2.52mg/L in low areas whereas Cl^- values were higher within low As areas (29-200mg/L) and lower within high As areas (3.9-78.4mg/L). Fe(t) and Fe^{2+} values at high and low As areas were 0-13.5mg/L, 0.01-0.11mg/L and 0-1.4mg/L, 0.04-0.06mg/L respectively. $\delta^{18}O$ and δD results revealed that monsoonal precipitation is the major recharge source in this area with some input from the surficial waterbodies as ponds in shallower depths within high As areas. The total As extracted from core sediments in these areas do not show much difference: total As in high and low As areas ranges from 6.4-18 mg/kg. Sequential extraction results revealed that majority of the sediment bound As is present in residual phases (>40%).

DOC in groundwaters in high and low As areas were 1.5-3.2 and 0.5-1.3mg/L respectively and they had positive correlation with As within the depth profiles. Dissolved organic matter (DOM) characterization studies indicated that microbial proteins (Tyrosine and Tryptophan) are the major components in the groundwaters in the low As region, whereas high

As area groundwaters tend to have higher content of humic DOM (A and C). Cl/Br molar ratio of high As wells were low compared to the low As wells. Current study revealed the importance of organic matters (and not the mineralogy of the sediments) both in sediments and groundwaters in controlling the release of As from sediment, at least in the shallow parts of Bengal delta aquifer and microbial mediated reductive dissolution of FeOOH in the presence of organic matter is the major mechanisms by which sediment bound As (<50m depth) is released into the groundwater. The darker organic matter rich sediments (OM both sediment bound and anthropogenically derived) existing at the depth range 20m-50m with reducing environment persisting in both high and low As areas are possible reasons for elevated levels of As in this region.

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For any errors or inadequacies that may remain in this work, of course, the responsibility is entirely my own.

"*Your right is to work only, but never to the fruit thereof. Be not instrumental in making your actions bear fruit, nor let your attachment be to inaction."*

Ch. 2, verse 47, Bhagavad Gita

Dedication

To the sons and daughters of Murshidabad

Chapter 1 - Introduction

People across the globe rely on groundwater as a major source of drinking water. The presence of high levels of geogenic and anthropogenic elements in groundwater can lead to various detrimental health issues for the consuming population, which might commonly develop over a gradual course of time. Arsenic (As) in groundwaters has affected roughly 43 million people in West Bengal, and one district within the state of West Bengal (i.e., Murshidabad) has produced groundwaters with As concentration as high as 4622 µg/L (Datta et al., 2011). In the late 1980s, surface water was the main source of drinking water in the region (Bengal Basin) and was severely polluted by various pathogens. With the help of funding from UNICEF, the West Bengal (India) and the Bangladeshi governments started exploring and promoting groundwater as an alternative source for drinking water in this region, and for this purpose they installed approximately 4 million tubewells. Unfortunately, this project is thought to be a cause of one of the worst environmental calamities (As toxicity) in Bengal delta (which covers part of West Bengal and Bangladesh). This situation is exacerbated by the recent discovery of the presence of dissolved Manganese (Mn) (McArthur et al., 2012; Biswas et al., 2012). Being a class I carcinogen, elevated levels of As in drinking water can cause various dermal lesions such as hyperpigmentation, peripheral neuropathy, skin cancer, bladder and lung cancers and peripheral vascular disease to the consuming population (Zaloga et al., 1985, Pierce et al., 2012). The WHO guideline value for As in drinking water is 10µg/L (WHO, 2011). Mn is a neurotoxin and it's toxicity is particularly harmful for newborns and children (Wasserman et al., 2006, Montes et al., 2008). Ingestion of high amount of Mn can cause various birth defects, impaired fertility in males and involuntary muscular movements (Ono et al., 2002) WHO guideline value for Mn was 0.4 mg/L prior to June 2011, but in the 4^{th} edition of WHO's guidelines for drinking water quality there is no guideline value (MCL) for Mn because none of the adverse health effects are associated with the usual Mn levels in the drinking waters. To avoid the adverse health effects caused by high Mn in drinking water, the Bureau of Indian Standards set 0.1 mg/L with 0.3 mg/L as the maximum permissible limit if there is no alternate drinking water source.

General geochemical characteristics and relation between Arsenic, Manganese and Dissolved Organic Carbon

Arsenic is the 3rd member of the 'VA' group of the periodic table. Atomic number is 33 and atomic mass is 74.9216 g/mol. As exists in -3, 0, +3 and +5 oxidation sates, however +3 (arsenite, As^{+3}) and +5 (arsenate, As^{+5}) oxidation states are common. General concentration of As in natural water is 1-2 µg/L (WHO, 2011). As is a major constituent in as many as 200 minerals. The ore mineral of As is arsenopyrite (FeAsS), realgar (As_4S_4) and orpiment (As_2S_3) (Smedley and Kinniburgh, 2002). In hydrothermal veins As occurs in native form. In the native form As^{+5} occurs in soils and sediments as $H_xAsO_4^{x-3}$, which adsorbed in to wide range of minerals like iron and aluminum hydroxides and aluminosilicate minerals (Ying et al., 2012). As^{+3} occurs as natural H_3AsO_3 species in non-sulfide environments and prefer to adsorb into iron hydroxides, iron oxides, ironoxyhydroxides (Gupta and Chen, 1978; Masue et al., 2007; Raven et al., 1998; Dixit and Hering, 2003; Herbel and Fendorf, 2006; Ying et al., 2012). As^{+3} is usually form weak complexes and upon the change in chemical conditions the bonds would break and As^{+3} go in to the solution (Tufano and Fendorf, 2008). Eh and pH conditions has got good control over As speciation in groundwater. $H_2AsO_4^-$ and $HAs_2O_4^{2-}$ minerals usually occur under oxidizing conditions (Eh >100mV and pH 6-7.5) (Smedley and Kinniburgh, 2002; Mukherjee et al., 2009). $H_3AsO_3^0$ used to exists under reducing conditions (Eh <100mV and pH 6-7.5) (Smedley and Kinniburgh, 2002; Mukherjee et al., 2009). When Eh<250mV then As can attached with sulfide species (HS^-, S^{2-}, and H_2S) to form the mineral Orpiment, As_2S_3. Arsenic exhibits very slow redox transformations and so both As^{3+} and As^{5+} occurs in natural conditions (Smedley and Kinniburgh, 2002; Mukherjee et al., 2009). The redox conditions greatly affects the ratio of As^{3+} to As^{5+} in groundwater and in strongly reducing (Fe^{3+} reducing and sulphate reducing) conditions As^{3+} species dominate over As^{5+} (Smedley and Kinniburgh, 2002). Under reducing acidic conditions As minerals (Orpiment & Realgar) and other sulphide minerals with coprecipitated As, can precipitate out from the solution (Cullen and Reimer, 1989; Smedley& Kinniburgh, 2002). It is expected that, if there is high concentration of free sulphide in water, then the As concentration would be much less (Moor et al., 1988; Smedley& Kinniburgh, 2002).

Mn is the first member of group VIIIB in periodic table with atomic number 25 and atomic mass 54.94 g/mol. It is the 12th most abundant element on the earth's crust. There are three possible oxidation states of manganese in soil, namely Mn(II), Mn(III) and Mn(IV)(

Gabriela et al., 2011). Among them most common are Mn^{3+} and Mn^{4+} (Pinsino et al., 2012). Most common Mn minerals are Pyrolusite (MnO_2), Braunite ($Mn^{2+}Mn^{3+}{}_6$)(SiO_{12}), Psilomelane ($Ba,H_2O)_2Mn_5O_{10}$) and Rhodochrosite ($MnCO_3$). Mn occurs in low concentration under natural pH and redox conditions and this is due to the low solubility of the most stable oxidation state Mn^{4+}(Björkvald et al., 2008). Oxidation of Mn is pH dependent and it is very slow in acidic condition (Stumm & Morgan,1996). Burning of fossil fuels is one of the major cause of Mn pollution and another one is volcanic activity (Stumm & Morgan,1996; Pinsino et al., 2012). The levels of manganese in groundwater from natural leaching processes can vary widely depending upon the types of minerals present at the aquifer. Mn is present in soil as a result of mineral weathering and atmospheric deposition, originating from both natural and anthropogenic sources. The divalent ion is the only form that is stable in soil solution, while Mn(III) and Mn(IV) are only stable in the solid phase of soil (McBride,1994). Mn mobility in soil is extremely sensitive to soil conditions such as acidity, wetness, organic matter content and biological activity (Gabriela et al., 2011). FeOOH can absorb As in their surfaces and occur in sediments as grain coating (Waychunas et al., 1993). H_2MnO_2 or $Mn(OH)_2$ (Manganese hydroxides) in alluvial sediments are examples of aquagene mineral formation or alluvial manganese mineralization (Silaev et al., 2000).

Dissolved organic matter (DOM) is a major component of natural waters and composed of a complex mixture of humic acids, fulvic acids, low molecular weight organic acids, carbohydrates and various bacterial derived proteins (Her et al., 2003). DOC form water soluble complexes with trace metals like As and Mn and it is very significant in their mobility and transport, among which fulvic acids show strong metal binding capacity and thus increasing metal solubility in natural water systems (McKnight et al.,1992; Anawar et al., 2003; Mladenov et al., 2008; Sharma et al., 2010; Reza et al., 2010).Fe and As reducing bacteria use DOC as an energy source (electron donor) and oxidize it and reduce Fe^{3+} to Fe^{2+} (or can cause reduce As directly). The reductive dissolution of FeOOH minerals cause As to be brought into solution. The humic substances in DOM have quinone moieties that act as electron shuttle (Scott et al., 1998) to accelerate Fe reduction (Lovely et al., 1996). Humic substances readily form complexes with Fe and form ternary complexes with Fe and As to keep As in solution. They can also compete with As for sorption sites (competitive sorption) (Lu et al., 1991; Mukhopadhyay and Sanyal, 2004. Warwick et al., 2005; Luo et al., 2006; Mikutta, and Kretzschmar, 2011; Liu et al., 2011)

Laboratory experiments by Lovely et al., 1996 have shown that the DOM act as electron shuttle between iron reducing bacteria and iron oxides and thus enhance iron reduction. Microbes in the water use DOC as the major source for their growth (Miettimen et al., 1999; Harvey and Swartz, 2002). DOC increases the solubility of iron oxides and can release adsorbed As onto the waters (Weber et al., 2006). Total nitrogen (TN) is another component in natural waters. It consists of all the available nitrogen species (NO_3^-, NO_2^-, NH_4^+) present in water. Amount of dissolved organic nitrogen (DON) can be calculated by subtracting the concentration of all the inorganic nitrogen species in the water from the TN content (Burdige and Zheng,1998; Burdige, 2000).

Natural organic matter in sediments enhance the release of sediment bound Arsenic into the pore water (Wang and Mulligan, 2006; McArthur et al., 2004; Acharyya et al., 1999). Organic matter in sediments can have various sources. The DOM in lacustrine and riverine environments was derived from various decomposed photosynthetic higher plants and micro-flora (Wetzel, 1992). Deltaic sediments account for roughly 45% of the global carbon burial and receives organic matter from both autochthonous and allochthonous sources (Hedges and Keil, 1995; Gordon and Goni, 2003).

Arsenic and Manganese Pollution (Global Scale)

Arsenic affected aquifers occur across the world and are present in all continents. As pollution (As concentration >10 µg/L) can be caused by geogenic or anthropogenic causes. The geogenic causes are mainly dependent on the proximity of As mineralized zones to the aquifers. The As from the mineralized zones can leach into the aquifer system and thus contaminate them, for example Canada (British Columbia; sulphide mineral deposits); Germany (Northern Bavaria; Sulphide mineralization) Smedley& Kinniburgh, 2002. Arsenic rich sediments in aquifer system can also leads to geogenic As contamination for example, Bengal Basin West Bengal, India and Bangladesh (quaternary aquifer sediments derived from Himalaya is enriched in shallow depth aquifers), USA (Tulare basin, California; Nevada; Idaho; South Dakota;), China, Taiwan and Mongolia (aquifer sediments enriched in arsenic) (Smedley& Kinniburgh, 2002). Volcanic ash could a source for As contamination in Northern Chile, Mexico (Smedley& Kinniburgh, 2002). Mining activities can affect natural systems and thus contaminate the aquifers example are USA (Fairbanks, Alaska); Canada (Moira lake, Ontario); Brazil and Thailand. Geothermal system can also cause geogenic As contamination and the cases are New Zealand, Japan, Russia, USA, Chile

and France (Smedley& Kinniburgh, 2002). First report on As contamination in drinking water was from Argentina in the year 1917 and main cause of the contamination was volcanic ash deposits and thermal springs (Mukherjee et al., 2006). In Australia As contamination is reported due to the leaching of As from As enriched country rocks and other anthropogenic activities like mining and extensive use of pesticides for agriculture (Mukherjee et al., 2006 references there in). The global distribution of As contaminated aquifers are depicted in the map (Fig.1) shown below by Smedley& Kinniburgh, 2002.

Figure 1: Distribution of Arsenic contaminated aquifers across the world (Smedley& Kinniburgh, 2002)

Mn is an emerging contaminant and it is the 12th most abundant element on the earth's crust. It is widely distributed in soil, sediment, water and other biological systems (Gabriela et al., 2011; Pinsino et al., 2012). Mn is an essential element for humans but high doses can lead to various fatal diseases. Mn, being an emerging contaminant, its distribution and affected population across the world is not yet clear. More studies are being done in various parts of Bengal Basin (BGS,2001;McArthur et al., 2012; Biswas et al., 2012; Neal et al., 2009, 2010a,2010b,2010c, 2011; Sankar et al., 2012, Sankar et al., 2013 submitted) to study the natural

occurrence of Mn. Lundy and Soule, 2012 reported naturally occurring Mn in Minnesota groundwaters, USA; Björkvald et al., 2008 reported natural Mn contamination in the snow melt driven boreal streams of Sweden. Nduka et al., 2008 reported anthropogenic Mn contamination in Niger delta, Nigeria; Homoncik et al., 2010 reported natural Mn contamination in Scottish groundwaters. Excessive Mn in water can result in having metallic taste in water, can cause stains on cloths and dishes, reduced water pressure in pipes due to the formation of Mn-oxide coating inside the pipe wall (Sly et al., 1990).

As and Mn contamination in the Bengal Basin

The current study explores the causes of As and Mn contamination in parts of the Bengal Basin (West Bengal) groundwaters. Mass poisoning of arsenic has affected roughly 60-70 million people in the Bengal Basin (Bangladesh and West Bengal, India). This is referred to as the greatest natural mass poisoning in human history (Bhattacharya et al., 1997; Nickson et al., 1998; Smith et al., 2000; McArthur et al., 2001; Dowling et al., 2002; Paul., 2004; Ravenscroft et al., 2005; Routh et al., 2005; Acharyya and Shah, 2007; Datta et al., 2011 and many references therein). Elevated levels of Manganese (Mn) is another alarming issue in the groundwaters of this region (McArthur et al., 2012,Biswas et al., 2012). In the late 1980s, surface water was the main source of drinking water in the region and was severely polluted. With the help of funding from UNICEF, India mostly the state of West Bengal and Bangladeshi governments started exploring and promoting groundwater as an alternative source for drinking water in this region. They installed approximately 4 million tube wells to provide safe drinking water during this time. Unfortunately, this project is thought to be a cause of one of the worst environmental calamities (As toxicity) in the history of the delta. The mechanism of As mobilization from Bengal Basin sediments to local groundwaters is complicated and poorly understood. However the common consensus is that the organic matter within the aquifer sediments drives dissimilatory iron reduction reaction and thus release As to the groundwaters (McArthur et al., 2001& 2004, Dowling et al., 2002). Bengal Basin covers most part of Bangladesh and West Bengal India and composed of Quaternary alluvial sediments. Seven districts in West Bengal and most part of Bangladesh is affected by Arsenic contamination. They are Malda, Murshidabad, Burdwan, Howrah, Hooghly, Nadia, North 24- Paraganas and south 24-Paraganas. Most of the As contaminated aquifers are at a depth range of 60 m (shallow to intermediate

depth) (McArthur et al., 2001 & 2004; Dowling et al., 2002; Datta et al., 2011). Many people in these areas are affected by arsenicosis in the form of various skin lesions. Major Quaternary sediments in this areas are classified as older sediments or Suja formation(Pleistocene age) and the younger alluvium or Bhagirathi-Ganga formation (Holocene age). Aquifers present in older alluvium or Suja formation are devoid of As however enriched in Mn. On the contrary aquifers present in younger alluvium or Bhagirathi-Ganga Formation are mostly enriched in As and depleted in Mn (Datta et al., 2011, Sankar et al., 2012). Source of As in Bengal Basin sediments are been described by various authors. Nickson et al., 2000 described that, as the Bengal Basin formed in the foreland basin of the Himalayan mountain chain and contains sediments derived from the Himalayas, source of As could be Himalayan rocks. Ghosh and De, 1995 explained Rajmahal and Chottonagpur plateau as the source of As rich sediments. Nickson et al., 1998 described that the base metal deposits present in the upstream areas of Bengal Basin could be a possible source, but later this idea was discarded, as these base metal deposits were too small in quantity to cause much of a problem. Nickson et al., 2000 explained that coal seams and basalts of Rajmahal Basin and isolated sulfides minerals (contains 0.8% As) present in the Darjeeling Himalayas and Gondwana coal seams could be the possible sources of As. Weathering of As minerals release As containing iron oxy-hydroxide minerals. These iron oxy-hydroxides can form grains coatings in the sediments. With time various geochemical processes can leads to the dissociation of Fe-oxyhydroxide grain coatings and thus release As into the groundwater containing them (Nickson et al., 2000; McArthur et al., 2001; BGS,2001; Dowling et al., 2002; Ravenscroft et al., 2005; Datta et al., 2011 references there in). McArthur et al., 2012 explained that microbial metabolism of organic carbon in sediments could cause the reduction of Mn oxides and Fe oxy-hydroxides and thus releasing Mn and As into the water along with other trace elements.

Regional Geology of Bengal Basin

Ganges Basin is an important part of the Himalayan foreland formed as the result of India-Asia collision. Flexural subsidence of the Indian lithosphere created the Ganges Plain foreland basin in front of the Himalayan orogen. This resulted in configuration during the late Quaternary (Singh, 2004, Sinha et al., 2005). The basin is composed of Quaternary sediments deposited by major meandering rivers like Ganges- Brahmaputra-Meghna and hence the name

of GBM delta (Morgan and McIntyre 1959; McArthur et al., 2011; Mukherjee et al., 2008; Hoque et al., 2011). The basin is bounded in the north by the Himalayan mountain ranges and in the south by the Precambrian, Peninsular Indian craton. It extends to the Bay of Bengal in the south, forming the great Bengal fan. Choronostratigraphically the basin holds two major types of sedimentary units; the older Pleistocene unit and the younger Holocene unit (Morgan and McIntyre 1959; Mukherjee et al., 2008; Datta et al., 2011; McArthur et al., 2008, 2011). During the Last Glacial Maximum (~20 ka before present), when sea level was substantially lower, the current highlands in the basin (i.e., current paleointerfluvial areas) were exposed and a thin layer of paleosol was deposited (McArthur et al., 2008). However, the low-lying areas (current paleochannels) were devoid of such deposits (McArthur et al., 2008; Hoque et al., 2011). Last Glacial Maximum of lowstand of sea level caused deep erosion in paleochannels by the paleorivers. Later the interfluvial areas were deeply weathered by high rainfall during the warmer climate regime and developed a widespread paleosol of impermeable clay that is found widely today across the Bengal Basin.

Western and northwestern border of the Bengal Basin is marked by Rajmahal hills. These are basalt lava traps of lower Jurassic in age and is a part of upper Gondwana system. The basin in the northeastern side is marked by Shillong plateau or Garo or Khasi or Jaintia hills. The basement of the plateau is composed of Archean quartzites, slates and schists with massive granitic intrusions with interbedded basaltic traps. Basement is overlain by Eocene sandstones and limestone beds. Eastern side of the basin is marked by Tripura hills at the north and Chittagong to the south. Western side of the basin is marked by Chottonagpur plateau composed of granites, amphibolites, carbonates and quartzites of Precambrian age (Morgan and McIntire, 1959 and references there in). Ganges river enters the Bengal Basin from northwest and brings sediments from the Himalayas. River Brahmaputra enters the basin from northeastern side of the basin from Himalayan mountains. Tsangpo river of Tibet (main tributary) joins Bharamaputra and together they discharge sediments into the basin (Morgan and McIntire, 1959). The Meghna river brings sediments from Shillong plateau and discharge them into the basin. Damodar river is another major river that joins from the western side after draining through the Chottonagpur plateau and discharge to the bay of Bengal through western border (Morgan and McIntire, 1959) (Fig.2)

Local geology of Murshidabad Sub Basin

Murshidabad district in West Bengal is the area under current research work. It forms south central portion of the Bengal Bain (Fig.2) covering an area of 5550 Km^2 and shares the border with Bangladesh. Geographically the area is alluvial plain and mostly the land is used for agriculture. The main climate type is tropical wet and dry climate with mean annual temperature is 27 and has a population of approximately 7.1 million people (Census 2011). The region's climate is characterized as a tropical wet-dry climate.

Murshidabad district forms a part of the lower Ganges valley of West Bengal and is covered by extensive deposits of Quaternary alluvium (Biswas and Saha, 1976).

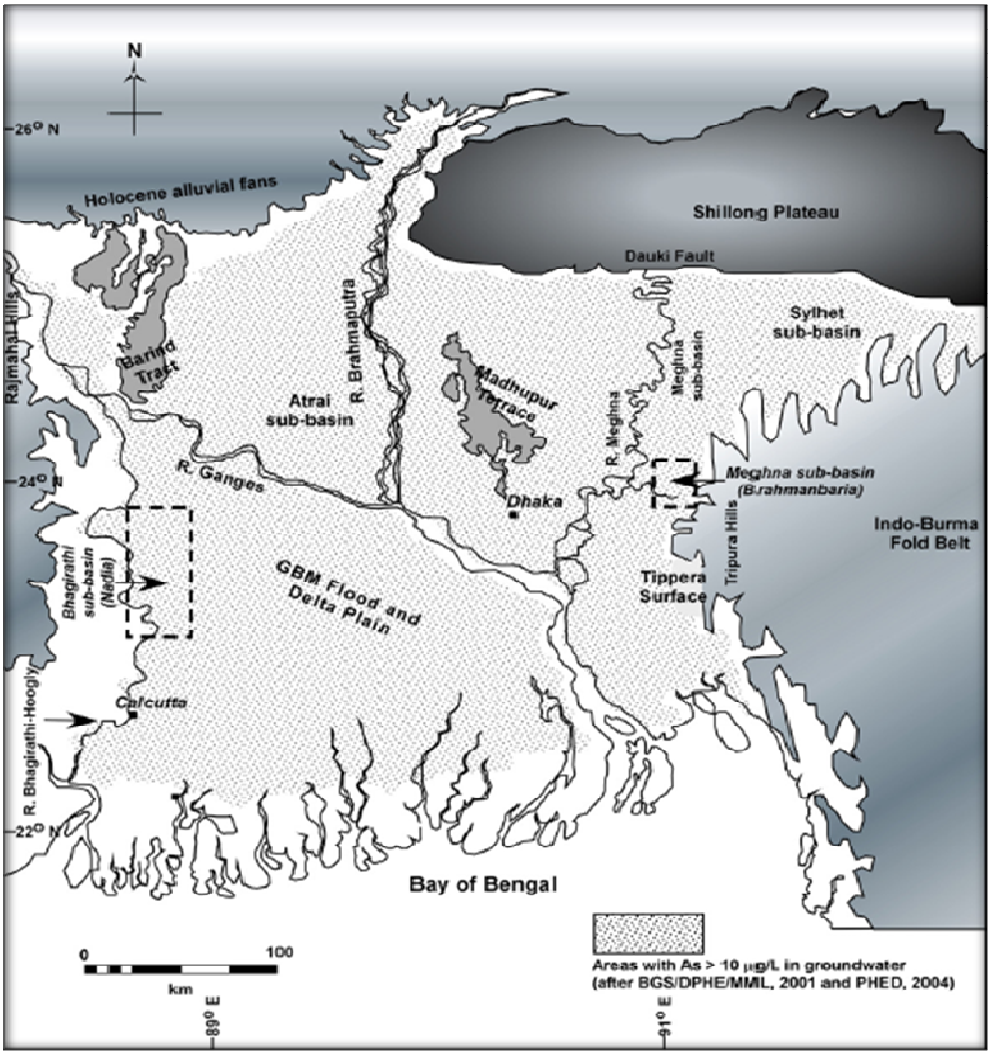


Figure 2: Location of Murshidabad sub basin is marked in dashed square, (Morgan and McIntyre 1959; Mukherjee et al., 2008, Hoque et al., 2011)

This district is transected by the river Bhagirathi, a tributary of the river Ganges, flowing N-S through Murshidabad. The western part of Bhagirathi river is mainly occupied by Suja formation which is older alluvium of Pleistocene age. This is mostly composed of oxidized ferruginous sand, silt and clay with caliche. On the other hand the eastern part of the river is occupied by Bhagirathi-Ganga formation, newer alluvium of Holocene age and composed of sand, silt and clay. Aquifers present in the eastern side of the river Bhagirathi; Bhagirathi-Ganga formation are contaminated with geogenic As. Whereas aquifers present to the western side of the river Bhagirathi; Suja formation is low in As in groundwater but are enriched in Mn to some extent.

Shallow level groundwater is the main drinking water source in this area and people extract groundwater by hand pumped shallow level tubewells drilled by local drilling companies. A total of more an 700 of them are present in this area (Mukherjee et al., 2011). Shallow depth groundwaters (<60m) are polluted with As whereas deeper groundwaters in these areas (80-300m) are considered safe for drinking (Mukherjee et al., 2011) purpose. The water bearing formations in this area are mainly grey colored sand beds and are unconfined to semi confined in nature (Mukherjee et al., 2011; Datta et al., 2011).

Ponds are another water source and more than 120 of them exist in this area (Mishra, 2006) and are contaminated by various anthropogenic pollutants, including enteric bacteria, due to overuse and additions of waste streams to the natural sources/channels via human practices. Neumann et al., 2010 indicated that ponds were one of the major source of groundwater recharge in Bengal Basin and ponds in these areas were enriched in biodegradable organic matter could be one of the major source of DOM in Bengal Basin. Sengupta et al.,2008 and Datta et al., 2011 based on oxygen isotope studies stated that ponds may not be the major recharging source for groundwater in Bengal Basin.

Chapter 2 - Background

Signs of chronic arsenic toxicity include dermal lesions (e.g., hyperpigmentation, hyperkeratosis, desquamation and loss of hair), peripheral neuropathy, skin cancer and peripheral vascular disease (Zaloga et al., 1985, Pierce et al., 2012). Among these symptoms, dermal lesions were most dominant, and were also known to occur within a period of about five years (Duker et al., 2005). The most affected organs are those involved in the absorption, accumulation and/or excretion of arsenic. Those organs are the gastrointestinal tract, circulatory system, liver, kidney, skin, tissues very sensitive to arsenic.

Manganese is another hazardous groundwater contaminant and a neurotoxin. Manganese toxicity is particularly harmful for newborns and children (Wasserman et al., 2006, Montes et al., 2008). Exposure to elevated manganese levels in drinking water during pregnancy may hamper the intellectual development of the child (Wasserman et al., 2006). Chronic exposure to manganese can lead to myoclonic involuntary movement (IVM) in adults (Ono et al., 2002). The presence of dissolved organic matter (DOC) in groundwater can improve the microbial growth and affect the water quality (Weinrich et al., 2010).

Previous studies (Neal et al., 2009, 2010, 2011 a&b, Datta et al., 2009, 2010a&b, 2011) show that the chemistry of the groundwater was dominated by anoxic conditions with relatively high amounts of $Fe2^{+}$ and As. Field work carried out as the part of present research work also confirmed that positive correlation of arsenic with Fe^{2+}, PO_4^{3-} and TDS content in most of the high As areas, whereas the Mn and Cl^{-} ions are negatively correlated with high As. Hydrochemistry is controlled primarily by carbonate dissolution, silicate weathering, FeOOH reduction, and some mixing with saline water.

The As concentrations in high As (10-1265 µg/L), low Mn (0-1292 µg/L) in the areas like Beldanga, Hariharpara (east bank of the river) and low As (0-30µg/L), higher Mn (0-2328 µg/L) in Nabagram, Kandi (west bank of the river). Maximum contamination level of Arsenic as per WHO standard is 10 µg/L. The WHO guideline value for Mn in drinking water was set at 0.4 mg/L prior to mid 2011 and in the recent edition of WHO guideline for drinking water quality has no guideline value for Mn. The DO, NO_3^{-} and NH_4^{+} do not show appreciable variation among the high and low As areas and they range from 1.5-5 mg/L, 0-2.7 mg/L and 0-0.06 mg/L respectively. The TDS and conductivity also do not show considerable variation among the high

and low As areas and their ranges are 0.001-6.2 g/L and 2.6-988 μS/cm respectively. The high As areas show a pH of 4.5-7.8 while pH in the low As areas is 5.1-8.2. Alkalinity (HCO_3^-) values range from 270-640 mg/L at high and 270-630 mg/L at low As areas. The PO_4^{3-} values of high As areas range 0.2-11mg/L and at low As areas the range is 0.3-1.3 mg/L. The Cl^- values are higher at low As areas (40-148 mg/L) and lower at high As areas (10-60 mg/L). The Fe^{2+}values at high and low As areas are 0.05-6 mg/L and 0.1-1.4 mg/L respectively. During the field work it was identified that there was a good correlation between tube well platform color and high As concentration areas which match with a recent study near Chakdaha, south of Murshidabad (Biswas et al., 2012). Over exploitation of groundwater in this region for irrigation during the past few decades has significantly distorted the regional groundwater flow. The low hydraulic gradient has led to a very slow flushing rate, which is thought to have a significant effect on the groundwater chemistry. The stable isotope data from the same region shows that the groundwater of this region is directly recharged by local precipitation without significant evaporation (Datta et al., 2011).

In the Gangetic plain, organic matter driven microbial reduction of Fe-oxyhydroxides is considered as the most plausible mechanism of As release into groundwater (Hery et al., 2010; Mladenov et al., 2010; Kar et al., 2011). However, the role of organic matter in the aqueous environment and its effect on As mobilization is not well understood and hence organometallic complex formations are not well understood either. Sharma et al., 2011 found that freshly extracted soil organic matter has a greater impact on As transport. There are different views regarding the source of DOM in Bengal Basin groundwater and they are:

a) The DOM is terrestrially derived and were released from shallow aquifer sediments over time (Mladenov et al., 2010)

b) The natural organic matter present in the peat layer above the aquifer sands and overlying confining unit and their subsequent release to the groundwater (McArthur et al., 2004)

Main focus of the current research was to study various possible sources and species of DOM in groundwater and their effects on groundwater As and Mn mobilization and retention. Hery et al., 2010 suggested that even very low concentrations of organic matter are able to support microbial arsenic mobilization via metal reduction and subsequent arsenic mitigation through sulphate reduction. As per Tipping et al., 1981; Davis, 1982; Warren and Haack, 2001; Weber et al., 2006 and Björkvald et al., 2008 DOC strongly associate with both dissolved and

particulate Fe species in water and also increases it's solubility. Studies show that the Mn species in water can form complexes with dissolved humic substances and are weakly bonded to DOC (Carpenter, 1983; Laxen et al., 1984; de Vitre et al., 1988; Graham et al., 2002; Björkvald et al., 2008). Fe species along with DOC are identified as the major carriers of trace metals in water (Tipping, 1981; Davis, 1984; Benoit, 1995; Pokrovsky and Schott, 2002; Pekka et al., 2004; Pokrovsky et al., 2006; Björkvald et al., 2008). The oxidized forms of Fe and Mn species are insoluble but if the environment turns reducing these species can dissociate and release various trace metals like Mn and As into the water. The mechanism of As mobilization from Bengal Basin sediments to local groundwaters is complicated and poorly understood. However the common consensus is that the organic matter within the aquifer sediments drives dissimilatory iron reduction reaction and thus release As to the groundwaters (McArthur et al., 2001& 2004; Dowling et al., 2002). The results from this study showed that sediments in both high and low As and Mn areas are enriched in As and Mn. Processes existing in highly polluted areas are responsible for the anomalous concentration of As and Mn in groundwater. Various studies also show that, deep level aquifers (>60 m) in Bengal Basin is not polluted with As or Mn and are quite safe (Burgess et al., 2010; Datta et al., 2011; Hoque et al., 2011).

Studies show that the dissolved organic matter (DOM) in natural waters is highly reactive toward both metals and was a clear candidate to influence arsenic mobility (Redman et al., 2002, Babuer and Blodau, 2006). Studies showed that litter and humus are the most important DOM sources in soils (Kalbitz et al., 2000). However, it is impossible to quantify the individual contributions of each of these sources to DOM release. High microbial activity, high fungal abundance, and any conditions that enhance mineralization all promote high DOM concentrations. There are strong indications that microbial degradation of DOM also controls the fate of DOM in the soil (Kalbitz et al., 2000). Knappet, 2010, explained leaching of surface DOC and pathogens in to the shallow level aquifers in Bangladesh and this explains surface sources for the DOC. There is still no common consensus over the source of organic matter in the Bengal Basin. Distribution of As and Mn in the Bengal Basin sediments are extremely patchy in nature due to the variable sediment properties. There is no consensus on the mechanisms accounting for the observed varied concentrations of As and Mn in similar types of sediments.

Studies show that arsenic contamination of groundwater aquifers is related to the content of dissolved organic matter (DOM). The presence of DOM can cause the desorption and redox

transformation of As from the iron oxyhydroxides (Bauer and Blodau, 2004; Sharma et al., 2010, Sharma and Kappler, 2011). Studies proved that organic anions (citrate, malate and oxalate) enhance the leaching of As from soils (Kalbitz and Wennrich, 1998; Lin et al., 2002; Zhang et al., 2005). The amount of arsenate and arsenite released were significantly correlated with release of Fe, Mn and Al in sediments and thus suggesting that arsenic was mainly released from Fe, Mn and Al hydroxides in soil (Zhang et al., 2005). Fulvic or humic acids block As from adsorbing to various sorption sites like Fe-oxides, alumina, quartz and kaolinite (Xu et al., 1991; Grafe et al., 2001; Grafe et al., 2002). Prominent metal binding sites were identified in well characterized fulvic acids (Murray and Linder,1984; Leenheer et al., 1998). Adsorption of fulvic or humic acids leads to the desorption of arsenate from the sorption sites and thus increase the As concentration in the solution (Simeoni et al., 2003; Gustafsson, 2006; Ko et al., 2007; Weng et al., 2009). From the current study both fulvic and humic acids were identified in Murshidabad waters. The competition for sorption sites between fulvic acid and As is much stronger than the competition between humic acids and arsenic (Weng et al., 2009). Mladenov et al., 2010 stated that DOM is a labile substrate for Fe and humic reducing bacteria and DOM at all depths in the Bengal Basin sediments contains terrestrial signatures. Polizzotto et al.,2008; McArthur et al., 2004 stated that near surface sediments rich in organic matter is main cause of As contamination in Bengal basin. The present research investigates the role of organic matter in the mobilization of As and Mn.

Cl/Br ratio is an effective tracer to identify the contaminated groundwater. Anthropogenically derived NaCl affects the Cl/Br ratio of groundwater (Davis et al., 1998; Vengosh and Pankratov, 1998). Various sources of NaCl in groundwater includes agricultural chemicals, septic effluent, animal waste, municipal landfill leachate, sea water, basin brines and road de-icers (Panno et al., 2006, Xie et al., 2012). The groundwater with higher Cl/Br ratio has higher concentration of potassium, boron, chloride, dissolved organic carbon and sulfate compared to the groundwaters with low Cl/Br ratio and indicates septic influence (Katz et al., 2011). McArthur et al., 2012 based on Cl/Br ratio studies revealed that there is a high percentage of waste water influence Bengal basin aquifers (Dasdia area, South of Murshidabad). Present research work also studied the influence of waste water on Murshidabad aquifers based on the Cl/Br ratio.

Studies show that the major recharge sources for Bengal Basin aquifers are monsoonal rain and surface water sources (rivers) and ponds were not the major recharge sources (Mukherjee et al., 2007; Sengupta et al., 2008; Datta et al., 2011). Mukherjee et al., 2007 stated that stable isotopic signatures of deeper groundwaters were similar to that of the shallow level groundwaters of this region (Murshidabad) thus indicating that groundwaters in this region are recharged by monsoonal rains .The current study also investigated the role of ponds in the recharge of aquifers in Murshidabad. Mukherjee and Fryar, 2008 stated that elevated levels of As in groundwaters in Bengal Basin are related to Fe^{3+} reduction and highly influenced by Fe-S-C redox cycle. Mukherjee et al., 2011 indicated that deeper groundwaters are non-brackish, potable ($Cl \leq 250$ mg/L).

Chapter 3 - Hypothesis and Objectives

Hypothesis

The processes that dissolved organic matter (DOM) within groundwaters of the Bengal Basin can efficiently drive bacterial mediated Fe and Mn oxyhydroxide reduction and the process of enhancing the release of adsorbed As into the Bengal Basin aquifer is not very clearly understood. The source of the dissolved organic matter has also been scarcely studied in this particular region. The main idea of this work is to understand the source of the organic matter both in sediments and waters compared between high and low Arsenic areas east and west of the river Bhagirathi that divides the district of Murshidabad in West Bengal. Since the study area is situated in a fluviodeltaic depositional environment of the River Ganges that originated and transported through high-grade granulites and Gondwana deposits, the aquifer sediments that feed into the fluvial plains consist of a wide variety of reworked minerals, dominated by quartz and feldspar mostly. Various authors have explained different sources of DOM and they are

1. Pond water rich in degradable organic matter having input from local sewage, reworked waters from irrigation and shallow tubewell pumping, percolate down into the shallow aquifers of Bengal Basin as result of heavy groundwater draw down by pumping (Neumann et al., 2010). This hypothesis is being retested in this work from detailed organic matter characterization from both sediment sources and water sources.

2. Mladenov et al., 2010 explained that there was a contrast in DOM characteristics of the surface waters from the shallow depth groundwaters within Bengal Basin. Terrestrially derived DOM of shallow depth groundwater were more reduced in nature compared to the surface waters in this region. Terrestrially derived DOM from the aquifer sediments gradually released to the groundwater over time. This DOM is a labile substrate for Fe and humic reducing bacteria in the Bengal Basin.

3. However Datta et al., 2011 based on the study of stable isotope studies of (δD) and ($\delta^{18}O$) and 1D transport modeling stated that ponds/surface water bodies in these regions may not be not the major source of DOM to the groundwater rather sediment-borne-/bound organic matter has also to be taken into consideration.

So the present research work evaluates the source of DOM in the shallow groundwaters (<50 m) of Bengal Basin. In order to evaluate this hypothesis following objectives have been set

for the current research that also includes detailed sediment characterization by various techniques in the field and state of the art geochemical instruments and also analyzing various geochemical parameters of the waters from this region.

Objectives

Several objectives have been targeted in this work in the light of proving or ground-truthing the above mentioned hypotheses:

1. Determine the chemical behavior of As and Mn in high and low As contaminated groundwaters and its relation to the source of OM
2. Determine a detailed groundwater geochemistry along with As speciation at various depths in the aquifer, surface waters, irrigation waters and shallow and deep tubewells
3. Understand the relation of As in water with various cations (Ca^{2+},Mg^{2+}, Na^{+}, Fe (t), K^{+}, Fe^{2+}) and anions (PO_4^{3-}, SO_4^{2-}, Cl^{-}, NO_3^{2-}, NO_2^{-}) in high and low As affected areas and their temporal relations in terms of variation in concentrations
4. Understand the sediment geochemistry via total bioavailable concentration of As and Mn; sequentially extracted As and Mn, organic matter bound As, Mn and solid state As speciation along with surficial sediment micro-topography to understand the sediment dynamics throughout the shallow and deep parts of the aquifer
5. Understand the distribution of DOC in high and low contaminated areas and its characterization and statistical evaluation of relations between various fluorescence components and with various hydrochemical parameters to evaluate DOC-As relation
7. Compare the oxygen and hydrogen isotopic ratios of surface and groundwater of this region in order to elucidate the recharge mechanism of these shallow As tainted groundwaters in this region.

Chapter 4 - Materials and Methods

Study area description

Murshidabad district (study area) is located in the south-central part of the Bengal Basin and is transected north to south by the river Bhagirathi, a distributary of river Ganges (Fig. 3). The district covers an area of roughly 5550 km^2 and has a population of approximately 7.1 million people (Census 2011). The region's climate is characterized as a tropical wet-dry climate. The basin is composed of Quaternary sediments brought by 3 major river systems, Ganges-Brahmaputra-Meghna and their tributaries and distributaries. Ultimately the whole river system discharge to the Bay of Bengal to the south to form the great Bengal offshore fan (Morgan and McIntire, 1959; Mukherjee et al., 2008).

There are two major choronostratigraphic units (sediments) in Bengal Basin. Pleistocene and Holocene sediments (Morgan and McIntire, 1959; Mukherjee et al., 2008; Neal et al., 2010; Datta et al., 2011; McArthur et al., 2008, 2011; Sankar et al., 2012). In Murshidabad district these two sediment types are present on either side of the river Bhagirathi (distributary of river Ganges). The eastern side of the river is occupied by Holocene sediments or younger alluvium also known as Bhagirathi-Ganga formation or over bank deposits. It is composed of sand silt and clay. These sediments are dark, loose with appreciable amount of organic materials and water content. These areas are identified with high As and low Mn concentration.

Western side of the river Bhagirathi is occupied by Pleistocene sediments. These are also known as older alluvium or Suja formation and are flood plain deposits. These sediments are generally oxidized and colored reddish or orange brown. They contains feruginous or calcareous nodules (Morgan and McIntire, 1959). Organic matter and water content of this Pleistocene sediments are less compared to the Holocene sediments (Morgan and McIntire, 1959, Sankar et al., 2012). The groundwater in this side is having low As and high Mn concentration in groundwater.

During the Last Glacial Maximum (~20 ka before present), when sea level was substantially lower, the current highlands in the basin (i.e., current paleointerfluvial areas) were exposed and a thin layer of paleosol was deposited over on top (McArthur et al., 2008). However, the low-lying areas (current paleochannels) were devoid of paleosols (McArthur et al., 2008; Hoque et al., 2012). Last Glacial Maximum of lowstand of sea level causes deep erosion in

paleochannels by the paleorivers. Later the interfluvial areas were deeply weathered by high rainfall during the warmer climate regime and thus caused the development of widespread paleosol of impermeable clay across the Bengal Basin (McArthur et al., 2008).

River Bhagirathi marks the border between these two separate geological formations to the west and east of Murshidabad (Neal et al., 2010, 2011 a&b; Datta et al., 2011; Sankar et al., 2012). Pleistocene and recent sediment surface can be easily distinguished in aerial photographs (Fig.3; Google map) on the basis of tone, texture and drainage pattern(Morgan and McIntire, 1959). Recent sediments surfaces (on the eastern side)are marked by major river activity and are composed of numerous abandoned channels, oxbow lakes and numerous sediment cover with less vegetation growth over it. Whereas the Pleistocene sediment surfaces (western side of the river) are marked by less riverine activity, less freshly deposited sediments, full of vegetation and no visible traces of oxbow lake or abandoned channels (Morgan and McIntire, 1959).

Murshidabad was the capital of Bengal during the Mughal period. District composed of 26 administrative blocks, 7 municipalities, 254 gram-panchayat and 1937 villages. Baharampur town is the district head quarter. 4 blocks are chosen for the current study.1 Beldanga (N 23° 56.379', E 88° 16.166') ; 2. Hariharpara (N 24° 03.692', E 88° 21.606'); 3.Nabagram (N 24° 11.846', E 88° 13.435'); 4. Kandi (N 23° 58.602', E 88° 06.682'). Beldanga and Hariharpara are situated in the eastern side of the river and occupied by Holocene sediments (Bhagirathi-Ganga formation) and concentration of As is high and Mn is low. Whereas Nabagram and Kandi are located on the western side of the river Bhagirathi and composed of Pleistocene sediments (older alluvium) and concentration of As is low and Mn is high.

Sample collection

Water sample

Two weeks of field work in Murshidabad was conducted for the current research work on January 2012. During the course of field work water samples were collected from 11 surface ponds, 37 shallow depth (10-40 m) hand pumped tubewells, 3 deeper depth tubewells (>40m); 11 irrigation wells (10-46 m) operated with electric pumps, 1 from Bhagirathi river (collected from the middle of the river while crossing the river) and 2 rain water samples (same rain water but from different places, Murshidabad and Kolkata). The depth classification (shallow tube wells (10-40 m) and deep tube wells (>40 m) were created for practical study purpose but both

were considered together as there were only a few deeper tube well sample collected (3 number) and both were used for drinking water. So where ever "tubewells" are mentioned in this thesis, it implies both shallow and deeper depth tubewells together. The ponds (surface water) were mostly dirty (anthropogenic input) and water was greenish in color due to the algal growth. Each village in this area had number of ponds and the local people use it for various domestic purposes. Irrigation wells are used for irrigation and they draw huge amount of groundwater.

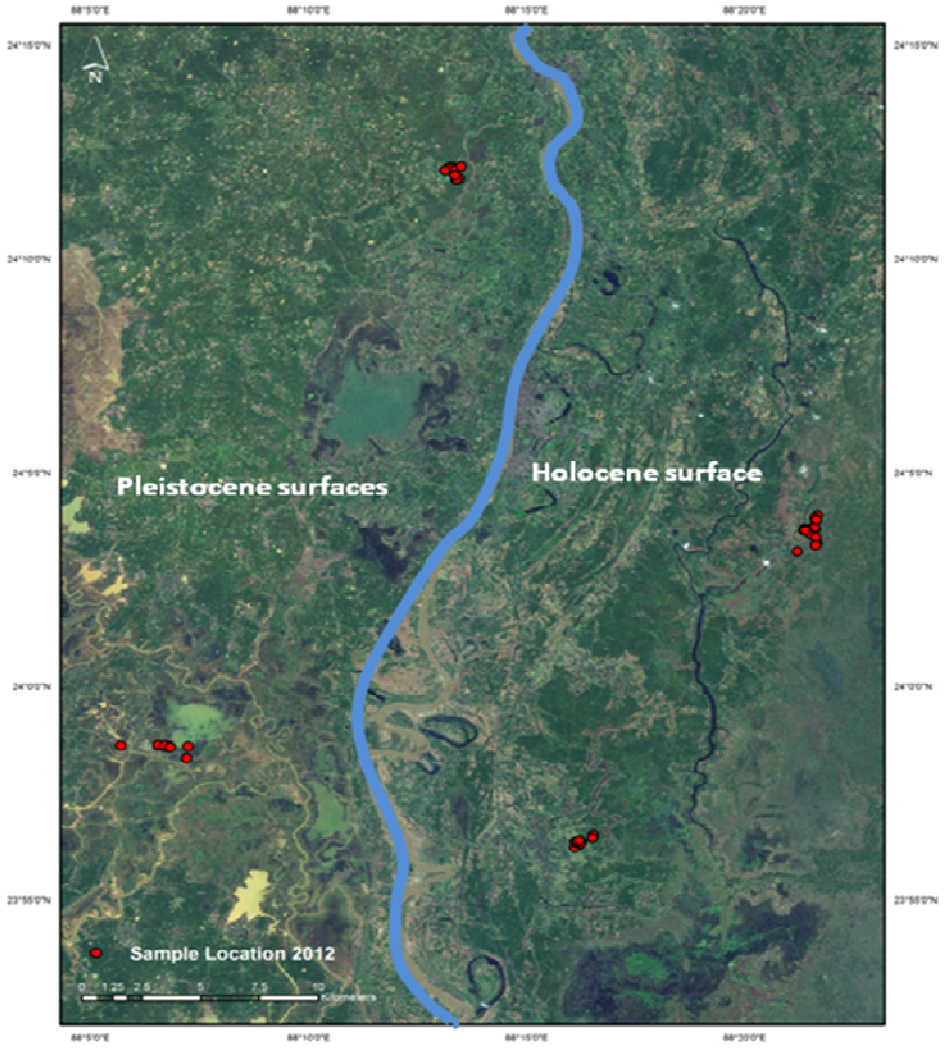


Figure 3: Google map showing the clear distinction between Pleistocene surface and Holocene surface. Blur line marks the river Bhagirathi. Red spots indicate the 4 sample locations

Ponds are used for taking bath, washing clothes, cleaning animals and growing fish (Fig.4). Shallow depth tubewells (10-40 m) and deeper depth tubewells (>40m) were mainly

used for drinking purpose (Fig.5). The irrigation wells, locally known as "deeps" are mainly used for irrigating the agricultural field. During the field work it was observed that, in a single day, the irrigation wells drew out huge amount of water from the deep aquifers. Water from these deep tube wells were channeled through numerous artificial cannel system to various agricultural fields across the area (Fig.5).

Figure 4: Local ponds in Murshidabad; Most of the ponds are within the villages and green coloration indicates high organic activity

Figure 5: Shallow depth Hand pumped tubewell (Left); Irrigation well (right)

Before proceeding to the field all the sample bottles were prewashed as per the EPA protocol. Each bottle was washed 3 times with tap water then 3 times with de-ionizer water . Then soaked in RBS detergent over night, rinsed 3 times again with de-ionized water. Later

socked in acid bath (10% trace metal grade HCl) overnight. Each bottle was then rinsed 3 times with de-ionized water and kept for air drying over the Kim-wipes.

In the field before collecting water from each tube well and irrigation well, it has been pumped for 5-10 minutes, to remove the pre existing water from well casing so as to collect the fresh water sample (van Geen et al., 2003). Pond water samples were collected from middle of the pond (bottom middle area after removing the dirt). Before collecting the samples, bottles were washed with the water to be collected 3 times. Location of each sample is marked with GPS co-ordinates (Garmin®, GPSmap 62s). It was ensured that each bottle was filled to the top leaving no space for the air and then sealed with black tape. Some of the samples were filtered in field using 0.45µm filter (Whatman® cat. no.6784-2504) and acidified (0.2% ultrapure nitric acid; Fisherbrand®, cat no. A509-P212). From each location most of the time, 7 water samples were collected, marked sample name, place and date as per the code (TW- tube well; PW-pond water; IW-Irrigation well; RW- River water, Rain water- Rain) and packet it together in a zip lock bag. Sample number and date were marked again over the zip lock bag. Details of the samples collected from each location are described in the Table-1 below.

Serial number	Bottle name	Brand and catalog number	Number of Sample collected	Remarks	Purpose
1	500ml HDPE narrow mouth plastic bottle	Fisherbrand® cat no.12-100-317	1	Unfiltered unacidified	Preservation
2	125ml amber plastic narrow mouthed bottle	Fisherbrand® cat no.02-923-5c	1	Unfiltered unacidified	Anions
3	125ml amber plastic narrow mouthed bottle	Fisherbrand® cat no.02-923-5c	1	Filtered and Acidified (0.2% ultrapure nitric acid, 250µl)	Cations

4	Flat top closure; 50ml centrifuge tubes	Fisherbrand®, cat no. 06-443-19	1	Unfiltered unacidified	Preservation
5	250ml Boston round narrow mouth clear glass bottle	Fisherbrand®, cat no. 05-719-163	1	Unfiltered & unacidified	Oxygen isotope and hydrogen isotope studies
6	250ml narrow moth amber glass boston rounds bottle	Fisherbrand®, cat no. 02-911-928	1	Unfiltered & acidified(0.2% ultrapure nitric acid, 500µl)	Preservation
7	20 ml glass vials sealed with a rubber stopper and crimp top	National Scientific® Vials, Cat. No. C4020-20 rubber stopper; Cat. No. C4020-34 Crimp top: Cat. No. Cat. No. C4020-5A	1	Unfiltered & unacidified	DIC (dissolved inorganic carbon)

Table 1: Types of water samples collected at each location during the field work, January 2012.

DIC vials were pretreated with an $HgCl_2$ (Acros Organics, Mercury(II) Chloride, 99.5%; Fisherbrand® Cat. No. 7487-94-7) solution and heated on a hot plate (Corning Remote Hotplate;~95°C) in the lab (KSU-Geology) so as to form a thin precipitate covering of $HgCl_2$ on the inside bottom of the vial to remove organic carbon from the sample (Zheng et al., 2005).

Sediment Sampling

During the course of field work drilling was conducted to recover aquifer sediments at 4 locations; 2 cores in Beldanga (CS-BM-102 &CS-BM-103); N 23° 56.376', E 88° 16.147' and N 23° 56.392', E 88° 16.206' were drilled to a depth of 140ft(43m) and 110ft(34m). 1 core in Hariharpara (CS-HK-105) N 24° 03.651', E 88° 21.395' to a depth of 140ft (43m); 1 core in Nabagram (CS-NB-104) N 24° 12.156', E 88° 13.492' to a depth of 140ft (43m) and Kandi (CS-KHN-106) N 23° 58.570', E 88° 06.814' drilled to a depth of 110ft (34m). Hand driven percussion drilling (Fig.6) (by local drilling company) was conducted to collect the aquifer samples. During the drilling operation samples were collected at regular intervals (5 to 10 ft interval). While collecting the sediments vinyl gloves (Fisherbrand® Powder-Free, Latex-Free, Vinyl Exam Gloves; Cat. No. 19-041-190C) were used. Then the sediments were placed inside in an O_2-impermeable Remel® bag (Mitsubishi Gas Company, Remel®, Cat No. 2019-11-02), along with an O_2 absorber pouch (Mitsubishi Gas Company, AnaeroPouch® Anaero; Cat. No. 23-246-379) flushed with nitrogen(N_2 gas) and later stored at 4°C (Fig.6)

Figure 6: Local hand driven percussion drilling method (left); Sediments preserved inside in O_2-impermeable Remel® bag with an O_2 absorber pouch inside. Flushed with N_2 gas and sealed (right)

The sediment samples (aquifer) were used for the following purpose

a. Total digestion to find out the concentration of As, Mn and Fe

b. Sequential extraction to find out the concentration of As Mn and Fe in various aquifer sediment fraction

c. Organic matter extraction to find out the Organic matter and organic bound As, Mn and Fe

d. Loss of Ignition test (LOI) to find out the organic matter concentration (%)

e. Synchrotron X-ray studies; XANES- X-ray absorption near edge structures and XAFS-X ray absorption fine structures for As speciation

f. SEM (Scanning electron microscopy) studies

Sample preservation and transport

In the field samples were stored in a fridge (water samples) and freezer (sediment samples). Later they were shipped to Kansas State university by express courier (DHL) and then again stored in hydrogeochemistry lab in K-State, department of Geology in the same way.

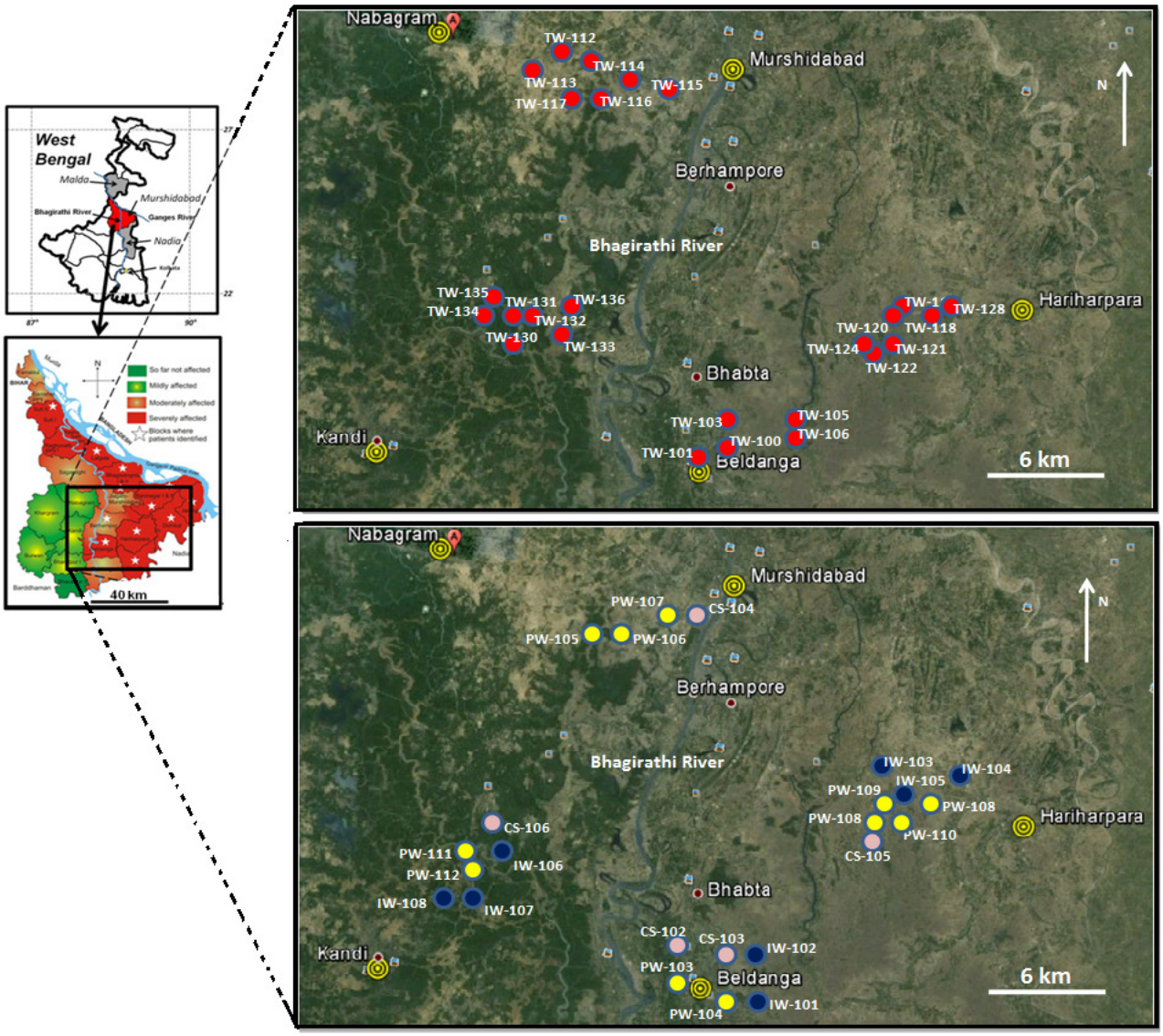


Figure 7: Map showing (top left)the location of Murshidabad (Marked red) in relation to West Bengal. Inset map showing As affected regions in Murshidabad(bottom left) (http://www.soesju.org/arsenic/wb.htm). Study locations and Sample locations , Red dots in the top right map indicates shallow depth tubewells (10-40m) and deeper depth tubewells (>40m). Yellow dots in map to the right bottom indicates the Pond water (surface water) ; Blue dots (map to the right bottom) indicates Irrigation wells (10-46m);Violet dots(map to the right bottom) indicates the bore hole locations. Beldanga and Hariharpara (high As and low Mn) and Nabagram and Kandi (High Mn and low As). Bhagirathi river flows to the south and divide the high As area to the left (Beldanga and Hariharpara) form the low As areas to the right (Nabagram and Kandi)

Analysis

Field Analysis

METTLER TOLEDO SevenGo™ for water parameters

In the field Temperature (°C), total dissolved solids (TDS) (mg/l), conductivity (µS/cm) , salinity (ppt) and resistivity (Ω cm) were measured using METTLER TOLEDO SG3-FK2-SevenGoTM (Mettler Toledo SevenGo™ Conductivity Meter SG3 with MT InLab® 731 Conductivity Sensor (Cat. No. 51344120). pH was measured using OAKPON® (Model WD-35801-00 pH 5 Acorn series). The water quality measurements were done only on the shallow and deeper depth tube wells (n=40). While collecting the water parameters the tube wells were pumped for 10-15 minutes into a bucket. Then after this pumping the bucket was emptied and continued the pumping. During this time all the above mentioned parameters were collected. During the measurement the pumping was continued until the machine was stabilized. Each tube well platform was photographed to study the platform color.

Field test kits for water chemistry

A total of 9 field test kits were used to measure *in situ* water chemistry at the place of collection. In the field water chemistry was measured mainly for the shallow and deeper depth tube wells (n=40). While collecting the sample a small field laboratory was set up near the tubewell to measure Arsenic (As), Manganese (Mn), Nitrate (NO_3^-), Sulfate (SO_4^{2-}), Phosphate (PO_4^{3-}), Chloride (Cl^-), Dissolved oxygen (DO) and Alkalinity.

Spectrophotometer, HACH DR 2800 ™ for water chemistry

Some of the parameters measured using field kits were rechecked and confirmed by analyzing the same sample over the spectrophotometer. Parameters measured were Manganese (Mn), Nitrate (NO_3^-),Iron ($Fe_{(T)}$), Sulfate (SO_4^{2-}), Phosphate (PO_4^{3-}) and Ammonia (NH_3-N)

Test kits

1. Arsenic concentration was measured using 2 different HACH test kits, they were

    a. Arsenic low range(0-500 µg/L As) test kit (HACH, Cat. No: 2800000)

    b. EZ Arsenic high range (0-500 µg/L & 0-4000 µg/L As) test kit (HACH, Cat No:2822800). In the current research we used two separate As field test kits as stated above to

measure high and low range separately. Appendix-A contains the details of test kit procedure to measure As

2. HACH® Manganese Test kit (Model MN-5, Cat. No: 1467-00): Mn test kit was used to find out Mn concentration in field. The details of the procedure of the Mn test kit is represented in the Appendix-A

3. Nitrate CHEMetrics® test kit (Cat. No. K-6909D): CHEMetrics nitrate test kit was used to find the nitrate concentration of groundwater samples in the field and the details of the test kit procedure is represented in the Appendix-A

4. HACH® Sulfate Test kit (Model SF-1, Cat. No: 2251-00): Sulfate concentration of ground waters were measured using HACH sulfate test kit and the details of test kit procedure is represented in the Appendix-A

5. HACH® Orthophosphate Test kit (Model PO-19, Cat.No: 2251-00): There are 3 different types of tests for Phosphate (PO_4^{3-}) they are a) . low range phosphate concentration (0-1mg/L) test procedure. b) . Mid range phosphate concentration (0-5 mg/L) test procedure c). High range phosphate concentration (0-50 mg/L) test procedure. Spectrophotometer test for phosphate concentration was conducted to determine the concentration of phosphate. Then based on concentration of phosphate measured from spectrophotometer, the test kit procedure was decided (low, mid or high range) to reconfirm the concentration. The details of test kit procedure for low range mid range and high range phosphate concentration is represented in the Appendix-A.

6. LaMotte® Chloride test kit (Model: PSC-DR. Code 4503-DR-01): LaMotte test kit was used to find the chloride concentration of groundwater samples during the field work and the detailed procedure to use the test kit is represented in the Appendix-A.

7. CHEMets® Dissolved oxygen test kit (Cat. No:K-7512; 1-12ppm): Dissolved oxygen of groundwater samples in the field was measured using CHEMets test kit and the detailed procedure to use the test kit is represented in Appendix-A.

8. HACH® Alkalinity test kit (Model AL-DT; Cat. No. 20637-00) Phenolphthalein and Total Alkalinity Method 8203 was used to measure alkalinity of the groundwater samples in this area. The detailed procedure to use the test kit is represented in Appendix-A.

Spectrophotometer HACH DR 2800 tests

Mn, NO_3^-, Fe (t), SO_4^{2-}, PO_4^{3-} and NH_3-N were analyzed using HACH® DR 2800 spectrophotometer. The values obtained for Mn, NO_3^-,SO_4^{2-} and PO_4^{3-} were evaluated using spectrophotometer in field. The details of reagents used and test procedures were represented in Appendix-A.

Sediment Characteristics and core logging in field

A total of 5 sediment coring were carried out for various lab analysis to measure As, Mn, Fe (t) and organic matter concentration. At the time of collection systematic core logging was carried out and recorded in field note book and schematic diagrams were prepared later for each core.

Lab analysis

Water analysis

Cations in water samples

Concentration of cations in water samples were measured using ICP OES (Varian 720-ES ICP Optical Emission Spectrometer) at soil chemistry lab in Agronomy department at Kansas State university (40 tubewell samples; 10 irrigation wells; 11 pond water; 2 rain water and 1 river water) and some samples (8 tubewells; 2 irrigation wells; 4 pond water; 1 river water and 1 rain water) were analyzed in HR ICP-MS (High Resolution Inductively Coupled Plasma Mass Spectrometry at Actlabs®, Canada). Five multi element standards and one blank were prepared for ICP OES analysis. Multi-element standard contains following elements Ca, Mg, Na, K, Fe and Mn with a very low range standard (Ca=10 mg/L, Mg=5 mg/L, Na=5 mg/L, K=10 mg/L, Fe=10 mg/L, Mn=2 mg/L); low range standard (Ca=50 mg/L, Mg=30 mg/L, Na=30 mg/L, K=40 mg/L, Fe=40 mg/L, Mn=4 mg/L); Medium range standard (Ca=100 mg/L, Mg=60 mg/L, Na=60 mg/L, K=60 mg/L, Fe=60 mg/L, Mn=6 mg/L); high range standard (Ca=150 mg/L, Mg=80 mg/L, Na=80 mg/L, K=80 mg/L, Fe=80 mg/L, Mn=8 mg/L) and a very high range standard (Ca=200 mg/L, Mg=100 mg/L, Na=100 mg/L, K=100 mg/L, Fe=10 mg/L, Mn=10 mg/L). The wave length for analysis of each element were chosen (Ca: 315.887 nm; Mg: 279.078 nm; Na=589.59 nm; K: 766.491nm; Fe: 259.940 nm; Mn= 257.61nm). Expected concentration of various elements in the samples were studied from various available literature and on the basis of this all the above defined standards were prepared. The standards were prepared in such a way that the concentration of the samples to be measured will fall almost in the middle of the best fit line (standard curve) created for each element with a good cluster. The 6 mL of samples were taken from preacidified with 0.2% ultrapure HNO_3 and filtered 125 ml amber plastic bottles (explained during sample collection) in to a 90 x 13 mm ICP vials in a sample-holder rack. Instrument was calibrated after analyzing every 20 samples for better accuracy and samples were analyzed for Ca, Mg, Na, K, Fe and Mn in mg/L. A duplicate and triplicate of the sample was kept after every tenth sample to recheck the accuracy of the analysis.

Fe^{2+} concentration of Murshidabad waters samples (tubewells =11; irrigation wells =4 and pond water=2) were analyzed using spectrophotometer (HACH®, DR 2800). The test started by making a blank by filling the sample cuvette (cell) with fresh water sample to be analyzed.

Then the sample was prepared by snapping the tip of the AccuVac® ampoule (cat. no.2514025) inside a beaker containing the sample to be analyzed. The ampoule was kept inside the beaker until it filled up completely with sample. Then ampoule was capped and the contents mixed well. The instrument timer was set for 3 minutes reaction period. The blank was inserted inside the cell holder of DR 2800 and the shutter was closed. Before inserting the blank it was made sure that the cells were wiped dry. Zero the instrument then display will show 0.00mg/L Fe^{2+} . Then ampoule was inserted into the cell holder after wiping it dry and the shutter was closed. The result was then read for Fe^{2+} in mg/L.

Anions in water samples

Anions in water samples were analyzed by Ion chromatograph (Dionex,ICS-1000 ion chromatography system) at the soil chemistry lab in department of Agronomy at Kansas State University. A total of 40 tubewells, 11 pond water and 10 irrigation wells were analyzed. After every 10th sample a duplicate and triplicate of the sample kept to check the accuracy of the analysis. Standards were prepared for Cl^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, F^- and NO_2^- and were analyzed for Murshidabad waters. 4 tubewell water samples and 1 pond water sample were send out to Actalabs®, Canada for anion analysis in Ion chromatography. Detection limit of the Actlab® IC were as follows. F =0.01 mg/L; Cl^-=0.03 mg/L; NO_2^-= 0.01 mg/L; Br^-=0.03 mg/L; NO_3^-=0.01 mg/L; PO_4^{3-}=0.02 mg/L and SO_4^{2-}=0.03 mg/L. The samples for anion analysis were taken from 125mL unfiltered unacidified amber plastic bottles. Later 2.5 mL of it has been filtered using 0.45µm filters (Whatman® cat. no.6784-2504) and transferred in to IC vials and then kept inside the auto sampler of the IC unit.

Arsenic Speciation

A total of 3 water samples, 2 tubewells and one pond water samples were used for As speciation. Part of the speciation procedure was done in field using pretreated resins. In the field Biorad® prefilled exchange columns AG® 1-X8 Resin, 50-100 mesh, chloride form (cat. no. 140-1431) were used. Columns were first pretreated with 10 mL of 1M NaOH (sodium hydroxide) for 3 times and once the whole NaOH solution was drained out, then the resins were rinsed with 10mL distilled water 3 times. Once the distilled water was completely drained out from the resin, the resins were then converted to acetate form by treating with 10 mL 1M CH_3COOH (acetic acid) for 3 times. Once acetic acid was fully drained out, it was then washed 3

times with 10 mL distilled water. The columns were then preserved in distilled water until they were ready to be used in field. In the field, water sample to be tested, were filtered through 0.45µm filters (Fisher scientific® cat. no. 2670500). In each site about 30-60 mL of filtered water was then passed through the column whereby arsenate (As^{5+}) adsorbed to the resin, and only arsenite (As^{3+}) passed through it. Then acidified the aliquot of As^{3+} with HNO_3^- to a pH of <2. Then the concentration of As^{3+} was measured using ICP-MS at Earth and environmental science department at Tulane University. The total As was also measured from acidified filtered samples of the same locations. Then As^{5+} was determined by difference: between total As and As^{3+} (Ficklin, W. H., 1983; Wilkie and Hering, 1998; Pohl and Prusisz, 2004).

δD and $\delta^{18}O$ of water samples of Murshidabad

Stable isotope values of δD and $\delta^{18}O$ for 23 tubewells; 11 pond water and 9 irrigation well samples were measured using Cavity Ringdown spectrometer (Picarro® G1301) at the Stable Isotope Mass Spectrometry Lab in the Department of Biology at Kansas State University. The precision of the Picarro® G1301 was ~50 ppm. Again some sample (9 tube wells; 9 pond waters and 7 irrigation wells) were analyzed in ISOTECH® laboratories Inc, Illinois to recheck the accuracy of the earlier analysis at Kansas State University, Biology lab. The samples for oxygen isotopes were collected in 250mL Boston round narrow mouth clear glass bottles. Before collecting the waters samples these bottles were washed with the same water with 3 times and the rinsed 2 times. Then water samples were collected till the top leaving no space for air in the bottle. Then the bottle was capped and sealed with back tape. In the lab 5 mL of samples were filtered though 0.45µm filter (Whatman® cat. no.6784-2504) to Piccaro® vials. From these vials approximately 2 µg of sample was injected into the Picarro water analyzer for determination of δ^2H and $\delta^{18}O$. Inside the instrument the injected water sample was converted to vapor and carried by a N_2 carrier stream to the analyzer where the relative abundance of heavy and light isotopes were measured. There was a slight memory effect between samples as water molecules from one injection adhere on the surface of the analyzers internal plumbing unit. In order to avoid such memory effect per sample a total of 6 injections were made and out of that 6 injections, the first 3 were removed from the analysis and the last three were averaged (as recommended in the Picarro® instrument user's manual). The average value represents a 'raw' data point that is then corrected to three secondary standards (Evian bottled water [δD = -78.07‰ and $\delta^{18}O$ = -

10.01‰], KSU de-ionized water [δD = -40.72‰ and $\delta^{18}O$ = -5.30‰], and KSU de-ionized enriched water [δD= -8.36‰ and $\delta^{18}O$ = 4.03‰]) that are analyzed along with each batch of samples. The standards have been calibrated to National Institute of Standards and Technology (NIST) accepted standards (Greenland Ice Sheet Precipitation (GISP: δD = -189.5‰ and $\delta^{18}O$ = -24.78‰), Standard Light Arctic Precipitation (SLAP: δD = -428.0‰ and $\delta^{18}O$ = -55.5‰), and Vienna Standard Mean Ocean Water (VSMOW: δD = 0‰ and $\delta^{18}O$ = 0‰)) (Coplen, 1994). The $\delta^{2}H$ and $\delta^{18}O$ values of the standards span the entire range of expected isotope values for the samples submitted. In order for correction of drift in the analyzer during a batch of samples, a working standard of known isotope ratios was analyzed every four samples. Finally, the raw isotope data was corrected to the three standards analyzed with the measured water samples.

Dissolved organic carbon, Total Nitrogen and Fluorescence spectroscopic Studies

A total of 40 tubewells, 9 pond waters and 9 irrigation wells were analyzed for dissolved organic carbon (DOC) and total nitrogen (TN) in water samples. All these samples were also analyzed for fluorescence spectroscopic studies to get excitation emission metrics (EEM) to find out various components of DOC. The fresh samples were taken from 500mL amber plastic bottles. The sample preparation started with preheating the Fisherbrand® Binder-free, borosilicate glass fiber filters with 0.7µm pore size (cat. no. 09-804-142H) to 400°C for 4 hrs in a muffle furnace. After 4 hrs the furnace was switch off and the filters were allowed to cool for some time (45 minutes) to avoid breakage of the fibers. The fibers were then taken out of the furnace and was allowed to cool inside a glass desiccator for a day. Then glass fiber filters were fixed inside the Fisherbrand® filter holder (cat. no. 09-753-2). With the help of a Thermo scientific® syringe 20 mL (cat. no. 03-377-24) 60 mL of water sample to be analyzed was taken and pushed though the syringe opening in filter holder containing the glass fiber filter. The filtered samples were collected in 2 separate centrifuge tubes (pre washed in acid bath and later dried; 50 mL in one and 10mL in another). 50 mL sample was later acidified to a pH < 3 with 12.1 molar HCl (assay 37.4%) hydrochloric acid Fisherbrand® (lot. no. 983618). The 10 mL sample was collected as such and no acidification was done on it. The 50 mL acidified samples were used for DOC and TN analysis in TOC-L SHIMADZU®, Total Organic Carbon analyzer and 10 mL unacidified sample was used for fluorescence spectroscopic analysis in HORIBA Aqualog® Benchtop Fluorometer both at Civil engineering Department, Kansas State university.

A total of 58 samples were loaded to sample holder disc of TOC-L SHIMADZU, Total Organic Carbon analyzer along with distilled water in between the samples. The samples were taken in the TOC sample glass vials. Vials were preheated by packing inside aluminum foil at 450°C for 4 hrs in a muffle furnace to remove organic carbon if present in it. To cross check the result 3 repeat samples were also loaded along with the samples. While analyzing water samples in TOC-L SHIMADZU, Total Organic Carbon analyzer following configuration was maintained. Number of injections per sample was 5. Out of 5 results the best 4 were used and averaged to calculate the final result. 50µL samples is used per injections. After each samples 2 wash steps were carried to flush out the system. The standard deviation maximum method set up was 1. Spurge gas flow was 80 mL and spurge time set up was 1.30 minutes.

58 samples were taken for fluorescence study in HORIBA Aqualog® Benchtop Fluorometer. The analysis starts with turning on the instrument (first the instrument and then the computer) and then allowing the fluorometer lamp to warm up approximately for 45 minutes before running each sample. Then rinsed the clean quartz cuvette (for sample) 20 times with ultrapure water. Then the sides of 3-Q-10 sealed ultrapure water samples (standard) were cleaned with Kim-wipes to make sure that no dust is present in the bottle. Then a folder was created in the desktop computer with the following format- year month date (YYMMDD). The Aqualog® software was then opened. When the fluorometer bulb was warmed up (after 45 minutes), to check the contamination, initially cuvette check has to be performed by choosing H_2O button of "Aqualog main experiment menu". Then "Spectra" and then "Emission 2D" were checked. After that Then load the experiment file "cuvette.xml" was loaded. The setting were then checked to make sure that the following are, integration time=0.25seconds; increment=3.28nm; Gain=high; Excitation=240nm and chose "sample only" box. The cuvette was then filled with ultrapure water (distilled water) and "run" the experiment and looked for any peaks between emission 300 and 400 nm. If there was any obvious peak, then clean the cuvette again and re-run this experiment again until there is no obvious peak. Once the experiment was finished, the peak value was observed by double clicking on the figure and then clicking on the "data reader" icon to select the peak. Then the highest peak between emission 300 and 400nm was recorded. Once the cuvette check is over then the second step was to carry out "Water Raman Scan" by clicking on "H_2O" button of the " Aqualog main experiment menu". Then clicked on the "Spectra" and then "Emission 2D". After that the experiment file "water ramn.xml" was loaded. Then

integration time=0.25second; increment=3,28nm; gain=high; excitation=350nm and chose 'sample only" box were checked. Cuvette containing ultrapure water (distilled water) was run again and recorded the Raman peak at ~397nm (Raman peak X and Y). The area under the Raman peak was then calculated by double clicking on the resultant graph. Then "data selector" arrow was selected, which allowed to narrow down the range of the emission wave length, so that only Raman peak was in view. Then the "analysis" button of the Aqualog main experiment menu and "Baseline" were selected. Then "Integrate peaks" was selected. Then the "Baseline mode constant" was checked to make sure that the "custom" and set Y=0 and then selected "Next" and again selected 'Next". Then checked "find" and clicked "next". Then selected "fixed width for all peaks" as the integration window width and set "left half width" to "25". Then the right half width will automatically get selected to "25". Then clicked "finish". Then moved on to the "integration result 1" tab to find the area. The area was in the 2nd column entitled "integral result of Sc/Rc, area". This value and area were recorded. After the "water Raman scan" then start the "3D EEM acquisition experiment". It started with selecting on the "H_2O "button of "Aqualog main experiment menu" followed by selecting "3D" then select the "EEM 3D CCD+absorbance". Then the experiment file "3Deem NEW.xml" was loaded. The setting ; integration time=0.25 second; increment=3nm and 3.28nm; Gain=high and make sure that "Sample and Blank" circle were checked. The ultrapure water (distilled water)was then inserted as sample to check any contamination on the cuvette or in the ultrapure water system and the Fluorometer was run to collect the data and the samples were named in the data identifier box. Then named the blank in the "collect blank" box and run the instrument. Then it will ask to insert the blank first and then the sample. Then the Raman certified Reference as blank (Starna Cells, Inc; cat. no. 3-Q-10/WATER) was inserted and collected the Excitation emission matrix(EEM). Then the sample containing the ultrapure water (distilled water) was inserted and collected excitation emission matrix. By subtracting EEM of blank from EEM of ultrapure water will show up as uncorrected waterfall plot. Mean while in the waterfall plot screen the "inner filter correct" button and "Rayleigh masking" button (select both first and second order and set wavelength to 12) were selected. Then "Normalize 3D" button was selected and the Raman area recorded earlier was entered into the "Divide by specific value" box. After this step the EEM contour plot was edited to make it easier to view by setting up the range from 0 to maximum intensity and changing the first layer to white color. Then contours at all major levels was

selected. Each of the samples were run by using the sample cuvette. Before each sample the 'Blank' from the saved file was selected (no need to run blank each time). It was carried out by selecting previous experimental setup and collecting EEM for each sample (Tube well, pond water and irrigation waters). The EEM was composed of two parts a map and a number matrix. From the number matrix we could calculate the following parameters (Table-2) based on Fellman et al., 2010

Parameter	**Calculation**	**Description**
Fluorescence Index (FI)	Ratio of emission wavelengths at 470 nm and 520 nm, obtained at excitation wavelength at 370.(Cory and McKnight (2005)	Fluorescence index explains the source of DOM in water, which is either: microbial (high FI ,1.8, derived from extracellular release and leachate from bacteria and algae) or terrestrially derived (low FI ,1.2, terrestrial plant and soil organic matter).
Freshness Index (β:α)	Ratio of emission intensity at 380 nm divided by the emission intensity maximum observed between 420 and 435 nm, obtained at ex 310 nm (Parlanti et al. 2000; Wilson and Xenopoulos 2009).	Indicator of the contribution of recently produced DOM, where β represents more recently derived DOM and α represents more decomposed DOM. If the ratio is high then DOM in the sample is fresh .
Specific Ultraviolet absorbance (SUVA) in a.u (absorbance unit or arbitrary units, L $mg^{-1}m^{-1}$)	Ultraviolet absorbance at 254 nm (or 255nm) divided by DOC in mg/l . This value is again divided by 0.01m (path length of the cell in meter, For the experiment path length is	SUVA is an indicator of reactivity of DOC. More humic component in DOC means more reactive . Humic components are more aromatic in nature.

	equal to the length of cuvette used and it is 0.01m, there for SUVA=UV 254nm/DOC (mg/l)/0.01 (Weishaar et al., 2003; Mladenov et al., 2010)	

Table 2: Fluorescence parameters calculated from number matrix

From the excitation and emission matrix peaks on EEM (map), the following parameters (Table.3) can be identified Parlanti et al., 2000; Fellman et al., 2010

Component	**Excitation wavelength (nm)**	**Emission wavelength (nm)**	**Letter used to represent the component in EEM map**
Humic like	330-350	420-480	C
Humic like	250-260	380-480	A
Tyrosine like, protein like	270-280	300-320	B
Tryptophane like, protein like or phenol like	270-280	320-350	T

Table 3: Major peaks(DOM) identified in EEM maps of Murshidabad waters

Sediment Analysis

Total digestion of sediment samples

Drill core samples (aquifer sediments) collected from Murshidabad were digested in two separate ways to find out the concentration of total As, Mn and Fe. At first 47 samples; 7 duplicates and 1 standard reference material (Montana, www.nist.gov/srm ; national institute of standards and technology US department of commerce NIST) were digested by reflux tube (Zarcinas et al., 1996) and analyzed over ICP-OES in dept of Agronomy at Kansas State University, and no results were obtained. Then 2 experiments were executed and those were 1. Total digestion by reflux tube soil digestion (Zarcinas et al., 1996) and 2. Microwave digestion, were carried out to digest 15 same samples in two different ways as mentioned above at the same

time. Again the reflux tube soil digestion did not give any results however the microwave digestion gave results for all samples. Then 43 aquifer sediments, 4 duplicates and 11 standard reference material (Montana II-2711, www.nist.gov/srm ; national institute of standards and technology US department of commerce NIST) were digested over microwave to get the results. The methods for both the procedures are described below.

Reflux tube soil digestion: Acid dissolution method (aquaregia) for the determination of total metals in soils sludge, ores , fertilizers etc. Reagents required were Concentrated Hydrochloric acid(trace grade); HCl (cat. no. Fisher Scientific®, cat. no. A5085K-212); concentrated nitric acid (trace grade) (cat. no.) and deionized water. The digestion method started by weighing out ~0.5g of <2mm soil in to very clean restricted neck digestion tubes . If the soil is >2mm in grain size then it has to be pulverized using agate mortar and piston. Mean while aquaregia (HNO_3: HCl; 1:3) been prepared (trace grade HNO_3, Fisher Scientific® cat. no.A509-P212 ; and trace grade HCl, Fisher Scientific®, cat. no. A5085K-212). Then 5mL of this prepared aquaregia was added to each of the digestion tubes containing samples. Then these digestion tubes were arranged over sample rack and left overnight inside running fume hood. Very next morning each digestion tube was gently swirled to make sure that there is no soil stuck on the bottom of the tubes. Then small glass funnels were placed in each of the digestion tubes for refluxing. Digestion blocks were sat to slowly ram up to 140°C and hold for 2 hrs. Checking was done at every 15-20 minutes, to make sure that the soils haven't bubbled up in the tubes. If soil stared bubbling up in the tubes, then remove the tubes from the block and wash the sides of the tube down with a small amount of 0.1% nitric acid. After this procedure the tubes were returned to the block and then watched for more bubbling. After 2 hrs of reflux period the tubes were removed from the block and let it cool. Then made up to 50 mL mark of the tubes with distilled water, mixed well with vortex and placed in the walk in refrigerator overnight covered with parafilm (BEMIS®). Next morning the solution was filtered through Wahtman® no.42 (cat.no. F1241-1) filter papers in to Fabrikal® pH cups. Then these solution were poured to ICP vials for finding the concentration of As, Mn and Fe in ICP-OES in Dept of Agronomy at Kansas State University. The left over samples were preserved in clean centrifuge tubes and kept it in hydrogeochemistry lab in dept of Geology at Kansas State University. For ICP-OES analysis one blank and 4 multielement standard containing As, Mn and Fe in aquaregia matrix were prepared. They include low range standard (As=10 mg/L; Mn=50 mg/L; Fe=50 mg/L); medium

range standard (As=25 mg/L; Mn=100 mg/L ; Fe=100 mg/L); high range standard (As=35 mg/L; Mn=200 mg/L; Fe=300 mg/L) and a very high range standard (As=50 mg/L; Mn=300 mg/L; Fe=500 mg/L). Aquaregia digestion did not show any results after running the samples in ICP OES.

The second method used for total digestion of aquifer sediment was Microwave digestion using by Fisher scientific® cat. no. A509-P212, trace grade nitric acid(70%) over microwave(US EPA, 1986b). Procedure started by weighing out ~0.5g of <2mm soil in to very clean microwave digestion tubes. Then 10 mL of 70% trace grade nitric acid (Fisher scientific® cat. no. A509-P212) was added to each of those microwave digestion tubes containing samples. The tubes were placed in Microwave (MARS® CEM) and ran it at 200°C for 15 minutes. Then the tubes were kept idle for 30 minutes for cooling. Then the solution was filtered through Whatman® no.42 (cat.no. F1241-1) filter papers in to Fabrikal® pH plastic cups. Then the solution was poured in to ICP vials and analyzed for As , Mn (with 50% dilution; 3ml of sample diluted with 3 mL of deionized water) and Fe (with 25% dilution; 1mL of sample diluted with 3 mL of deionized water) in ICP-OES at Dept of Agronomy, Kansas State University. Single element standards were prepared and analysis were performed separately. For As run, 4 standards and one blank were prepared and they are Blank (As=0), low range standard (As=2 mg/L); medium range standard (As=4 mg/L); high range standard (As=8 mg/L) and a very high range standard (As=20 mg/L). Mn standards include a blank (Mn=0); a low range standard (Mn=10 mg/L); medium range standard(Mn=20 mg/L); high range standard (Mn=40 mg/L) and very high range standard (Mn=50 mg/L). Fe standards include blank (Fe=0); very low range standard (Fe=15 mg/L); low range standard (Fe=30 mg/L); medium range standard (Fe=60 mg/L); high range standard (Fe=100 mg/L) and very high standard (Fe=200 mg/L). Microwave digestion gave results for all samples and hence followed for this study.

Sequential extraction of Aquifer Sediments

5-step method of He et al., 2010 was most relevant and therefore was chosen for this study to find out concentration of As, Mn and Fe at various soil phases . Aquifer samples from each location were selected for the study. A total of 27 samples, 2 duplicates and one standard reference material (Montana II 2711, www.nist.gov/srm ; national institute of standards and technology US department of commerce NIST) were used for the experiment. From Beldanga 8 samples and 1 duplicate, Hariharpara at 7 samples and 1 duplicate, Nabagram 6 samples and

from Kandi 6 samples at different depths were chosen for the study. The samples were selected based on the values obtained from microwave total digestion results.

Sample Preparation started by measuring of ~1 g subsamples of the wet samples were placed in previously weighed (to 0.001 g precision) plastic 50 mL centrifuge tubes in a N_2 glove box for a few days for drying

Step-1 Procedure; for Non-specifically sorbed As, Mn and Fe

(a) Prepare 0.05 M $(NH_4)_2SO_4$, was made by adding 6.574 g of $(NH_4)_2SO_4$ powder to 1L of de-ionized water.

(b) Once samples were dried then weigh to nearest 0.001 g

c) 25 mL of the 0.05 M $(NH_4)_2SO_4$ were added to the samples via pipette

d) Place the Samples over the shaker for 4 hours to react with the ammonium sulfate.

e) Prepare 7 multi-element standards (As, Mn, Fe) were prepared in the 0.05 M $(NH_4)_2SO_4$ matrix near expected concentrations.

f) After 4 hours of shaking, samples were removed and centrifuged at ~2100 rpm for 10 minutes

g) The solution was decanted into a disposable syringe and passed through a 0.45 µm filter into a 13 mm x 90 mm plastic vial for analysis by ICP-OES.

h) Preserve the remaining solution by filtering into small Evergreen vials for future analysis (by GFAAS).

i) 3 wash step with 15 mL of de-ionized water was done at ~2100 rpm for 10 minutes. The remaining solution was decanted and saved in 50 mL centrifuge tubes. Centrifuge tubes with sample were weighed to account for contribution from this step onto the following step.

j) 4 multi-element standards were prepared (low range Standard, As=0.5 mg/L, Mn=0.5 mg/L, Fe=2 mg/L; medium range standard, As=1 mg/L, Mn=1 mg/L, Fe=4 mg/L, high range standard, As=2 mg/L, Mn=2 mg/L, Fe=8 mg/L; very high range standard, As=3 mg/L, Mn=5 mg/L and Fe=10 mg/L) and one blank(As=0, Mn=0, Fe=0) were prepared for As, Mn, and Fe using the 0.05 M $(NH_4)_2SO_4$ as the matrix

Step-2 procedure : For specifically sorbed As, Mn and Fe

The extraction of the specifically sorbed ions using 0.05 M $NH_4H_2PO_4$. $NH_4H_2PO_4$ was used because As and P have similar electron configurations and form triprotic acids with similar dissociation constants (Wenzel, et al., 2001), and at equal concentrations phosphate outcompetes

arsenate for adsorption sites in soils (Swartz et al., 2004) because of smaller size and higher charge density of phosphates (Manning et al., 1996).

a) 0.05 M strength was prepared by adding 5.746g of $NH_4H_2PO_4$ granules to 1L of de-ionized water.

b) 25 ml of 0.05 M $NH_4H_2PO_4$ solution was added via pipette to each 50 mL centrifuge tube and placed on the shaker overnight for 16 hours

C) Run the standards and samples with dilution factor 25 from Step 1 (during shaking for the second step) on ICP-OES using wavelengths of 193.76, 257.61, 259.94 nm for As, Mn and Fe, respectively.

d) After 16 hours of shaking, samples were centrifuged at ~2100 rpm for 10 minutes

e) Decant and filter the solution (using and Evergreen vials into a disposable syringe and passed through a 0.45 µm filter) into a 13 mm x 90 mm plastic vial for analysis by ICP-OES

f) 3 wash step with 15 ml of de-ionized water was done at ~2100 rpm for 10 minutes each. The remaining solution was decanted to 50ml centrifuge tubes and saved. Then Centrifuge tubes (with sample) were weighed to account for contribution from this step onto the following step.

g) 4 multi-element standards were prepared (low range standard As=0.5 mg/L, Mn=0.5 mg/L, Fe=2 mg/L; medium range standard, As=1 mg/L, Mn=1 mg/L, Fe=4 mg/L, high range standard, As=2 mg/L, Mn=2 mg/L, Fe=8 mg/L; very high range standard, As=3 mg/L, Mn=5 mg/L and Fe=10 mg/L) and one blank (As=0, Mn=0, Fe=0)were prepared for As, Mn, and Fe using the 0.05 M $NH_4H_2PO_4$ as the matrix

Step-3 procedure: To find the concentration of As, Mn and Fe present in amorphous and poorly crystalline hydrous oxides of Fe and Al

This step starts with the preparation of a 0.2 M NH_4^+-oxalate buffer at pH 3.25 in the dark.

a) 0.2 M NH_4^+-oxalate buffer strength was achieved by adding 28.422g of NH_4^+-oxalate buffer granules to ~500 mL of de-ionized water, adjusting pH to 3.25 by adding ~16mL of concentrated HCl (trace metal grade). De-ionized water was added to bring the final volume of solution up to 1L to make the 0.2 M NH_4^+-oxalate buffer. Then wrap the beaker with aluminum foil to create darkness.

b) 25 mL of 0.2 M NH_4^+-oxalate buffer at pH 3.25 was added to each centrifuge tube with a pipette and placed in a rack in a cardboard box and covered with aluminum foil (for darkness) then placed on a shaker for 4 hours

c) Standards and samples were ran with dilution factor 25 from Step 2 on ICP-OES

d) 4 multi-element standards were prepared (low range Standard, As=0.5 mg/L, Mn=0.5 mg/L, Fe=5 mg/L; medium range standard, As=1 mg/L, Mn=1 mg/L, Fe=25 mg/L, high range standard, As=2 mg/L, Mn=2 mg/L, Fe=50 mg/L; very high range standard, As=3 mg/L, Mn=5 mg/L and Fe=100 mg/L) and a blank (As-0, Mn=0, Fe=0) for As, Mn, and Fe using the 0.2 M NH_4^+-oxalate buffer at pH 3.25 as the matrix .

e) After 4 hours of shaking, samples were centrifuged at ~2100 rpm for 10 minutes.

f) Decant and filter the solution (using and evergreen vials into a disposable syringe and passed through a 0.45 µm filter) into a 13 mm x 90 mm plastic vial for analysis by ICP-OES

g) 3 wash step with 15 ml of de-ionized water was done at ~2100 rpm for 10 minutes each. The remaining solution was decanted to 50 mL centrifuge tubes and saved. Centrifuge tubes (with sample) were weighed to account for contribution from this step onto the following step.

Step-4 procedure: to target well crystalline hydrous oxides of Fe and Al.(e.g. goethite, hematite)

a) Prepare the extractant by adding 28.422 g of 0.2 M NH_4^+-oxalate granules and 17.648 g of ascorbic acid to ~500 mL of de-ionized water. Solution pH was adjusted to 3.25 by adding ~13 ml of HCl (trace metal grade) and bringing the volume up to 1L ml with de-ionized water to achieve proper strength

b) 25 mL of the extractant solution was added carefully via pipette to each centrifuge tube with sample

c) Placed the centrifuge tubes in a rack in a water bath and heated at 90°C ± 5°C for 30 minutes

d) Prepare 4 standards(low range Standard, As=0.5 mg/L, Mn=0.5mg/L, Fe=5 mg/L; medium range standard, As=1 mg/L, Mn=1mg/L, Fe=25 mg/L, high range standard, As=2 mg/L, Mn=2 mg/L, Fe=50 mg/L; very high range standard, As=3 mg/L, Mn=5 mg/L and Fe=100 mg/L) and one blank (As=0, Mn=0, Fe=0) using the 0.2 M NH_4^+-oxalate solution adjusted to pH 3.25 as the matrix prepared for step 4.

e) Run the standards and samples with dilution factor 25 from Step 3 on ICP-OES

f) Centrifuged the samples two times at ~2100 rpm (10 minutes first time and 15 minutes second time)

g) Decant and filter the solution (using and Evergreen vials into a disposable syringe and passed through a 0.45 µm filter) into a 13 mm x 90 mm plastic vial for analysis by ICP-OES)

h) 3 wash step with 15 ml of de-ionized water was done at ~2100 rpm for 10 minutes each. The remaining solution was decanted to 50ml centrifuge tubes and saved. Centrifuge tubes (with sample) were weighed to account for contribution from this step onto the following step.

Step-5 procedure: Residual phases excluding silicates

a) 10 mL of 1:1 HNO_3 (5 ml HNO_3:5 ml de-ionized water) was added to each centrifuge tube.

b) Cover the centrifuge tube with a watch glass and placed in a water bath at ~90°C for 15 minutes

c) After the 15 minutes samples were removed for cooling

d) 5 mL of concentrated HNO_3 was added to each sample, watch glasses were replaced, and samples were returned to water batch to reflux for 30 minutes

e) Keep the samples in water bath at 90°C ± 6°C for ~2 hours to evaporate (No brown fumes were observed)

f) The Standards and samples were analyzed with dilution factor 25 from Step 4 on ICP-OES under same conditions as earlier steps.

g) Remove the samples from water bath after 2 hours and let it cool

h) Add 2 mL of de-ionized water to the samples, followed by 3 ml of 30% H_2O_2 to facilitate effervescence

i) Return the samples to water bath and heated at 90°C ± 5°C for two hours. During the first hour, a total of 13 mL of H_2O_2 was added in 1mL aliquots to each sample due to continued effervescence of the samples.

j) After two hours, samples were removed from water bath and centrifuged, decanted and filtered as done in the previous steps (using and Evergreen vials into a disposable syringe and passed through a 0.45 µm filter) into a 13 mm x 90 mm plastic vial for analysis by ICP-OES)

k) Final weights of samples were recorded, and samples were stored in refrigerator.

l) 4 multi element standards were prepared (low range Standard, As=0.5 mg/L, Mn=0.5mg/L, Fe=5 mg/L; medium range standard, As=1mg/L, Mn=1mg/L, Fe=25 mg/L, high range standard, As=2 mg/L, Mn=2 mg/L, Fe=50 mg/L; very high range standard, As=3 mg/L, Mn=5 mg/L and Fe=100 mg/L) were made using same concentrations as other steps in a 10:13:7 HNO_3:H_2O_2:de-ionized water matrix and one blank (As=0, Mn=0, Fe=0) run along with samples with dilution factor 25 in the ICP-OES.

Organic matter Extraction of Aquifer Sediments

Organic matter extraction was performed to find out the approximate amount of organic matter and organic bound As, Mn and Fe. During this test, total amount of organic matter present in the sediments were also calculated using combustion method. A total of 14 aquifer samples (Beldanga=4 and 1 duplicate; Hariharpara=4, Nabagram=3 and one duplicate , Kandi=3) 2 duplicates and one standard reference material (Montana II 2711, www.nist.gov/srm ; national institute of standards and technology US department of commerce NIST) were used for the experiment. The experiment started with the preparation of 0.7 *M* NaOCl (adjusted to pH 8.5 with HCl) by adding 790.067 mL of NaOCl in deionized water and adjusted to pH 8.5 by adding 5 mL of trace grade HCl. By adding NaOCl to the soil cause digestion of organic matter present in the sediments and during this process the organic bound As and Mn will also comes to the solution and both can be measured. (Hettiarachchi et al., 2003). Steps for the organic matter extraction is as follows

1. Weighed out 1g sample (dry weight basis) placed in a 50-mL plastic centrifugal tube
2. Removed the inorganic carbon by adding few drops (~10) of 0.005 *M* HCl
3. Added 20 mL 0.7 *M* NaOCl (adjusted to pH 8.5 with HCl) to each centrifuge tube containing the samples.
4. Heated the tubes to 90°C in a water bath for 2 hr with occasional mixing
5. After cooling, the sample were centrifuged at 2100 rpm for 10 minutes and collect the supernatant and This procedure is repeated for 2 times and collect the supernatant separately
6. Then wash step with 0.01 M Ca $(NO_3)_2$ 4 H_2O (prepared by mixing 2.3363g of Ca $(NO_3)_2$ 4 H_2O in one litter of deionized water) by adding 20mL of this solution to each of centrifuge tubes that has been treated with 0.7M NaOCl solution. (the extractant from this step is saved for future analysis if necessary). Mixed the contents in the test tube in a shaker and centrifuged at 2100 rpm for 10 minutes and collected the supernatant separately and preserved inside the fridge.
7. Analyzed the supernatant separately (if the concentrations are really low in each of extractant then mix them together (5mL of extractant each) and analyzed them in ICP-OES and later results were combined to get the total As, Fe and Mn removed by this extraction. Prepared single element standards (As, Fe and Mn) using 0.7 *M* NaOCl (adjusted to pH 8.5 by adding HCl) as the matrix. 4 numbers of standards and one blank (0.7M NaOCl pH 8.5 for As, Fe and Mn. As (very low range=2 mg/L, low range=5 mg/L, Medium range=8 mg/L, high range=10 mg/L); Fe standard (very low range=15 mg/L, low range=40 mg/L, medium range=80 mg/L, high

range=100 mg/L) and Mn standard (very low range=2 mg/L, low range=5 mg/L, medium range=8 mg/L, high range=10 mg/L). While making Mn standard there was heavy precipitation of MnO_2 in the 0.7M NaOCl solution (pH 8.5). This was the reason for making single element standards separately and the concentration of Mn standards prepared were really low to avoid precipitation of MnO_2 .

8. Analyzed the supernatant by combining supernatant from both extractions of step-5, (2 mL of each extractant and diluting with 18 mL of distilled water) in the proportion, 1:10 to avoid instrumental damage by NaOCl in TOC analyzer for dissolved organic carbon (DOC)

10. Same sediments were analyzed for total organic carbon (TOC) in soil testing lab in department of agronomy by combustion method. TOC is determined using LECO TruSpec CN analyzer. The samples were treated with 1N phosphoric acid to remove carbonates prior to analysis.

Scanning Electron Microscopy (SEM)

SEM analysis was performed to find out the concentration of various trace elements in the aquifers sediments. 3 samples (aquifer sediments) were chosen (Beldanga=2, Nabagram=1) for the study. Samples are taken from various depth in the aquifer (Beldanga 43m and 27m depth; Nabagram 24 m depth). Each sample was mounted on a separate aluminum SEM stub with a carbon coating. The detailed description of SEM analysis is present in Appendix-A, detailed materials and method.

Loss of Ignition test for High As Aquifer sediments

Organic matter content (concentration) of sediments can be roughly determined by measuring weight loss of the sediments in question after burning. A total of two drill core samples (core#2 and core#3) collected during January 2010 from Beldanga (high As area) were engaged in LOI test. The position of these drill cores were very near to the drill core collected during January 2012 for the present study (both from Beldanga, high As area). During the time of LOI test (September 2011) the field work for the present study was not been executed. The loss of weight during burning of soil samples for loss-on-ignition (LOI) test is due to the conversion (oxidation) of organic carbon to CO_2. In high clay soils, water of hydration may be lost during the burning resulting in additional error. If the samples are from saline environments, additional steps must be taken to subtract weight loss due to the oxidation of sulphur to SO_2. Protocol for LOI has been

developed from Reeuwijk (2002); Matthiesen (2005). The protocol followed for LOI experiment is shown below.

1. Set the muffle furnace temperature to 450°C and leave the porcelain crucibles in it for 8 hours
2. Remove crucibles from furnace and allow cooling in a glass desiccator.
3. Weigh the crucibles using the mass balance (resolution 0.001 g) (**A** gram)
4. Transfer 5g fine soil (< 2mm) into the crucibles and re-weigh crucible and sample (**B** gram). Difference yields the water content
5. Dry crucible with sample in the oven at 105°C until dry (overnight).
6. Remove crucibles from oven and cool in a desiccator and weigh (**C** gram)
7. Place the crucibles in a preheated muffle furnace at 450°C and leave the crucibles in it for 4 hours.
8. Remove crucibles from furnace and allow cooling in a glass desiccators and re-weigh (**D** gram). The difference from the dry state yields the organic content.

Calculations

Moist(%)=[(B-C)/(C-A)]x100 The result should be expressed in Wt%

Moisture correction factor (mcf)= [(100+Moist%)/100]

Loss on ignition: LOI (%)=[(C-D)/(C-A)]X100

Ash content , Ash(%)=100-LOI(%)

Organic matter content (%)=[(C-D)/5]X100

Synchrotron beam line studies of Aquifer Sediments (XANES and EXAFS)

X ray absorption spectroscopy (XAS) covers both X ray absorption near edge structures (XANES) and X ray absorption fine structures (EXAFS). XAS studies were conducted in Murshidabad aquifer sediment samples to speciate As ($As^{3+}$and As^{5+}) and Sulfur (SO_4^{2-} and S^{2-}). XANES was used to find the various As and sulfur species (oxidation states) in sediments. EXAFS were used to find the local molecular structure of a particular element in question within the sample. Sulfur is very good redox sensitive element and by studying the various sulfur species in aquifer sediments will give insight about the redox condition of the aquifer. All the studies were carried out at Brookhaven National lab- National Synchrotron Light Source (BNL-NSLS) and 3 separate beam lines were used and they were X27A (energy range:4.5-32 keV); X 15 B (energy range:1.2-8 keV) and X11A (energy range:4.5-40 keV). X27A and X11A were

used for As speciation and X15B was used for sulfur speciation. The sample prepared for X15B beam line is shown is the Figure-8. The samples for the beam line were selected based on total digestion data of aquifer samples. Those samples with high As concentration and selected for the study. Before the analysis, all the samples were dried inside a nitrogen glow bag in a nitrogen environment to avoid oxidation. Later these samples were transferred to 50 mL centrifuge tubes and flushed with nitrogen to keep the sample environment inert. One sample from Beldanga was analyzed in X27 A. For X11A, 3 samples from Beldanga, Hariharpara and Kandi and 1 sample from Nabagram were analyzed. In X15B two samples from Beldanga; one sample from Hariharpara and Nabagram and 3 samples from Kandi were analyzed. The description and standard operating procedure for each beam line is represented in Appendix-A; detailed materials and method.

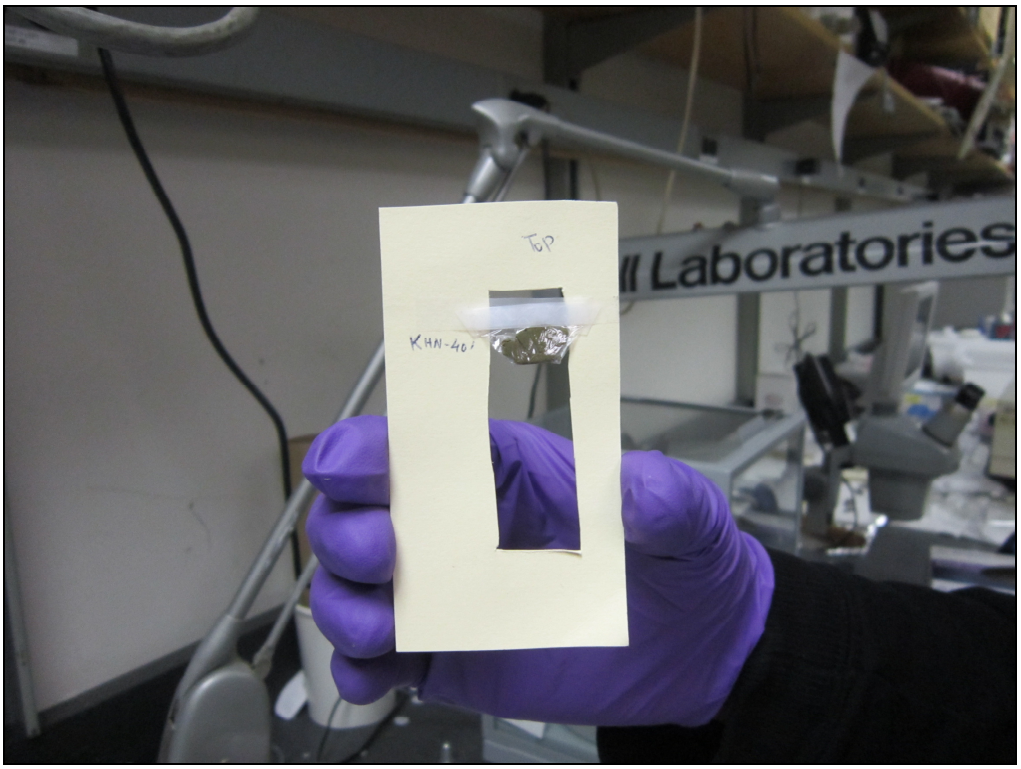


Figure 8: Sample prepared and mounted for X15B beam line

Chapter 5 - Results

Sediment Analysis in field

Sediment coring and lithologs

Sediments characteristics of high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi) were entirely different. Bhagirathi river marks the boundary between two main different chronostratigraphic units. The sediments on the eastern side of the river is Holocene in age and are grayish in color. The comprehensive lithologs (2 from Beldanga and 1 from Hariharpara) prepared for the drilled sediments on the eastern side of river Bhagirathi is described below. 2 cores from Beldanga (high As area) and one core from Nabagram (low As area) were described in the main text and rest of the cores (Hariharpara and Kandi) were described in the Appendix-B.

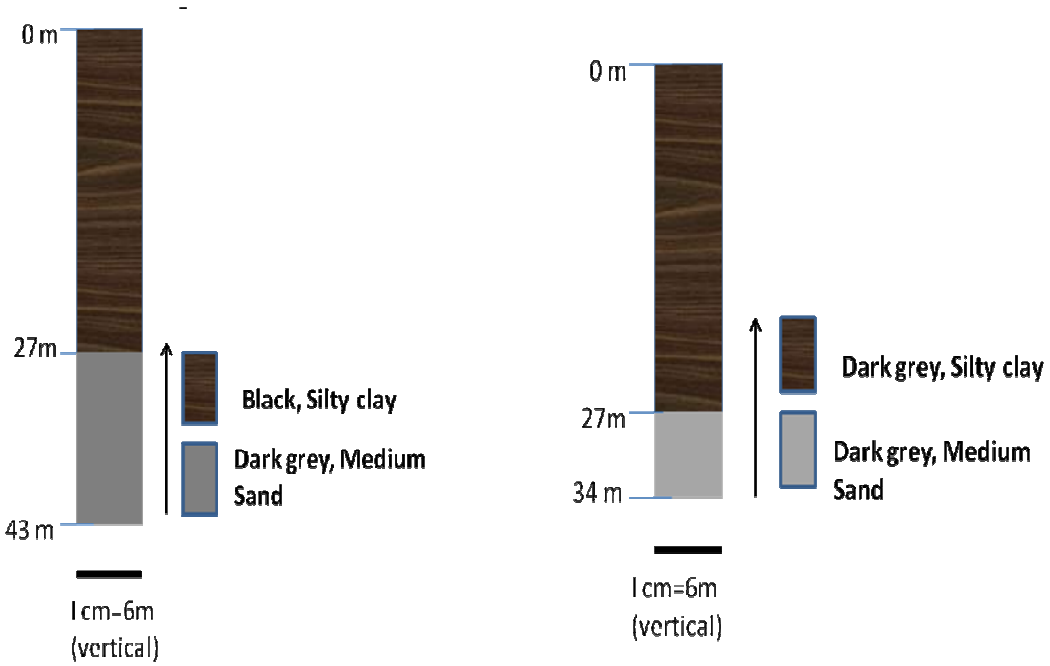


Figure 9: Comprehensive lithologs for Beldanga core, CS-102 BM (left) and CS-103 (right)

Both the logs were almost similar in sediment characteristics as they are both from the same place (Beldanga, high As area) (Fig. 9). The slight color difference in upper silty clay sequence may be due to the water (moisture) content or slight variation organic matter concentration.

CS-102 BM- Borehole drilled on 01/01/2012 (Fig.9, left). The sequence started with black clay sequence and was very sticky in nature. At 12m depth from the surface in CS-102 core very fine grained sand cay mixture was encountered and it was continued for almost 3m and again the black cay formation started. At this time red colored spots (oxidation of iron oxides spots) were observed on the clay surface and it disappeared after 3 m depth and the clay formation continued till 27m depth. After the black sticky clay sequence dark grey medium grained sand sequence was encountered till 43m depth. This sand formation is the aquifer in this region. This sequence consisted of abundant mica (muscovite); organic matter (plant) and various mafic minerals. Sand is very loose in nature. The main mineral composition of sand was quartz.

CS-103 BM- Borehole drilled on 01/02/2012 (Fig 9, right). Comprehensive lithology of this borehole is similar to that of CS-102. This core started with dark greyish sticky clay formation and it was continued to a depth of 3m till a very loose clay with very minor amount very coarse particles (quartz) were reached. It was grayish in color with high content of water. This bed continued for another 3m depth until a medium grained, greyish, loose sand with abundant muscovite mica; fragments of organic matter particles and some dark mafic minerals were reached. This bed continued for another 3m depth then a dark grayish sticky clay bed was encountered and it continued for 9 m depth. After that, the same clay bed was continued, but red colored spots over the dry clay surface were observed and continued for another 3 m depth and then it changed to clay (major) with minor amount of coarse grained particles (minor quartz sand fraction) with red colored spot over the dry surface and extended for another 3 m depth. The total length of the overall clay bed observed was 27 m. After the clay bed medium grained greyish sand with abundant muscovite mica , organic matter particles (plants) and some mafic minerals was encountered , which is same as the sand formation encountered in CS-102.

Sediments on the western side of the river Bhagirathi is Pleistocene in age and As content of groundwaters in this region were very low (<10ppb). Two borehole sediments has been collected from 2 separate study locations in this side, and they were Nabagram (CS-104 NB) and Kandi (CS-106 KHN).

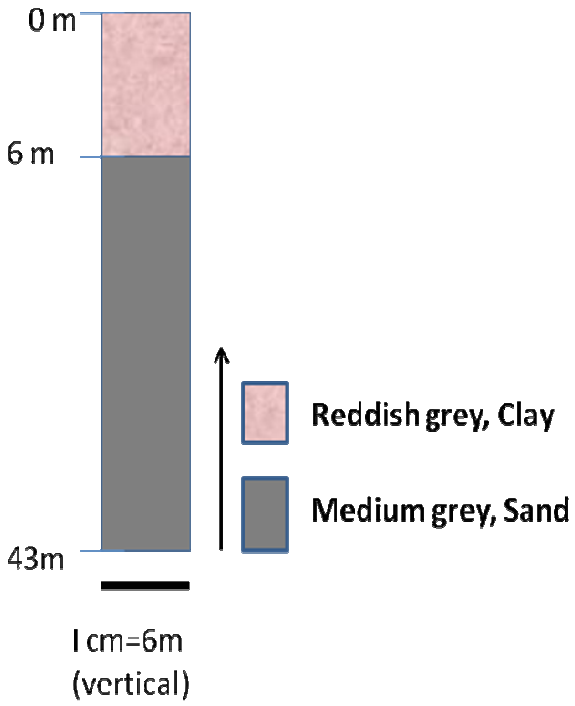


Figure 10: Comprehensive litholog for Nabagram core (CS-104 NB)

CS-104 NB (low As area): Borehole drilled on 01/04/2012 (Fig.10): The first bed encountered during drilling was reddish gray sticky clay and it extended to a depth of 6m. But after 3 m from the surface to a depth of 6m the same reddish grey clay bed contained some muscovite mica flakes. After the reddish clay bed, a medium grained, greyish colored sand bed had started, which continued till 43m (maximum depth drilled) depth. Within this sand bed, (stared from the base of the reddish clay bed) till to a depth of 15 m, abundant mica (muscovite); organic matter (plant) and some mafic minerals were observed. After 15m to a depth of 18m with in this sand bed, the size of the muscovite mica flakes became larger compared to other parts but rest of the characters remained same till 43m that is medium grained sand with abundant mica (muscovite) and organic matter (plant) and mafic minerals. However at lower depths (30m to 43m) occasional dark spots (decayed organic matter)were observed in same medium gray sand bed.

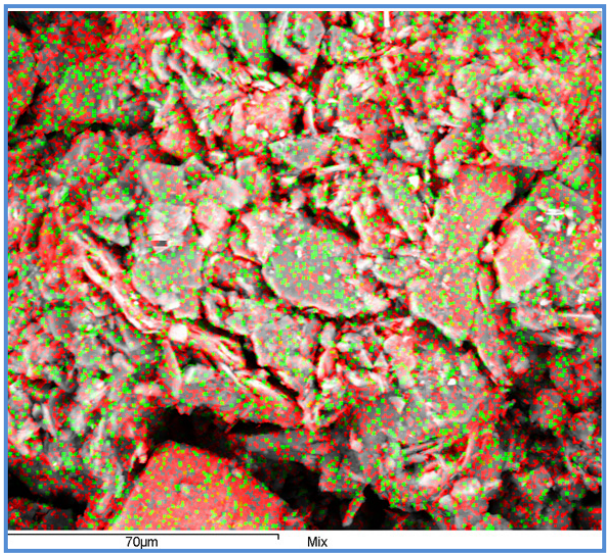
All the lithologs were showing a generalized fining upward sequence (fining of grain size towards top). Fining upward sequence of sediment were characteristics of sediments deposited by meandering streams and oxbow lakes. The litho-logging includes detailed recording of color, grain size, visual identification of organic matter.

Sediment analysis in the lab

Scanning Electron Microscopy(SEM) of Aquifer sediment Samples

SEM analysis of the selected aquifer sediments (solid phase) were carried out to study the a). characteristics of various sediment fractions; b). Arsenic and other elemental concentration associated with those fractions; c).the relationship of As with other elements. Each sample has been magnified and analyzed for As at various regions with in the sample. A total 3 aquifer sediment samples were analyzed. They were BM-140 (43m depth)(4 spots), BM-90ft (27m depth)-(3 spots) both from Beldanga (high As area), CS-102 borehole and NB-80 (24m) (6spots) from Nabagram (low As area), CS-104 drill core. These depths were selected because majority of the tubewells in this area were of the same depth.

Majority of sediment constitute clay fraction with quart grains spread throughout. Oxygen (O) and Silicon (Si) constitute the major elements present in these sediments. High As concentration was expected in Beldanga (high As area) sample, but the concentration of As (weight %) in the areas analyzed in those samples were less or below detection limit; but still there was presence of As in low concentration. In the contrary, Nabagram being low As area, the SEM results shows comparatively higher concentration of As (weight%) than Beldanga. A number of spots where analyzed for As concentration in each samples and those regions were photographed as well. SEM photomicrographs (Fig.11) and the concentration of As content in those photos were represented in the corresponding table on the side. For some of the analysis spectra showing elemental proportions were also taken. The detection limit of EDS is 0.01%.



Element	Weight %
O (K)	55.08
Si (K)	23.78
Al (K)	8.65
K (K)	3.21
Fe (K)	6.52
Mn (K)	0.06
As (L)	0

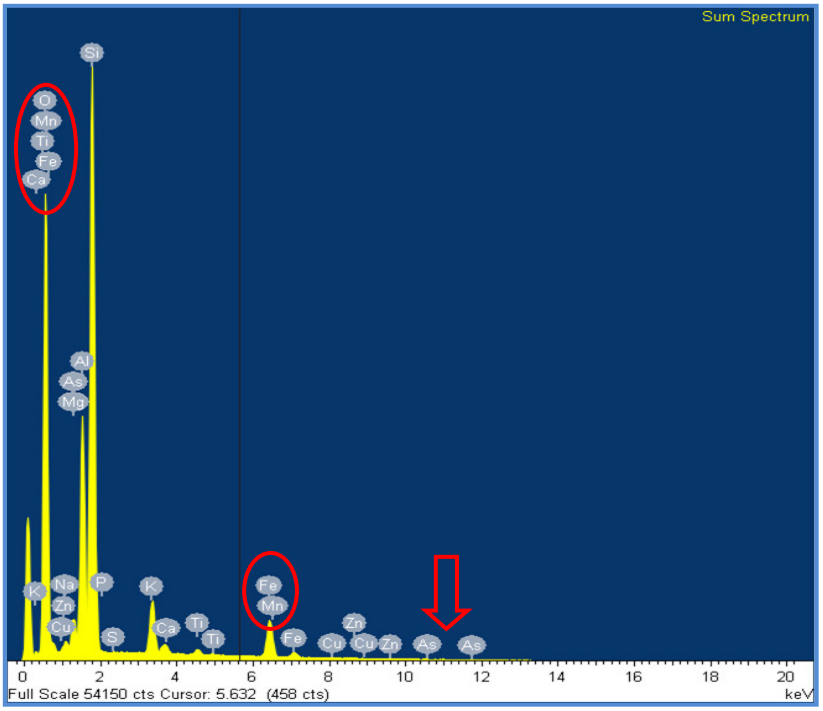


Figure 11: SEM photomicrograph of selected area in sample no.BM-140 (43m; high As area) and distribution of Mn (green spots) and Fe (red spots) over the selected area is shown. Yellow spots shows their coexistence. Corresponding table on the right shows the major elements and their weight % in this selected area, clay. The weight % are obtained from the ionization intensity peaks obtained from the major sub shells (represented inside the bracket) of a particular element. Spectra (bottom)showing elemental proportions. As is present as very minute concentration and it is below detection limit, but Fe and Mn shows association.

Several areas in each sample is analyzed to study the sediment characteristics and elemental concentration (weight %). The detailed information is attached to Appendix-C.

Loss of Ignition Test (LOI) for Beldanga cores sediments Results

The organic matter (OM) concentration have been measured for 2 drills cores from Beldanga (core#2 & core#3; high As area) . Based on depth the sediments were classified into 3 and they were; a). shallow depth (0-10m); b) intermediate depth (10-30m); c) deep depth (>30m) . For core#2; the organic matter concentration varies from 2.46% at shallow depth (0-10m) to 0.25% at deeper depths (40m). Maximum value of 3.28% OM is present at a depth of 24.4m (intermediate depth). Where as in the core#3 (Beldanga) the OM concentration varies

from 1.8% at the top to 0.26% at the bottom (40m) with maximum OM content 22.20% present at 18.3 m (intermediate depth) depth (Fig. 12).

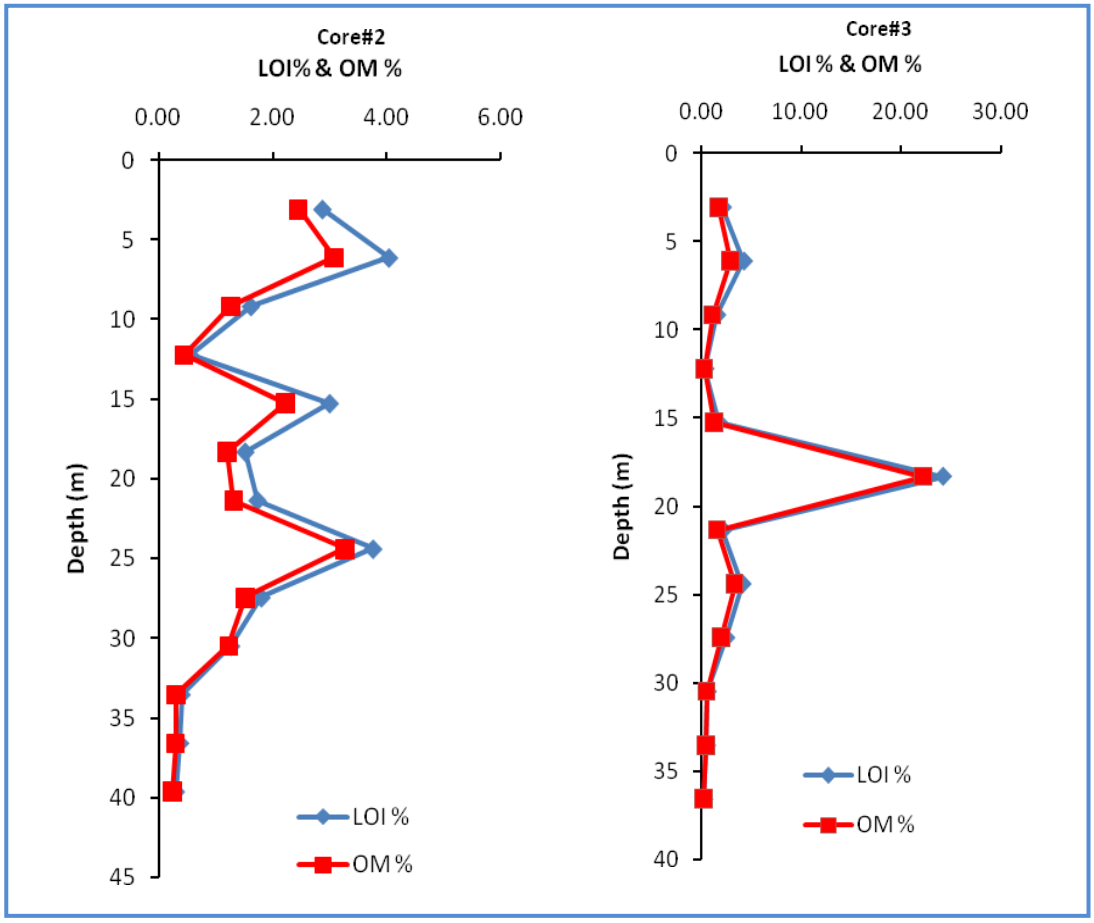


Figure 12: Plot showing the variation of LOI % and calculated OM % for Core#2 and Core #3 (Beldanga) with depth (m)

The percentage of ash from the LOI test for both core#2 and core# 3 are represented in the Table 4 blow.

Core #2		Core #3	
Depth (m)	Ash %	Depth (m)	Ash %
3.048	97.12	3.048	97.81
6.096	95.95	6.096	95.70
9.144	98.37	9.144	98.39
12.192	99.45	12.192	99.56
15.24	96.99	15.24	98.21
18.288	98.47	18.288	75.81
21.366	98.26	21.366	97.77
24.384	96.23	24.384	95.85
27.432	98.19	27.432	97.47
30.48	98.72	30.48	99.32
33.528	99.59	33.528	99.39
36.576	99.62	36.576	99.67
39.624	99.69		

Table 4: Table showing the Ash % (LOI test) for core#2 and core#3 with depth.

Both of the core show similar characteristics (trend) in OM%, LOI% and ash % . OM% is comparatively higher in the intermediate depths and gradually decreasing towards the bottom deeper depths. OM% is almost similar in concentrations at the top because of the equal amount of distribution of the soil humus layer. The OM % is high in clays compared to sand.

Total Digestion of Aquifer Sediments Results

Total digestion by 70% Nitric acid in microwave at 200°C for 15 minutes (US EPA, 1986b) was conducted to determine concentration of As, Mn and Fe via ICP-OES of aquifer sediments collected from 4 bore holes. Among those 4 cores 2 are from High As areas, Beldanga(CS-103 BM) and Hariharpara (CS-105 HK) and the other 2 are from low As areas, Nabagram (CS-104NB) and Kandi (CS-106 KHN). The variation of As, Mn and Fe concentration (mg/kg) with depths (m) of the sediments in high As area (Beldanga, Hariharpara) and low As area (Nabagram, Kandi) are represented in Figure.13, 14 &15.

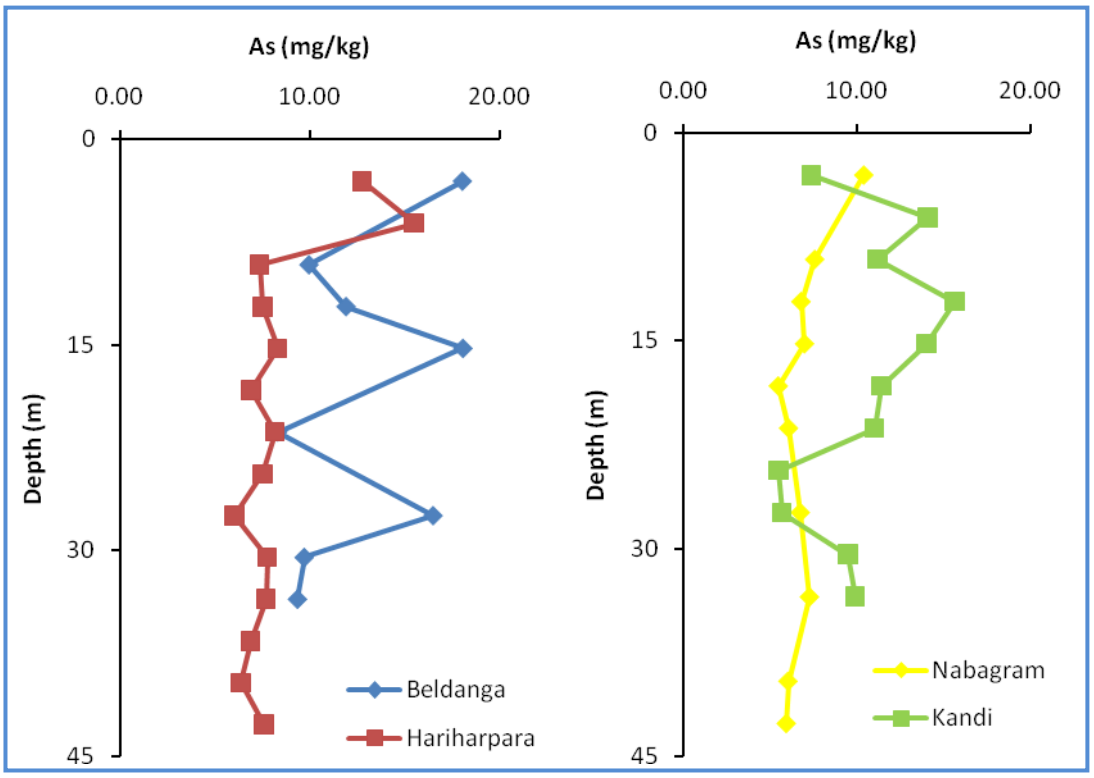


Figure 13: Depth-wise distribution in concentrations of As (mg/kg) in high As areas (Beldanga, Hariharpara) and low As areas (Nabagram, Kandi)

The depth wise classification for the cores are;

a) shallow depth (0-10m)

b) intermediate depth (10-30m)

c) deeper depths (>30m)

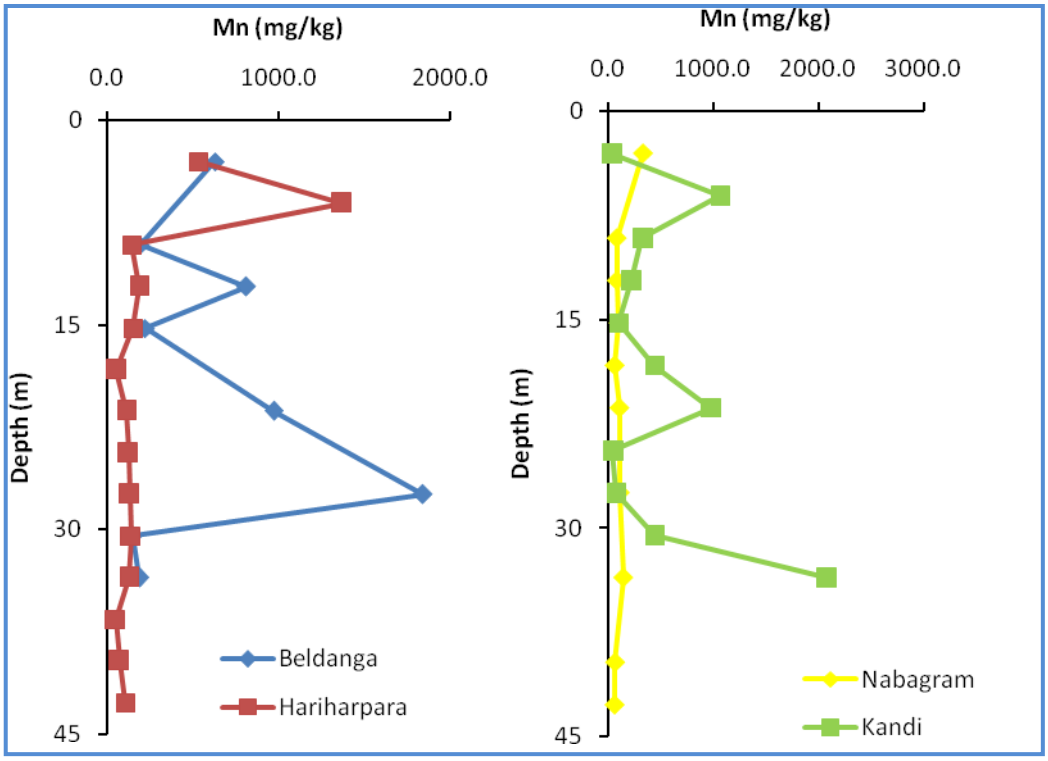


Figure 14: Depth-wise distribution in concentrations of Mn (mg/kg) in high As areas (Beldanga, Hariharpara) and low As areas (Nabagram, Kandi)

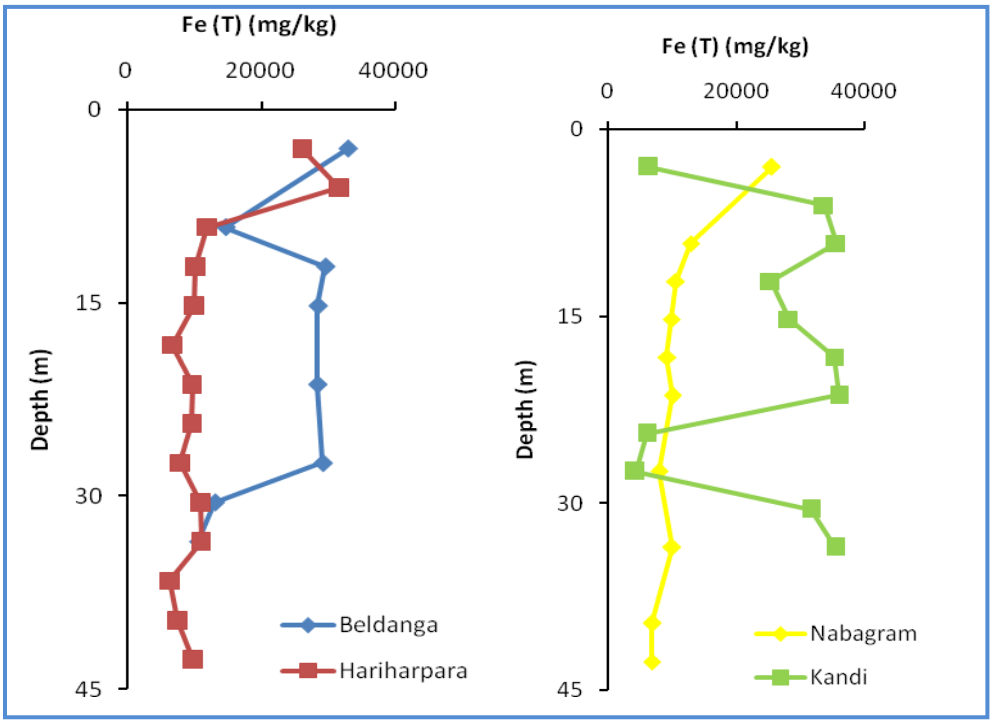


Figure 15: Depth-wise distribution in concentration of Fe(t) (mg/kg) in high As areas (Beldanga, Hariharpara) and low As areas (Nabagram, Kandi)

In Beldanga (high As area) the maximum As concentration is observed in black colored silty clay bed present at shallow to intermediate depths and the concentrations were 18.06 mg/kg; 18.09 mg/kg and 16.52 mg/kg at 3 m ;15 m and 27 m respectively. The sand bed below (27-34 m) has lower As concentration; 9.71 mg/kg being the maximum observed at 30.5 m depth. The coring has been done for a maximum depth of 34 m in this area. As per the observations As concentration is high in clay rich sediments (shallow to intermediate depths) compared to the sand (Fig. 13). Hariharpara (high As area) the maximum As concentrations, 12.78 mg/kg and 15.54 mg/kg are at 3m and 6m depths and both were in dark grey sticky clay bed. Whereas in the dark grey colored medium grained sandstone bed, which extends from intermediate to deep depths, has less As concentration compared to the As concentration above (clay bed). The concentration of As ranges from 8.3 mg/kg (maximum) at 15m depth to 6.03 mg/kg at 27.4 m, both within intermediate depth (Fig.13).

In Nabagram (low As area) the maximum As concentration was observed in the top reddish gray colored clay and it is 10.42 mg/kg at 3 m depth (shallow). Then As concentration ranges between 5.48 mg/kg to 7.29mg/kg in the grey colored medium grained sandstone which extends from the base of the red colored clay bed at 9.1 m depth to 43m depth (intermediate to deep). In Kandi the As concentration changed with change in lithology. In the red colored (oxidized) medium grained sand bed the concentration of As was 7.4 mg/kg . Followed by reddish grey colored clay formation (3-21 m; shallow to intermediate depths) and the As concentration ranges from 14.12 mg/kg at 6 m (shallow) to 11.04 mg/kg at 21m (intermediate) depth with a maximum As concentration of 15.67 mg/kg at 12.2 m depth (intermediate). Then the reddish gray clay bed changes to dark gray colored fine-medium grained sand bed (21-27 m, intermediate) and the As concentration range is 5.5 mg/kg to 5.7 mg/kg. Then the dark gray fine to medium grained sandstone changed to a dark grey colored sticky clay bed and As concentration in this bed changed from 9.51 mg/kg to 9.92 mg/kg at 30.5 m to 33.5 m (deep depths) (Fig.13).

Both Mn and Fe(t) concentration in Beldanga are also changing with depth and lithology. The concentration of Mn and Fe (t) in black colored sticky clay ranged from 8.3 mg/kg to 18.09 mg/kg and 14721 mg/kg to 32972 mg/kg respectively, which extends from shallow to intermediate depths. When the lithology changes to dark grey medium grained sand (27-34 m) the concentration of Mn and Fe (t) concentration ranges are 151.4-192 mg/kg and

10689-13140 mg/kg. In Hariharpara the Mn and Fe (t) concentration ranges from 533-1369.5 mg/kg and 26227-31731mg/kg respectively in the top most dark gray colored sticky-clay bed present at the shallow depths (0-6m). Later the lithology changes to dark grey colored medium grained sand bed which extends from 6-43m (shallow to deeper depths)and the concentration of Mn and Fe (t) are 59-1369.5 mg/kg and 6871-31731 mg/kg respectively (Fig.14&15).

The Mn and Fe(t) concentration in Nabagram also changes with depth and lithologies. The concentration range for Fe (t) and Mn in reddish-grey colored clay bed (0-9.1 m, shallow depth) are 89.2-332.8 mg/kg and 12962-25613 mg/kg respectively. Then it changes to 69.4-150.3 mg/kg and 6927-10598 mg/kg in grey-colored medium grained sands beds (9.1-43m, intermediate depth). In Kandi the Mn and Fe(t) concentration ranges from 35.2mg/kg and 6463mg/kg in reddish colored medium grained sands. Mn and Fe(t) ranges are 224.2-10703mg/kg and 25390-36121mg/kg in reddish grayish colored clay bed (3-21m, shallow to deep). After this the clay formation changes to dark grey colored fine- medium grained sand bed (21-27 m, intermediate depth) and the concentration of Mn and Fe (t) in these beds are 51.9-81.9 mg/kg and 4404-6182 mg/kg respectively. Later this sand bed grades into a dark grey sticky clay beds which extend from 27-34m (intermediate to deep depths) and the Mn and Fe(t) concentrations are 444.7- 2081.5 mg/kg and 3174.8-35508mg/kg respectively (Fig.14 & 15).

In these cases there is a sharp change in concentration of As, Mn and Fe (t) with change in lithology. In both high and low As areas the Fe (t) concentration shows linear correlation with As and Mn content. The r^2 values for As vs. Fe (t) for high and low As areas are 0.757 and 0.676 respectively. Whereas the r^2 values for Mn vs. Fe (t) for high and low As areas are 0.628 and 0.464. It is interesting to note that in all areas (both high and low As areas) the sediment As and Mn concentrations are almost similar (Fig.16). The details of total digestion results are represented in the Appendix D.

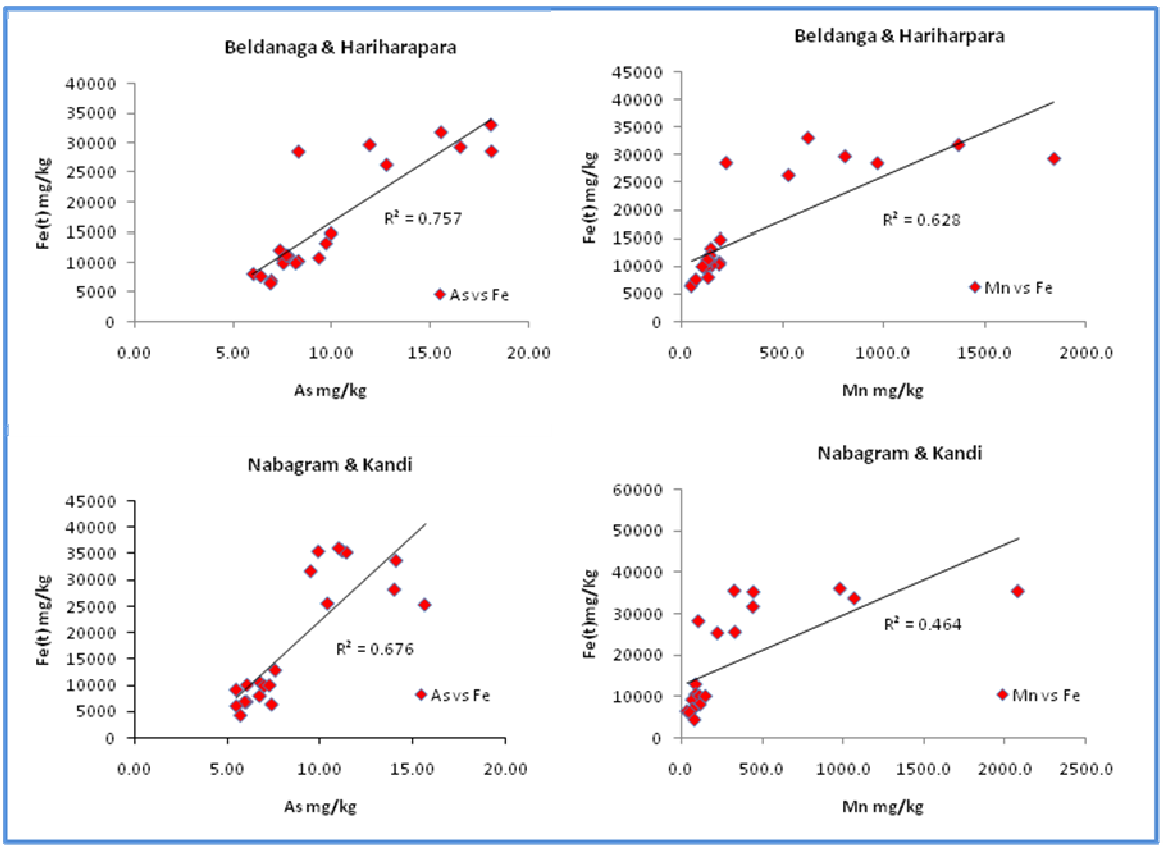


Figure 16: Correlation (linear) plots for As and Mn vs. Fe(t) for Beldanga & Hariharpara (high As) and Nabagram & Kandi (low As)

Sequential Extraction Results of Aquifer sediments

Sequential extractions were performed on both high As cores (Beldanga(CS-103), Hariharpara (CS-105) and low As cores (Nabagram (CS-104), Kandi (CS-106) to find out relative proportions of As, Mn and Fe in 5 different sediment fractions and they are a) non specifically sorbed; b) specifically sorbed; c) amorphous and poorly crystalline hydrous oxides of Fe and Al; d) well crystalline hydrous oxides of Fe and Al; e) residual phases (quartz and feldspar etc.). All leachates were analyzed immediately after the extractions and the analysis were continued the last step to avoid the precipitation of the trace elements. Only Beldanga and Nabagram results were only represented in the text, other 2 cores, Hariharpara and Kandi are in the Appendix-E.

In Beldanga core(high As area),CS-103 BM at shallow depths (0-10 m , BM-10& BM-30) occupied by dark grey colored sticky clay formation , no As concentration is observed in the nonspecifically sorbed phases. up to 30% As is found in specifically sorbed phases shallow

depths. Up to 30% As is found in amorphous and poorly crystalline hydrous oxides of Fe and Al.20% of As is present in well crystalline hydrous oxides of Fe and Al. Up to 40% As is present in residual phases. In the intermediate depth (10-30 m, BM-40 to BM-100) the concentration of As is totally absent in the non specifically sorbed phases. But in the next specifically sorbed phases the concentration of As decreases gradually from top(10m) 25% to bottom (30 m) 15% with a maximum of 30% at 15.2m (BM-50). Then again As concentration increases to 27% in the deep depth >30m(BM-110). In amorphous and poorly crystalline hydrous oxides of Fe and Al at intermediate depths the As concentration is more or less equally distributed(~20%) (BM-40-BM-100) with a maximum of ~30% at 27.4 m (BM-90).In the deep depth (>30 m) the concentration of As is around 20% in amorphous and poorly crystalline hydrous oxides of Fe and Al phase. In well crystalline hydrous oxides of Fe and Al phase at shallow depth the concentration of As is nearly sample and it is 20%. In the intermediate depths the concentration of As in this phase changes considerably. At 12.2 m depth the concentration of As is 10% where are in the middle region of intermediate depth the concentration is less ~2-3% and increase again towards the deeper regions of intermediate depths 27.4m and 30.5 m are 15% and 25%. In the deeper depths for this phase the As concentration is ~20%. There is sharp variation of As concentration in the residual phases from shallow depths (~30-35%) to the intermediate depths (~40%-50%) . At deeper depths (>30 m) the concentration of As is ~55% (Fig.17)

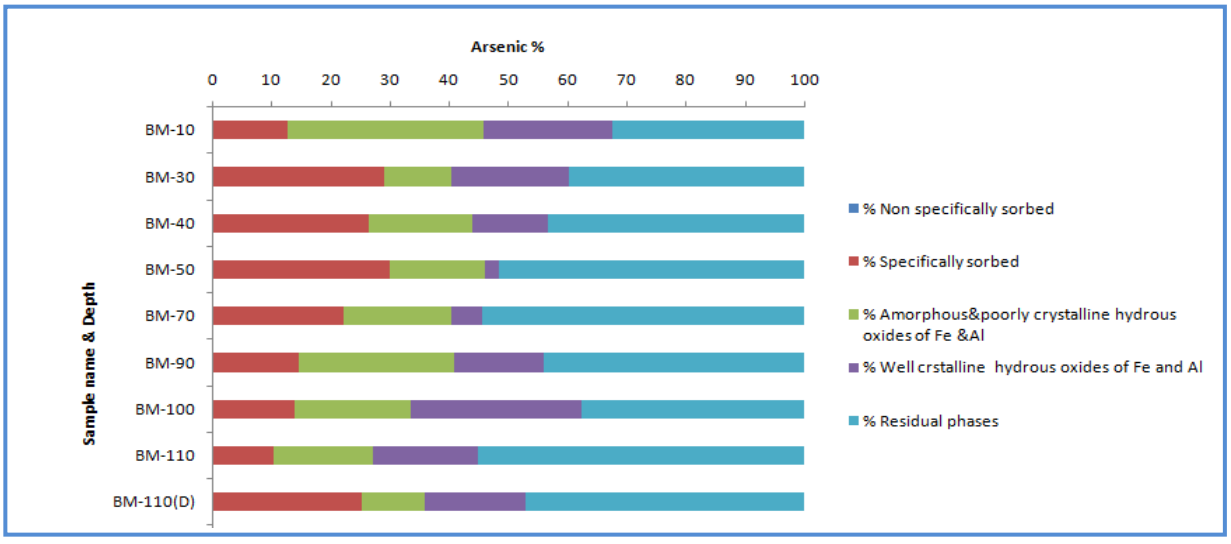


Figure 17: Distribution of As in various sediment fractions in Drill Core CS-103 BM from Beldanga, Total depth of core 34 m (e.g. BM-10 = 10 ft (~3 m) depth; BM-110 = 110 ft (~34 m) depth)

Mn concentration in Beldanga is showing considerable variation with depths in various sediment fractions. Majority of Mn (~75%) is present in the amorphous and poorly crystalline oxides of Fe and Al in the shallow and middle depths. It is almost equally distributed in the non specifically sorbed phases and the concentration is less (~2-10%) at all depths. In the specifically sorbed phase at shallow depth (0-10m) it is ~10% and at the intermediate depths the concentration was very less ~2% at 10 m and 1% at 27m depths. In the deeper depths (>30 m) the concentration of Mn is around 15%. Mn concentration in well crystalline hydrous oxides of Fe and Al phase was almost equally distributed in all most all depths. In the residual phases Mn concentration is around 45% in the top layer (3 m) then it very less at 9-10 m depths <1% and it increased(~62%) in the intermediate and remained almost same concentration in the deeper depths(~50%) (Fig.18).

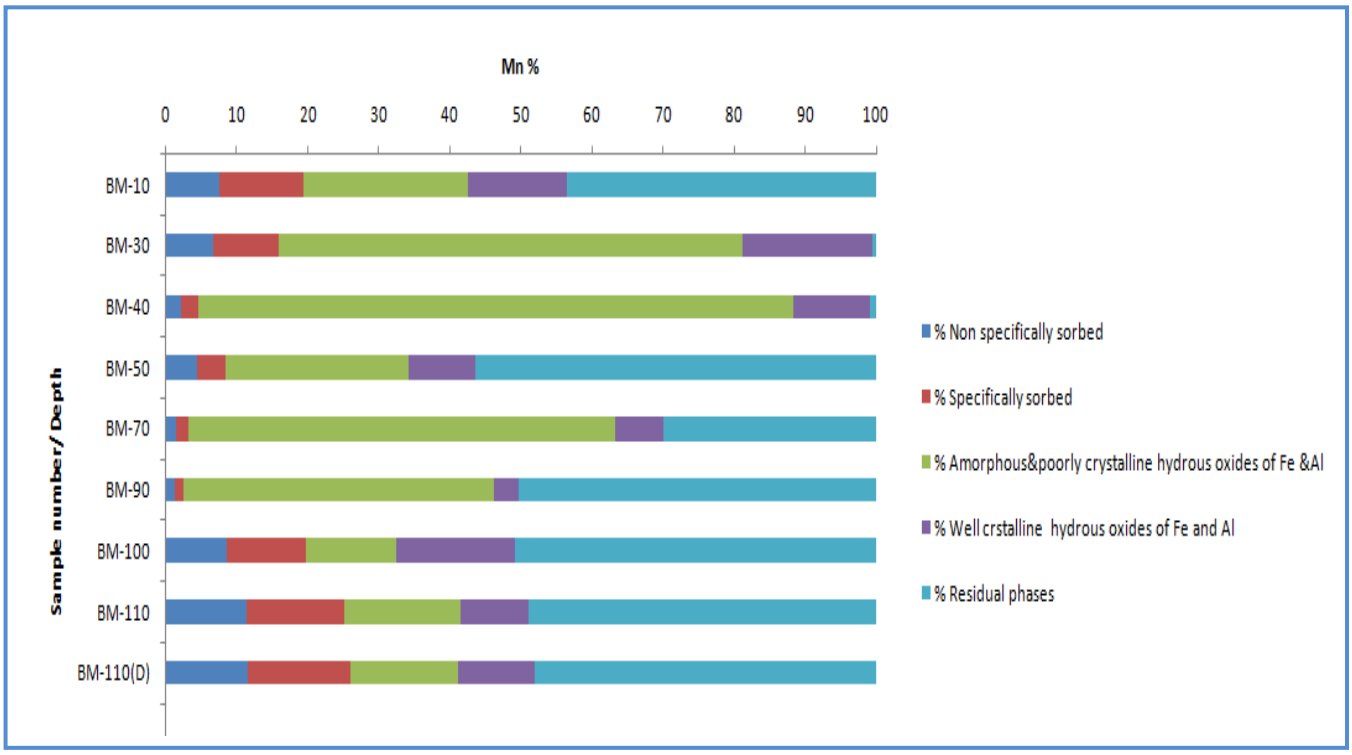


Figure 18: Distribution of Mn in various sediment fractions in Drill Core CS-103 BM from Beldanga, Total depth of core 34 m (e.g. BM-10 = 10 ft (~3 m) depth; BM-110 = 110 ft (~34 m) depth)

Concentration of Fe (t) was absent in nonspecifically sorbed phases at all depths. Very less concentration (~1%) of Fe (t) is observed in the specifically sorbed phases and was present at shallow (~3 m) and intermediate (15.2 m) depths. It was unevenly distributed in amorphous

and poorly crystalline hydrous oxides of Fe and Al with a maximum of 65% at shallow depth (~9m). The maximum concentration of Fe (t) observed in this phase at intermediate depths were 52% (21.4m) and 63% at (12.2m) and a minimum of 20% observed at 15.24m depth. At deeper depth (34m) the concentration of Fe (t) was 10% in amorphous and poorly crystalline hydrous oxides of Fe and Al phase. It was almost equally distributed at all depths in the well crystalline hydrous oxides of Fe and Al phase. At shallow depth (3 m)the Fe (t) concentration is ~52%. Then at 9m depth the concentration decreased to ~1%. There was an increase of Fe(t) concentration in the intermediate depth (from top bottom) ~3% to 60%, which is about ~95% increase in Fe (t) concentration in residual phases at intermediate depths. At the deeper depth (34 m) the Fe (t) concentration in residual phase was around 63% (Fig. 19)

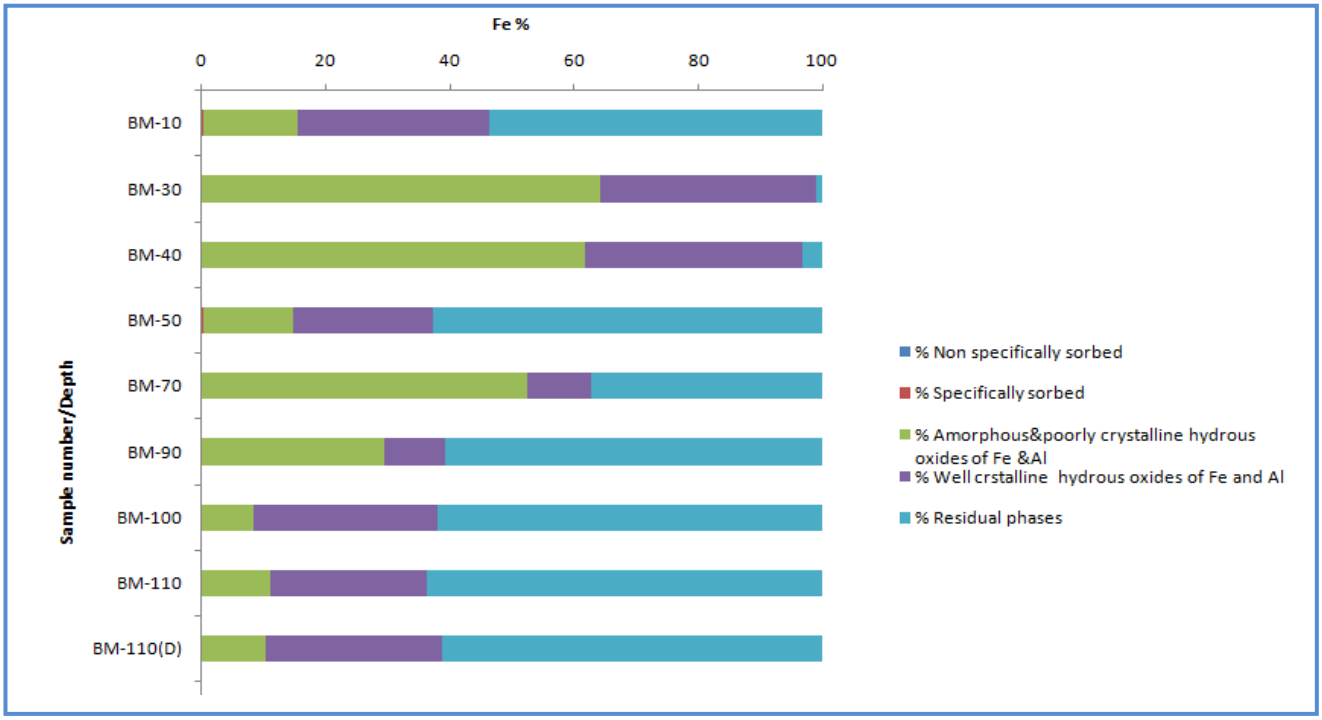


Figure 19: Distribution of Fe(t) in various sediment fractions in Drill Core CS-103 BM from Beldanga, Total depth of core 34 m (e.g. BM-10 = 10 ft (~3 m) depth; BM-110 = 110 ft (~34 m) depth)

The sequential extraction results for the Nabagram (low As area) aquifer sediment ore (CS-104NB) shows more or less similar characteristics like that of high As area cores (Beldanga and Hariharpara). The depth wise classification is as follows a) shallow depth (NB-10, 10ft, 3 m); intermediate depth (NB-40, 12 m to NB-90, 27.4m) and deep depths (NB-130, 40 m to NB-140, 43m). As concentration was totally absent in nonspecifically sorbed phase at all depths in

Nabagram. Arsenic concentration in specifically sorbed phases was unequally distributed and also not similar at all depths. Maximum concentration of 30% was present at 15.24m (HK-50) and least concentration was ~3% and was present at 12 m depth (NB-40). Whereas in amorphous and poorly crystalline hydrous oxides of Fe and Al and in well crystalline hydrous oxides of Fe and Al, the concentration of As changed from shallow to deeper depths. High concentration (~17% and 30%) was present in shallow depth and very less concentration (~4% and 3%) was present in deeper depths. There was an overall increase in As concentration in the residual phases from shallow to deeper depths and the ranges were 25% (3 m) to 70% (43m) (Fig.20).

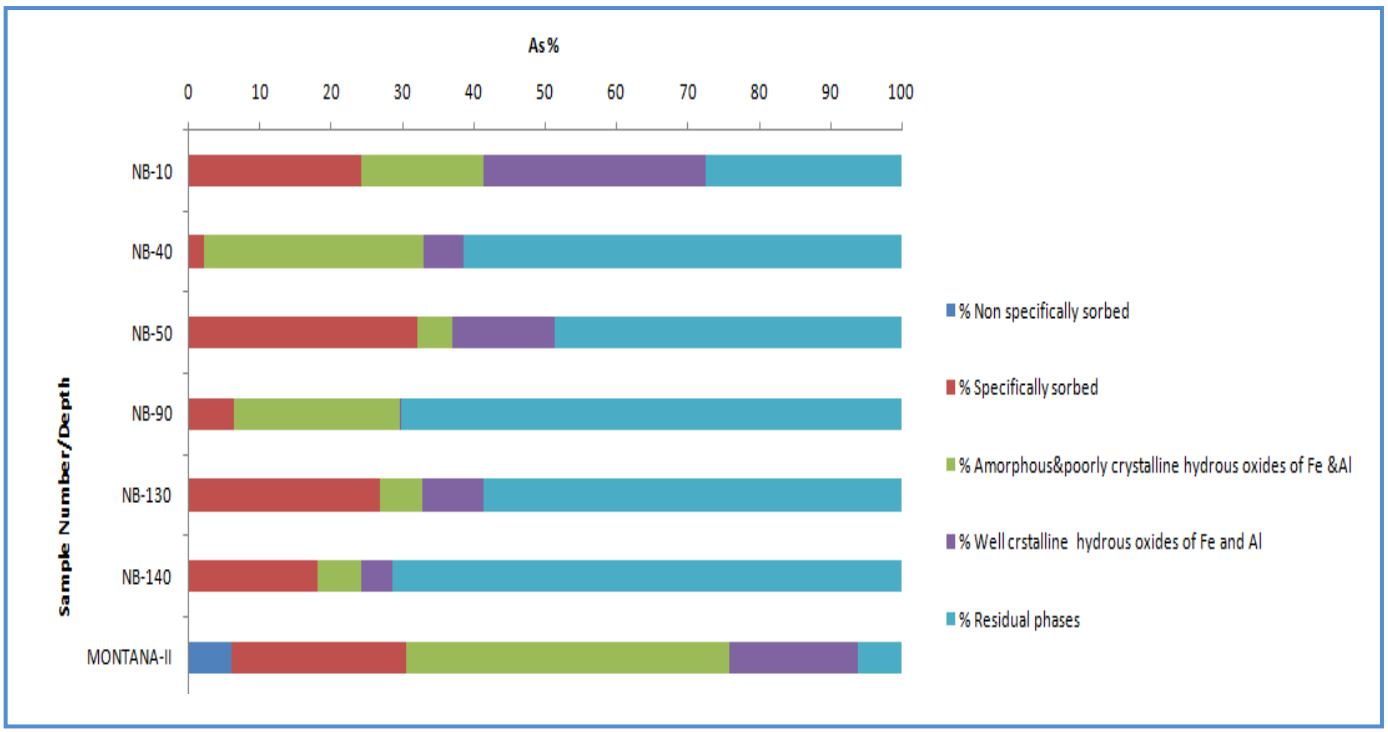


Figure 20: Distribution of As in various sediment fractions in Drill Core CS-104 NB from Nabagram. Total depth of the core 43m. (e.g. NB-10 = 10 ft (~3 m) depth; NB-140 = 110 ft (~43 m) depth)

Mn was distributed in all sediment fractions throughout all depth ranges. The maximum concentration was observed in nonspecifically sorbed phases and there was an overall increase in Mn concentration in nonspecifically sorbed phases with depth (12%-50%). It was almost equally distributed in specifically sorbed phases at all depths (~20%). Mn concentration in the amorphous and poorly crystalline hydrous oxides of Fe and Al phase and well crystalline

hydrous oxides of Fe and Al were almost similar (~5%) at all depths, except at shallow depth (3 m) and were 45% and 15% respectively. Mn concentration in the residual phase at shallow depths ranged from 9-25% (3 to 12.2 m). At the top portion of intermediate depth, 12 m the concentration was ~27% and at 15.24 m and at the bottom portion of intermediate depth 27m, the concentration decreased to 15%. Then again at deeper depth, there was a gradual increase in Mn concentration and it was 20% at 40 m and 25% at 43 m. (Fig. 21)

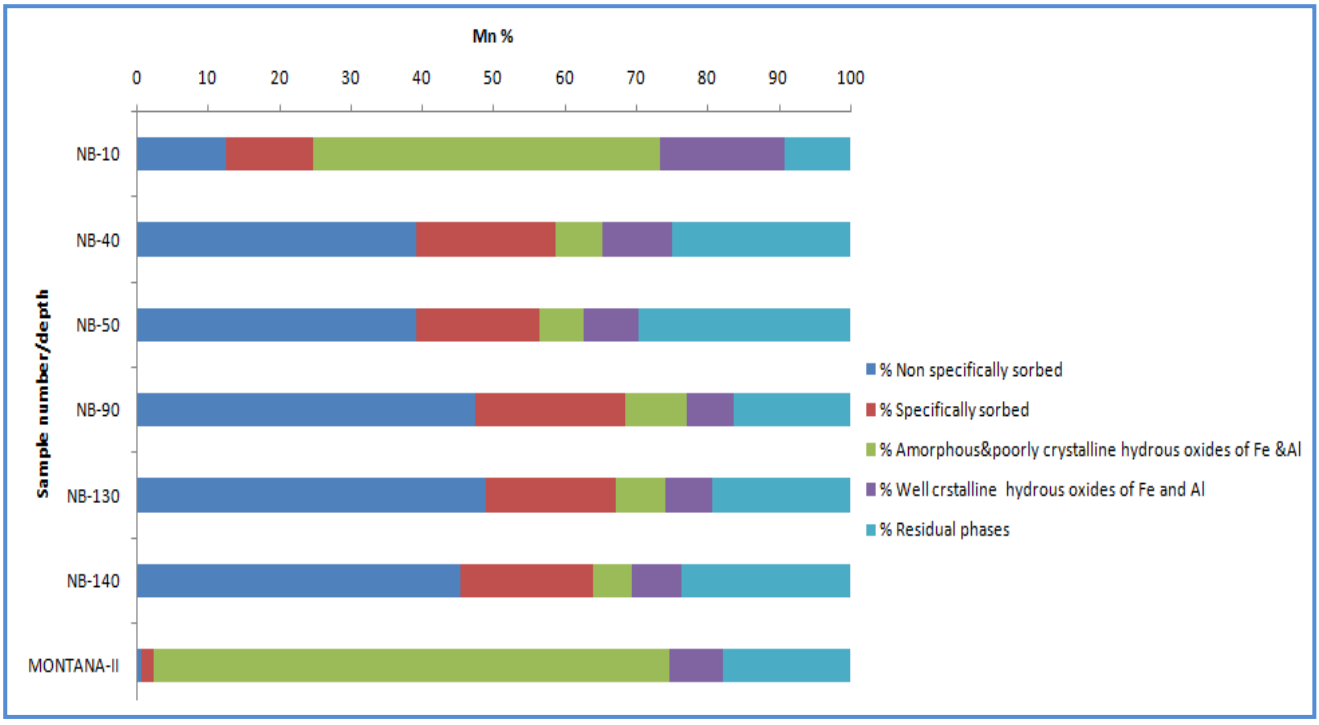


Figure 21: Distribution of Mn in various sediment fractions in Drill Core CS-104 NB from Nabagram. Total depth of the core 43m. (e.g. NB-10 = 10 ft (~3 m) depth; NB-140 = 110 ft (~43 m) depth)

Concentration of Fe (t) in various sediment fractions at various depths of Nabagram core was almost equally distributed except in nonspecifically sorbed fraction, where the concentration of Fe (t)was absent at all depths. Very less concentration of Fe (t) was observed in specifically sorbed fractions. It was absent in shallow depth (3m) and there was a gradual increase of Fe(t) in the intermediate(<1%) to deeper depths (~2%) in specifically sorbed fractions. Maximum Fe (t) in specifically sorbed fraction was observed at 40m depth and again it decreased to 1% at 43 m. It was equally distributed (~5%)in the amorphous and poorly crystalline hydrous oxides of Fe and Al phase throughout all depths. In the well crystalline hydrous oxides of Fe and Al, the Fe (t) concentration was more or less equally distributed (~25%) in all depths except at 3m depth

(shallow) and the concentration was 35%. There was a gradual increase of Fe(t) concentration from shallow to deeper depths in the residual phase 15% at 3 m to 30% at 43 m (Fig.22).

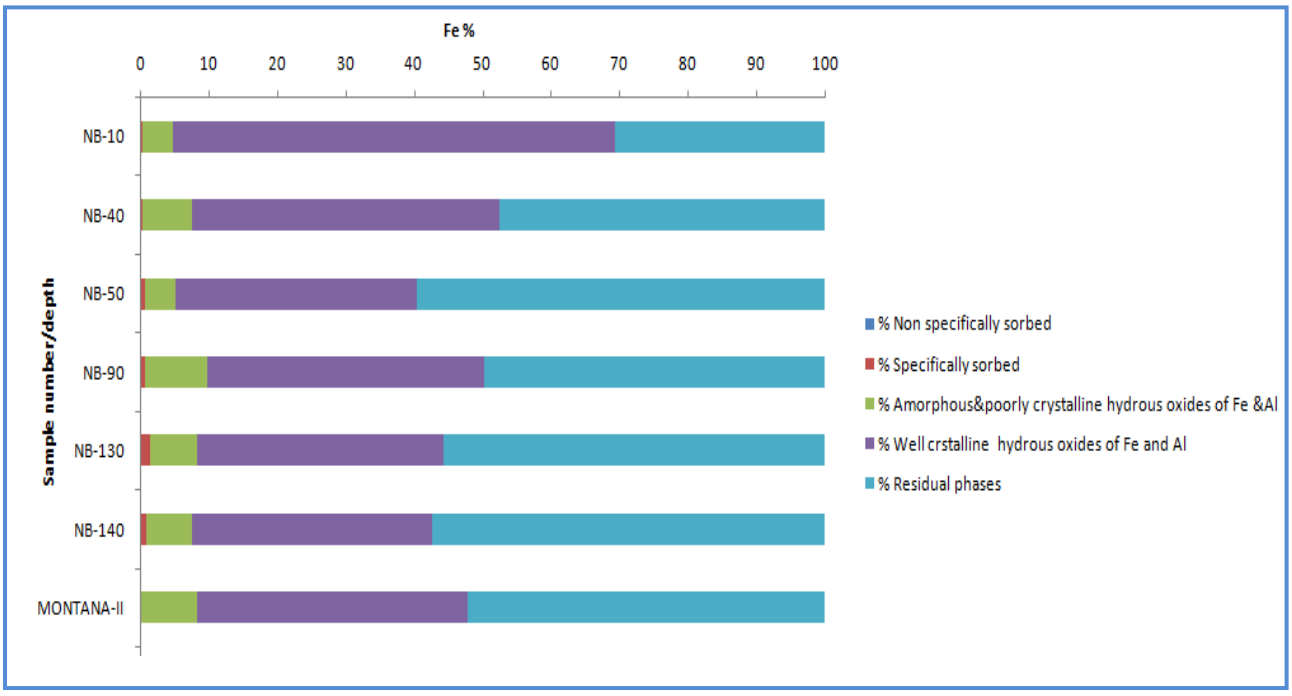


Figure 22: Distribution of Fe(t) in various sediment fractions in Drill Core CS-104 NB from Nabagram. Total depth of the core 43m. (e.g. NB-10 = 10 ft (~3 m) depth; NB-140 = 110 ft (~43 m) depth)

The results of sequential extractions are represented in appendix-F

Organic matter Extraction results of Aquifer Sediments

Organic matter extractions from sediment cores were performed based on Hettiarachchi et al., 2003, in two high As cores (Beldanga(CS-103 BM)and Hariharpara (CS-105)) and low As cores (Nabagram (CS-104), Kandi(CS-106)) to find the following

a) Concentration of As, Mn and Fe released during organic matter digestion using 0.7M NaOCl (via ICP-OES)

b) Quantify the amount of organic matter that came out in solution during NaOCl digestion, using a TOC analyzer

c) To find the total concentration of organic matter in sediment

Only As, Mn and Fe(t) concentration of Beldanga and Kandi aquifer sediment cores after OM extraction were represented in the main text. The As, Mn and Fe (t) concentration after OM extraction of Hariharpara and Nabagram were in Appendix-5. However the DOC concentration

(obtained from OM extraction) and TOC & TN concentration obtained from LECO TruSpec CN analyzer for all sediments cores from high As areas (Beldanga; Hariharpara) and low As areas (Nabagram and Kandi) are represented in the main text.

The concentration of As, Mn and Fe (t) resealed during digestion of Beldanga aquifer sediments using 0.7M NaOCl pH 8.5 is represented in the figure below. The concentration of As, Fe(t) and Mn

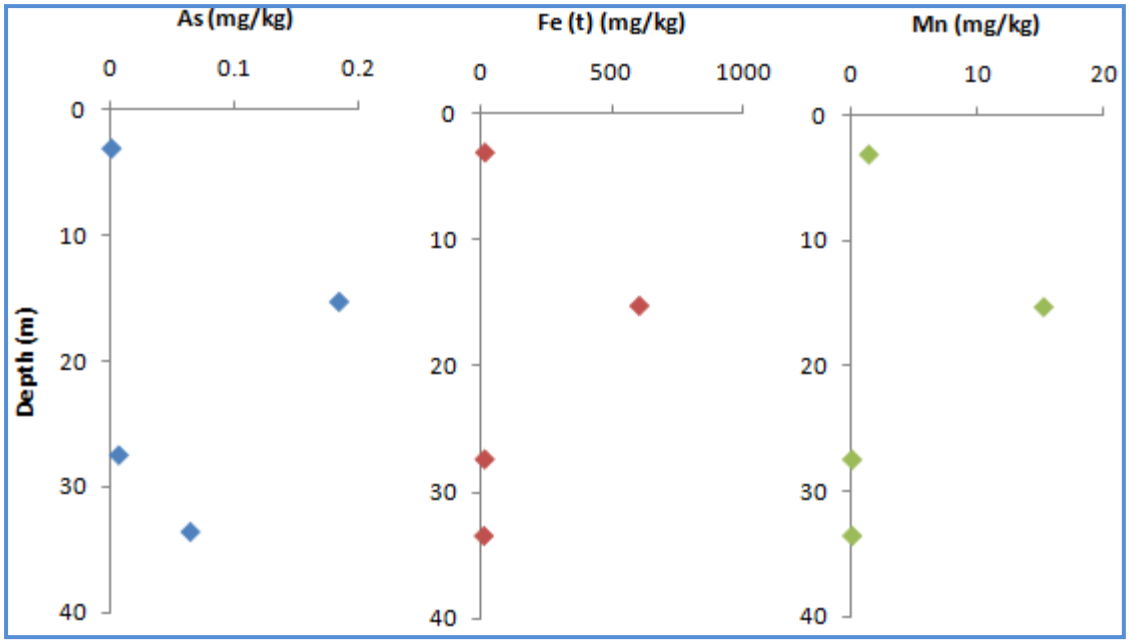


Figure 23: Depth variation of concentration(mg/kg) of As, Fe(t) and Mn in Beldanga aquifer core sediments (CS-103 BM; high As area). Depths are in meters and concentrations are in mg/kg. (depth classification, shallow: 0-10m, intermediate:10-30m; deep:>30m)

in Beldanga core (CS-103 BM; high As area) showed similar trend with depth. The concentration of As, Fe (t) and Mn were high at 15.2 m depth (intermediate depth) which is represented by a sharp peak at 15.2 m depth (As=0.18mg/kg; Fe(t)=604.7mg/kg; Mn=15.24mg/kg). Then the concentration (As, Fe(t) and Mn) decreased at 27m (intermediate depth). Both Mn and Fe (t) concentration remained low (Fe(t)=8.9mg/kg, Mn=0). But the concentration of As again increases0.063mg/kg at 34 m (deep depth) . A duplicate sample (BM-110 D) was included in the analysis which gave similar results(As=0.052 mg/kg; Fe (t)=8.71 mg/kg; Mn=0) (Fig. 23).

Concentration of As, Fe(t) and Mn obtained for Kandi aquifer sediments (CS-106 KHN; low As area) after organic matter extraction showed similar trend with depth, like that of Beldanga. Fe (t) and Mn concentrations were maximum at intermediate depths (18.3 m) and were 33.23 mg/kg and 9.12 mg/kg respectively. The concentration of As was maximum at 30.5m depth and the trend showed increase in concentration at deeper depths. Whereas the Fe (t) and Mn concentration decreased after 20 m depth. (Fig.24)

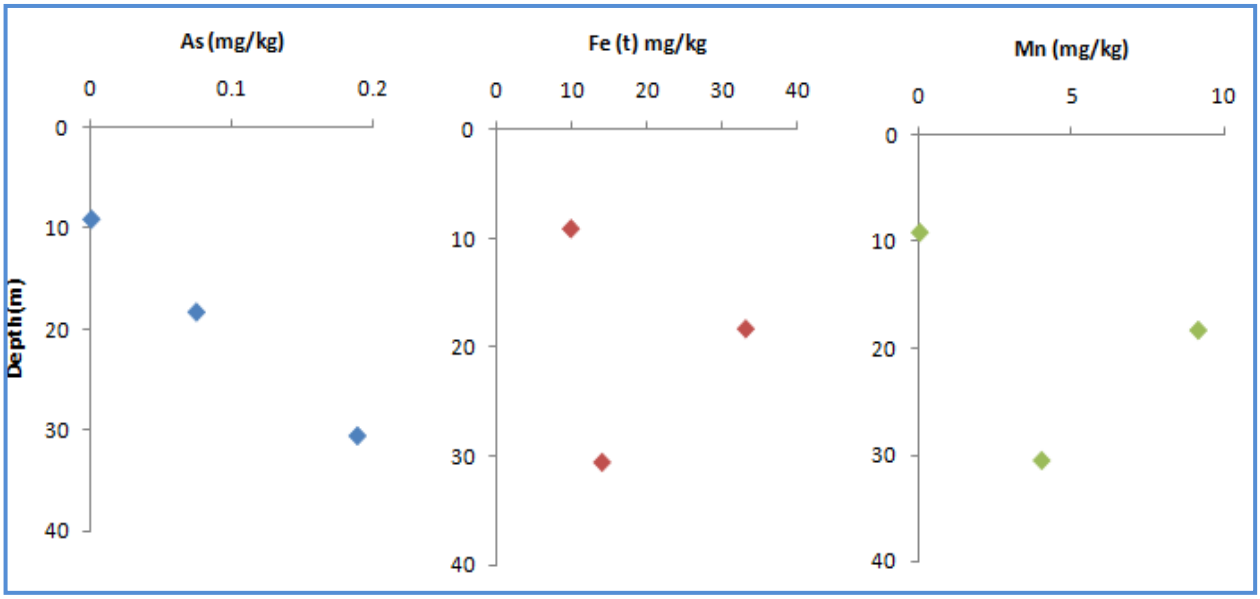


Figure 24: Depth wise change in concentration of As, Fe(t) and Mn mg/kg in Kandi aquifer core sediments (CS-106 KHN; low As area). Depths are in meters and concentrations are in mg/kg

Measurement of the DOC (part of the TOC came out in to solution during OM extraction) analysis of the aquifer sediment(1:10 dilution) extractant (0.7M NaOCl pH8.5) using TOC analyzer gave DOC data for all samples but total nitrogen (TN) was absent for most of the samples. For high As area cores; Beldanga (CS-103 BM) and Hariharpara (CS-105 HK) the DOC values ranged between 57.7-171.4 mg/kg and 55.58-61.15 mg/kg respectively. Whereas for the low As area cores; Nabagram (CS-104 NB) and Kandi (CS-106 KHN) the DOC concentration ranges were 62.78-74.64 mg/kg and 118.9-122.4 mg/kg. Results showed total nitrogen only for 2 samples and they were BM-10 (Beldanga; 3 m depth) and NB-130 (Nabagram; 40 ft depth) and the values were 0.0479 mg/kg and 0.0237 mg/kg. Total nitrogen was absent in rest of the samples. The DOC concentration vs. depth plots shows similar trend as

that of As concentration vs. depth for all of the areas. High As at a particular depth shows high extracted DOC (Fig.25). The data for Nabagram and Hariharpara were represented in appendix-G.

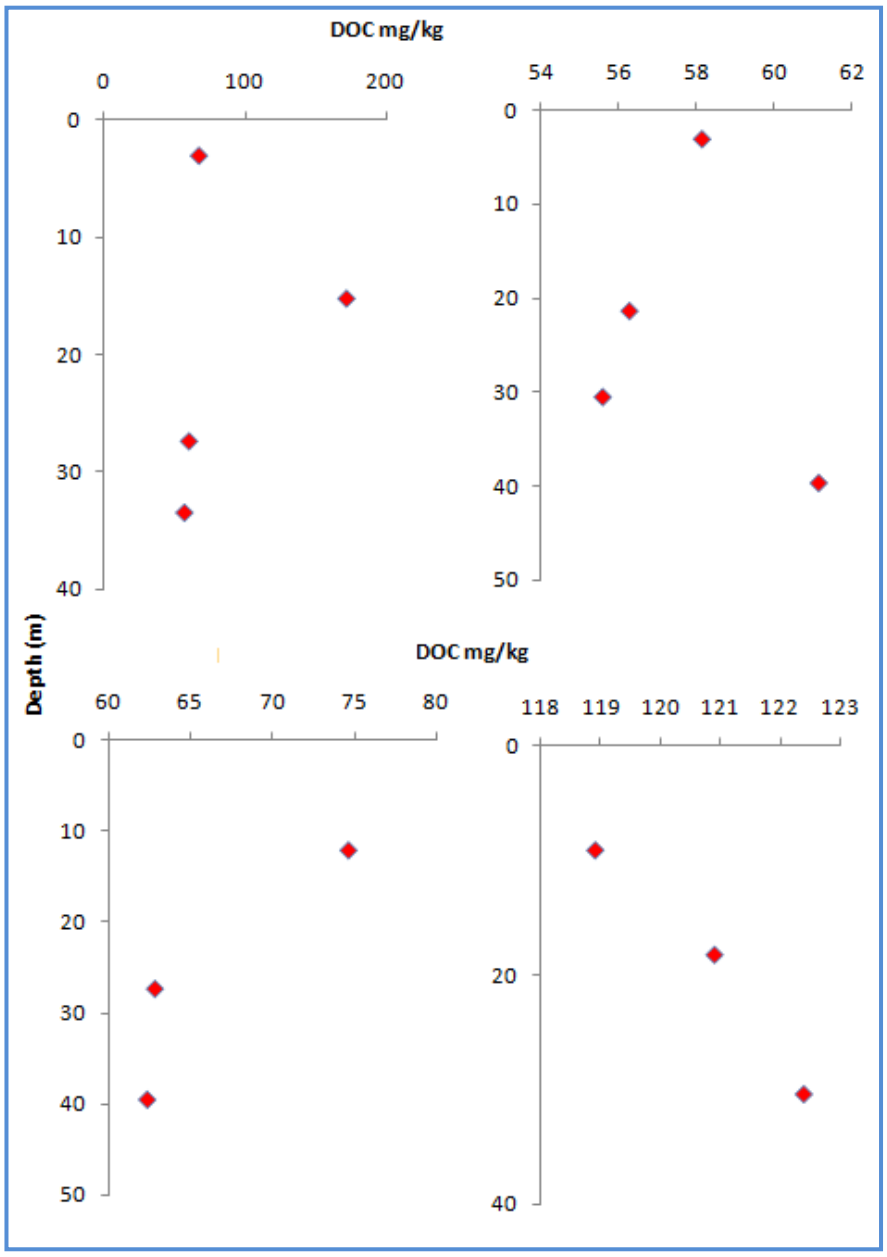


Figure 25: Depth wise distribution of DOC mg/kg in high As areas like Beldanga (CS-103 BM; top left); Hariharpara (CS-105 HK; top right)and low As areas like Nabagram (CS-104 NB; bottom left) ; Kandi (CS-106 KHN; bottom right) aquifer core sediments. Depths are in meters .

The same samples which were extracted for OM bound As, Mn and Fe (t) those same samples from same depths were analyzed for total organic matter (TOC) content (%) by LECO TruSpec CN analyzer after treating with 1N phosphoric acid to remove carbonates prior to analysis and showed similar kind trends for TOC as that of Arsenic with depth of sediments.

The depth distribution of TOC% in high As area drill cores (Beldanga; CS-103BM and Hariharpara; CS-105HK) showed similar kind of trend (Fig.26) as that of As concentration with depth in the same core samples (Fig 23). Maximum TOC (4.34%)in Beldanga core (CS-103BM) was found at intermediate depths (15.2m). For this core (CS-103BM) As concentration was also maximum (0.183mg/kg) at intermediate depth. Both Fe (t) and Mn concentration were also maximum at intermediate depth levels and were 604.667mg/kg and 15.24 mg/kg respectively (Fig 23). In Hariharpara drill core (CS-105HK) the maximum amount of TOC was present at shallow depth (3m) and it was 0.78% and at this depth the As concentration was 0.076mg/kg . The minimum TOC % of 0.2% was observed at 30m depth and the concentration of As at this depth was minimum and was 0. The TOC remains almost unchanged in the deeper depth (0.21% at 40m). However the As concentration increased to 0.063 mg/L at 40m depth. Both Fe (t)and Mn were showing maximum concentration (23.6mg/kg and 0.091mg/kg) at 30 m depth in this core and then decreased to 17.1 mg/kg (Fet) and 0 (Mn) at deeper depths (40m)(Appendix-G). The concentration of Total nitrogen (TN) looked similar in trend and concentration with depth (shallow, intermediate and deep) in both high As cores (Beldanga and Hariharpara). Maximum concentration of TN are 0.28% at 15.2 m for Beldanga and 0.06% at 21.3 m for Hariharpara (both intermediate depths). The concentration changed to low levels at deeper depths in these areas (Fig.26).

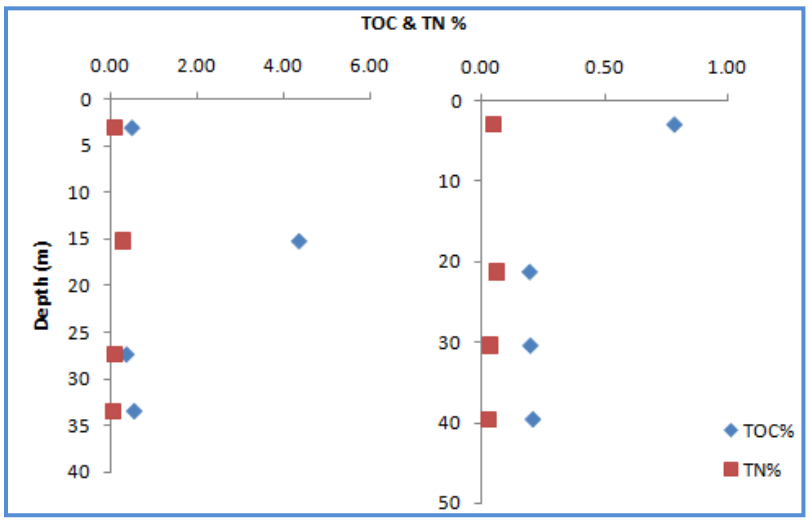


Figure 26: Change in concentration of TOC % and TN with depth of sediments for Beldanga core (CS-103BM)left; and Hariharpara core (CS-105 HK) right

The depth distribution of TOC and TN% for low As cores ; Nabagram (CS-104NB) and Kandi (CS-106 KHN) were represented in Figure.30. Among all the cores analyzed the concentration of TOC was minimum in Nabagram aquifer sediments. The concentration of TOC was 0.18% at shallow depths and increased to 0.26% at intermediate depths (27.43 m) then again decreased to 0.18% at deeper depths (40m). As and Mn concentration (0) were absent or below detection limit at all depths ranges in this area but the concentration of Fe(t) was maximum at intermediate depths (27.4 m) and was 14.4 mg/kg. The Fe (t) concentration in the top parts of intermediate depths (12.2 m) and deeper depths (40m) were low and were 10.6mg/kg and 12.5 mg/kg respectively. In Kandi the concentration of As with depth was similar to the change in concentration to TOC (%) with depth of the drill core. TOC % was very low at shallow depths (9.1m) and it increased to 0.93% at intermediate depths (18.3m) and again very slightly decreased to 0.81% at deeper depths (30.5m). The corresponding concentration of As , Fe(t) and Mn at shallow intermediate and deeper depths are 0,0.07,0.18mg/kg; 9.84, 33.22, 13.99mg/kg and 0, 9.12, 3.99 mg/kg respectively. The TN% was showing similar trend in both of the low As cores. Low concentration of TN was observed at shallow depths in both of the areas (Nabagram -0.04% ; Kandi-0.06%) then it gradually increased in the intermediate depths (Nabagram-0.05%; Kandi-0.08%) and then remained same at Nabagram (0.05%) and increased in Kandi (0.1%) at the deeper depths (Fig.27).

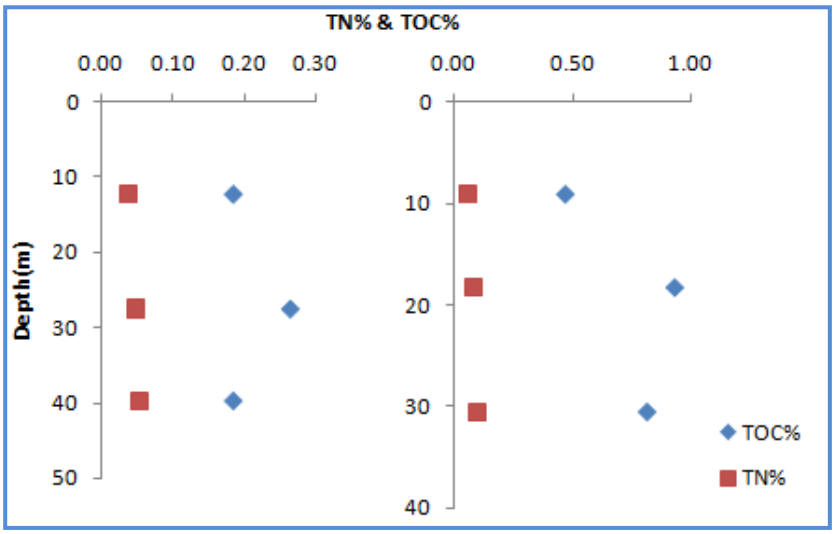


Figure 27: Change in concentration of TOC % and TN with depth of sediments for Nabagram core (CS-104NB) and Kandi core (CS-106 KHN)

The detailed results are presented in the Appendix-G

Synchrotron studies of aquifer sediments (XANES and EXAFS data on specific samples)

Aquifer sediments from Murshidabad were analyzed in 3 separate beam lines, X27A; X11A and X15B.

X27A: High As sample from Beldanga core; CS-103; BM-120 (37m depth). X ray mapping was carried out on this sample at an energy level 12200 eV which resulted in getting high As hot spots (golden yellow bright spots) (Fig .28). Among these 2 best spots were analyzed for As XANES (spot-1 and spot-3) at 11750eV. Correlation diagrams (As vs. Fe(t) and As vs. Mn) were plotted for spot-1. XANES results (peak) showed that the As species present in the Beldanga sediments were mostly As^{5+} and at the peak it was 11874eV (Polizzotto et al., 2006) (Fig.29). The correlation diagrams shows good relation between As with Mn and Fe (t) (Fig.30).

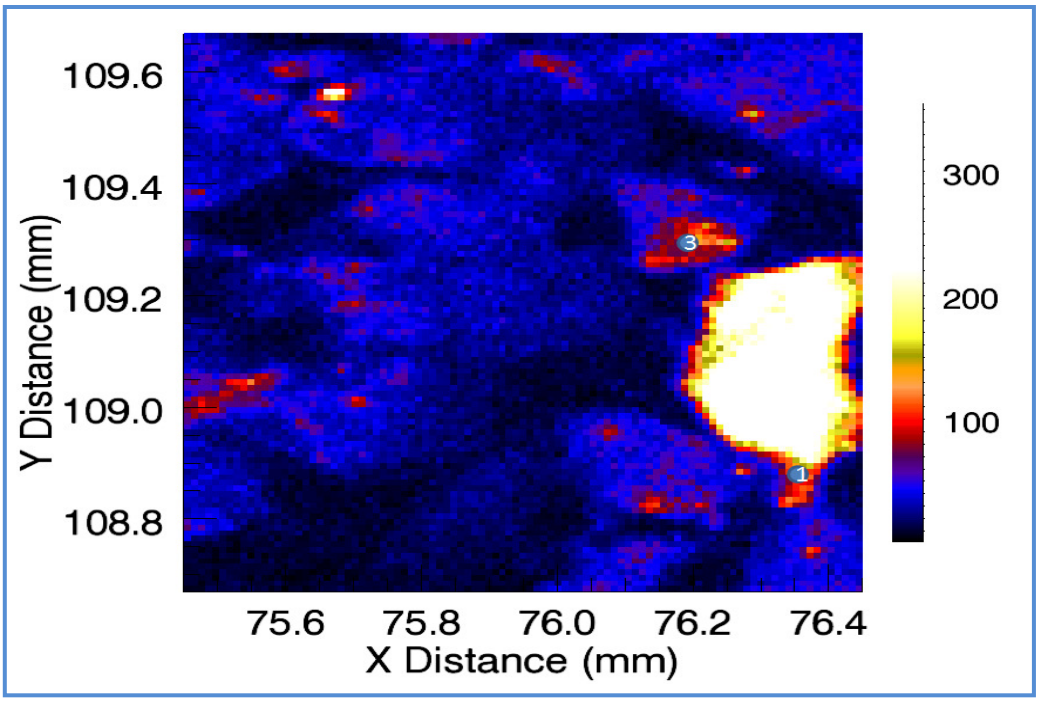


Figure 28: µX Ray map of Beldanga aquifer sediments (BM-120, 37m depth) analyzed in X 27A beam line, energy 12200 eV. The spots analyzed for XANES and correlation plots are marked 1 and 3 on the map.

The standard used for analyzing the As peak (solid state speciation) is $NaAsO_4$ the white lines for As $^{5+}$ was present for spots -1 and 3 (Fig.29)

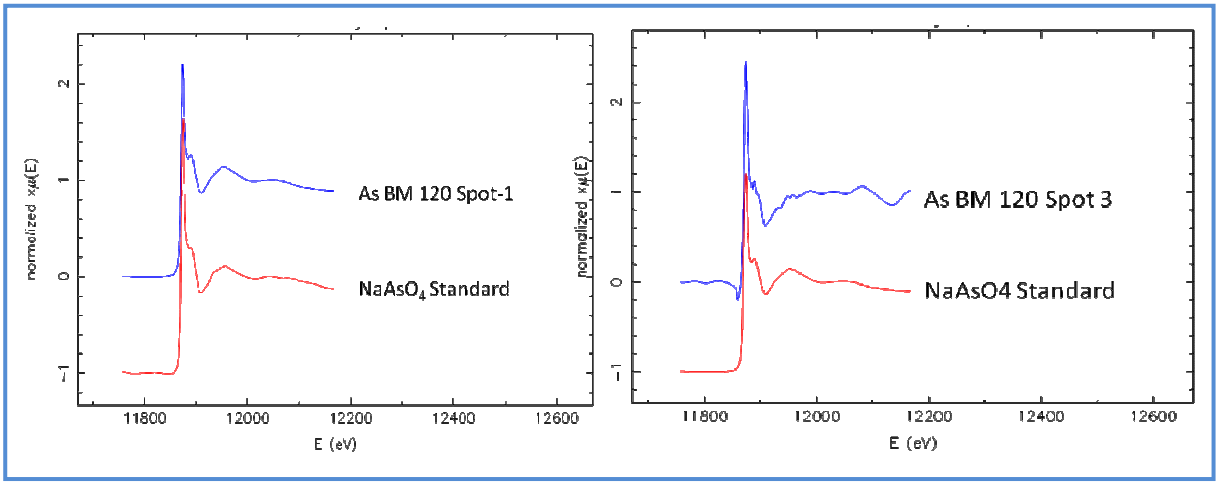


Figure 29: XANES for spot-1 (left) and spot-3(right) for BM-120 sample (Beldanga core CS-103, 37m depth) XANES for the sample is in blue and the standard in red ($NaAsO_4$). Energy levels are represented in the X axis and normalized peak heights in the Y-axis. The white line is at 11874eV.

The correlation plots for As vs. Fe (t) and As vs. Mn for the spot-1 are represented below. The correlation analysis shows good positive correlation of Fe and Mn with As. (Fig.30). It is to be noted that it is very hard to get correct distribution of Mn when there is more Fe (t) in the samples.

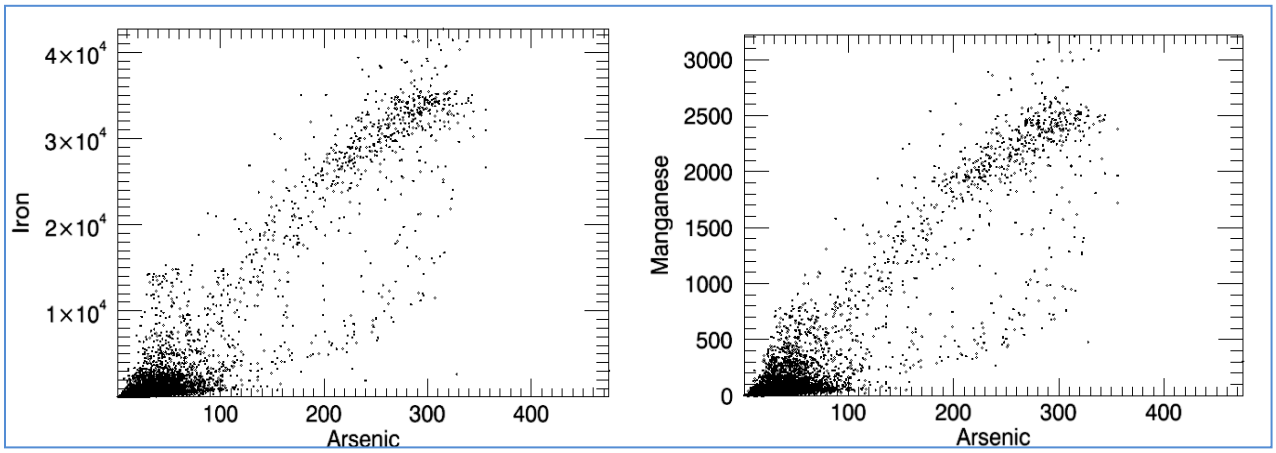


Figure 30: Correlation diagrams for As vs. Fe (t) (left) and As vs Mn (right) for spot-1 (fig-32) . Values in the X and Y axis represents the spot counts for the elements in the area analyzed.

X11A beam line: A total of 5 samples were analyzed in this bulk beam-line for solid state As speciation. The 5 samples included 3 from Kandi (KHN-40(12.2m depth); KHN-100 (30.5m depth) and KHN-110 (34m depth)) one from Beldanga (BM-30 (9.1mdepth)) and one from Hariharpara (HK-20 (6.1m depth)). The XANES peaks for the samples were compared with the standards peaks; 11871eV for As^{3+} and 11874for As^{5+} (Polizzotto et al., 2006). The results showed a broad peak covering both 11871ev and 11874eV values. So in these samples both As^{3+} and As^{5+} could most likely be coexisting (Fig. 31)

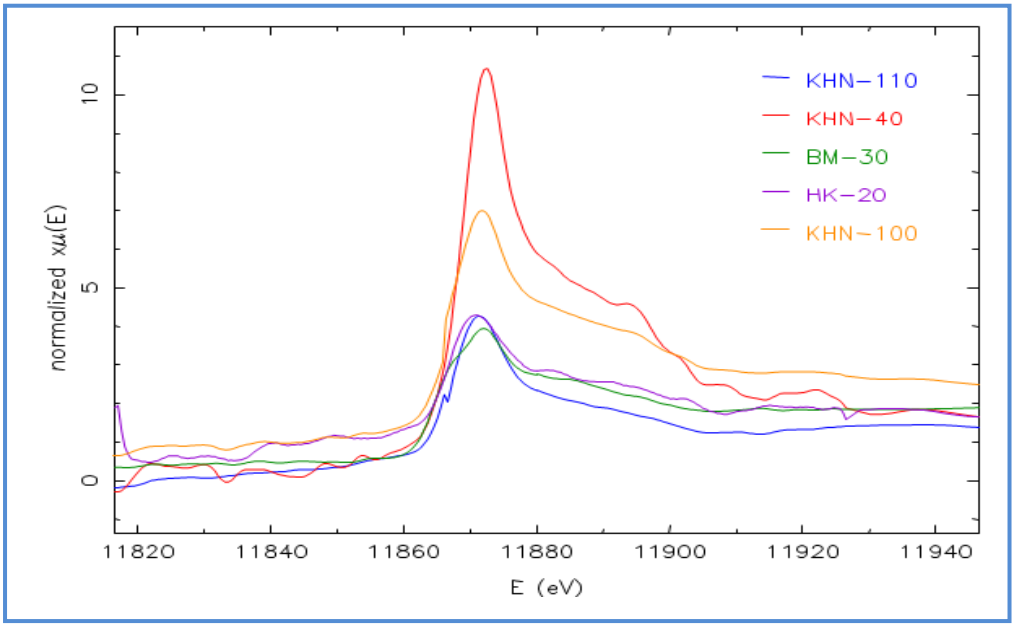


Figure 31: XANES for Murshidabad sediments from X11 A beam. The peak (white line) covers both 11871 eV for As $^{3+}$and 11874 eV for As^{5+}. X axis represents the energy level (eV) and Y axis represent the normalized peak values.

X15B Beam line: Sulfur speciation was done using X15B beam line. 2 Kandi (KHN-40(12.2m depth); KHN-100(30.5mdepth))and one Nabagram(NB-100 (30.5m depth)) samples were analyzed for this study. The results showed that major sulfur species present in the sediments were Sulfate (SO_4^{2-}) represented by the peak value 2482 eV (Prietzel et al., 2006) (Fig. 32).

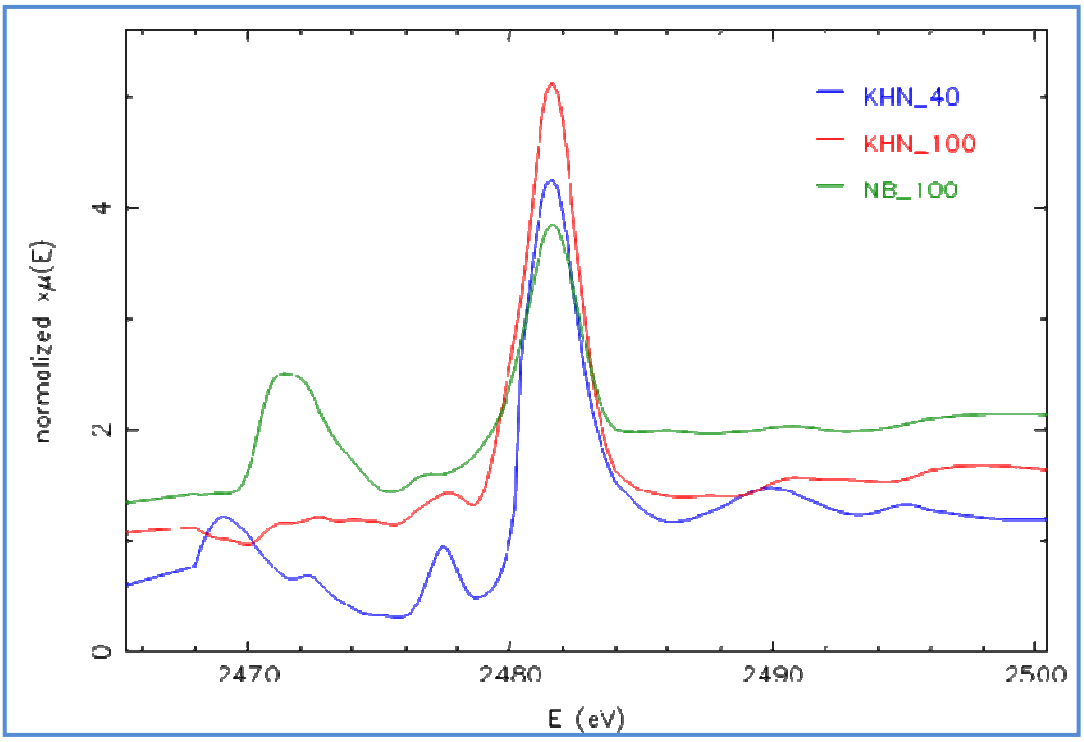


Figure 32: XANES for Murshidabad sediments from X11 A beam. The white line value is 2482 eV, which shows Sulfate species in the sediments Kandi (KHN-40,100) and Nabagram (NB-100) . X axis represents the energy level (eV) and Y axis represent the normalized peak values

Water analyses Results in-field

METTLER TOLEDO SevenGo™ for water parameters

Water quality (groundwater) parameters were measured using METTLER TOLEDO SevenGo probe. The parameters measured and the quantity at both high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi) are shown in the Table-5. The details of results for each tubewells (shallow and deeper depth) are in Appendix-H.

	High As Areas		Low As areas	
	Beldanga	Hariharpara	Nabagram	Kandi
Salinity (ppt)	0.01-7.21	0.44-12.02	0.43-5.91	0.45-0.47
Resistivity (Ωcm)	8.1-271000	49.6-1080	95.9-1140	10.7-1090
TDS	5.55 mg/L-5.82 g/L	455 mg/L-10.08 g/L	448 mg/L -5.21 g/L	457-482 mg/L
Conductivity (µS/cm)	2.6-155.5	12.68-990	7.21-950	912-988
Temperature (°C)	24.6-27.1	24.1-27.5	26.5-27.1	24.7-27.6
pH	7.6-7.84	6.6-7.85	6.59-7.53	7.9-8.27

Table 5: Water quality (groundwater) parameters for high and low As areas measured during January 2012 (data represent only tubewells ie. both shallow depth tubewells;10-40m and deep tubewell; >40m)

Field test kits and Spectrophotometer, HACH DR 2800 ™ results for groundwater chemistry for tubewells depths (both shallow & deeper depth tubewells)

Cations (in-situ analysis)

Mn from test kits: Mn values are measured using HACH kit: Model MN-5, cat. no: 1467-00. The details of the analysis was explained in the method session. For Mn, the ranges in the high As areas are 0-1.2 mg/L in Beldanga; 0.2-1.4 mg/L in Hariharpara and low As areas are 0.4-2.8 mg/L in Nabagram; 0-0.4 mg/L in Kandi.

Mn Results from Spectrophotometer: The Mn values in high As areas are 0-1.5 mg/L in Beldanga; 0-1.6 mg/L in Hariharpara and the values in low As areas ranges from 0.2-14.5 mg/L in Nabagram; 0.5-1.5 mg/L in Kandi.

As results from Test kit: As values are calculated from both test kits (HACH kits: low range; cat no. 2800000 and high range; cat no:2822800). As values are calculated by taking the average value from both the results (high and low range test kits). The As range high As areas

are 10-500 µg/L in Beldanga; 5-400 µg/L in Hariharpara and low As areas are 5-15 µg/L in Nabagram and 5-40 µg/L in Kandi.

Fe(t) Results from Spectrophotometer : Fe (t) values for groundwater samples from both high and low As areas in Murshidabad area calculated using spectrophotometer. The results in the high As area are 0.09->6.33 mg/L in Beldanga; 0.05->30 mg/L in Hariharpara and Fe (t) ranges in the low As areas are 0.15-1.4 mg/L in Nabagram and 0.21-1.03 mg/L in Kandi.

NH_4^+ Results from Spectrophotometer : NH_4^+ (ammonium) values for groundwater samples from both high and low As areas in Murshidabad were calculated using Hach DR 2800 spectrophotometer. The results in high As areas were 0-0.02 mg/L in Beldanga; 0-0.01 mg/L in Hariharpara and in low As areas it was 0.01-0.04 mg/L in Nabagram; 0-0.06 mg/L in Kandi.

The details of cations (field data) is represented in appendix-I.

Anions (in-situ analysis)

In field all most of the anions are measured using HACH and CHEMetrics test kits. Some of the results obtained using test kits are again reconfirmed using HACH DR2800 spectrophotometer. The concentration of various anions found out by using field test kits and spectrophotometer at high As areas and low As area are represented in the Table-6 below. The data represent for tubewells only (both shallow depth and deeper depth tubewells) together because the number of deeper depth tubewells was very less (only 3 number). The details of anion data (field) is represented in appendix-J.

		High As area		Low As area	
		Beldanga	Hariharpara	Nabagram	Kandi
NO_3^- *(nitrate)(mg/L)*	Test kit	0	0-4	0-4	No analysis
	Spectrophotometer	0-0.1	0-2.7	0-2.1	0-0.5
SO_4^{2-} *(Sulfate) (mg/L)*	Test kit	0	0-95	0-65	0
	Spectrophotometer	0-2	0->90	11-55	0
PO_4^{3-} *(phosphate) (mg/L)*	Test kit	0-3.5	0-11	0-0.4	0.2-1.5
	Spectrophotometer	0.18-1.91	0.56 - >50	0.31-1.04	0.4-1.34
Cl^- *(Chloride) (mg/L)*	Test kit	18-60	10-56	40-80	100-148
Dissolved oxygen (DO)(mg/L)	Test kit	1-5	3-5	1.5-5	4 (only 2 tests performed in Kandi due to the lack of test reagents and both gave same results
Total Alkalinity (as HCO_3)(mg/L)	Test kit	270-648	324-486	270-486	370- 630

Table 6: Results of in-situ analysis of various anions in field using various field test kits and spectrophotometer, HACH® DR 2800

Hydrogeochemistry of the waters: Laboratory Data (surface and groundwater)

All water samples (pond waters; tubewell waters (10-40 m and >40m) and Irrigation wells (10-46m)) were analyzed for cations, anions, isotopes, DOC, TN and fluorescence and are stated here.

Cations

Total Arsenic and As III results:

*Surface waters (Pond water):*Four pond waters were analyzed in lab (HR ICP MS in Actlabs®, Canada and Tulane University) and the results for high As areas are 110.27 µg/L (PW-102 BM); 25.57 µg/L (PW-103BM); 25.12 µg/L (PW-104 BM; Beldanga); 15.6 µg/L (PW-109 HK) and in the low As area is 4.69 µg/L (PW-106 NB, Nabagram)

Tube wells(10-40m &>40m depth): A total of 8 tubewells (3 from Beldanga; 2 from Hariharpara; 2 from Nabagram and 1 from Kandi) were analyzed in HR ICP MS at Actlabs for As(t). In this study both lab and field data (where no lab data was available) were used. Where ever there was both field and lab data, lab data is used instead of field data. The As(t) ranges in high As areas are 275.9-1263.73 µg/L in Beldanga and 237.56-400.11µg/L in Hariharpara. In low As areas the ranges are 0.4 µg/L in Nabagram and 10.21µg/L in Kandi.

Irrigation wells (10-46 m): Only 2 irrigation wells in high As areas were analyzed for As(t) and 42.9 µg/L in Beldanga (IW-102BM) and 433.02 µg/L in Hariharpara (IW-104 HB).

As III (As^{3+}) was analyzed in Tulane university for one pond water from high As area (Hariharpara) and 2 shallow depth tube well (<40 m) waters; one each from high As area (Beldanga) and low As area (Nabagram). The As III for PW-109 HK (Hariharpara) is 16.83 µg/L and As (V) or $As^{5+}$was 13.25 µg/L. The concentration of As^{3+} and As^{5+} for Beldanga shallow depth tube well in Beldanga (TW-102 BM, high As area) is 206.25 µg/L and 58.97 µg/L respectively. The As^{3+} and As^{5+} for Nabagram shallow depth tube well (TW-112 NBK, low As area) were 15.37 µg/L and 0.17 µg/L.

To study the changes in concentration of As(t) in high and low As areas of Murshidabad with depth and time, the As (t) data from tubewells (both shallow and deep) for years 2009 through 2013 were compared. 2009, 2010 data were taken from (Neal, 2010) and 2012 and 2013 data are been generated for this current study. The tubewells sampled by Andrew Neal 2010 during the years 2009 and 2010 study were very close or similar to the tubewells samples for the current study (2012 and 2013) Table-7. The data contains both field kit data and ICP OES lab data (Fig.33). The lateral distribution of As concentration in shallow depth tube wells in Murshidabad area for the years 2009, 2010, 2012 and 2013 in high As areas, Beldanga; Hariharpara and in low As areas, Nabagram; Kandi are represented in Figure.34, 35, 36 & 37 respectively.

As (t) (µg/L); Years	**High As area**		**Low As area**	
	Beldanga	Hariharpara	Nabagram	Kandi
2009	1-4622	250-630	0-8	No sample collected
2010	3-1299	19-695	1-3	10-11
2012	10-346.03	5-400.11	5-15.5	10-50.04
2013	5-75	10-60	5	5

Table 7: As concentration from 2009 through 2013 in Murshidabad tubewells (shallow and deep)

The details of the results for 2009, 2010, 2012 and 2013 were represented in the Appendix-K. Over all the data shows a decrease in As content from 2009 through 2013. However impossible to interpret in such way because samples were collected from different tubewells for these years (2009 though 213) even though their locations were close to each other.

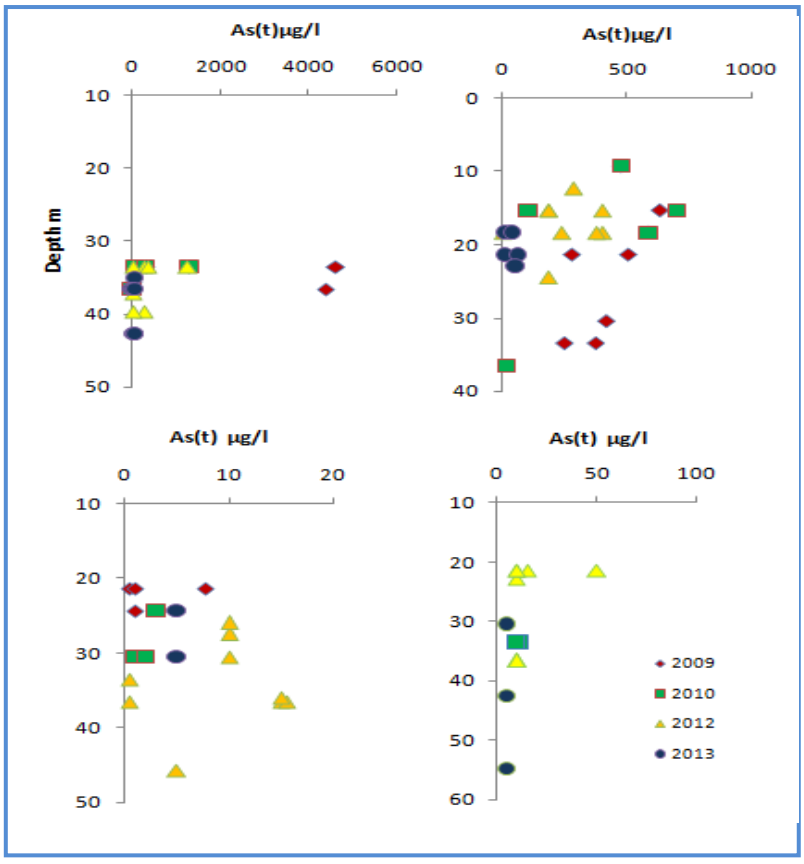


Figure 33: Plot showing the change in concentration of As(t) with depth for the years 2009, 2010, 2012 and 2013 in high As areas, Beldanga (top left); Hariharpara (top right) and in low As areas; Nabagram (bottom left), Kandi (bottom right)

Mn Results

Mn was analyzed for all water samples, 2012; pond water (surface water); tubewells (10-40m and >40 m depths) and irrigation wells (10-46 m) in ICP OES. In high As areas the Mn values for pond waters in high As areas are 0-0.47mg/L in Beldanga;0-0.53 mg/L in Hariharpara and in the low As areas are 0-0.145 mg/L in Nabagram; 0.2-0.63 mg/L in Kandi. (Fig 38)

For tubewells (both shallow and deep), in high As areas the Mn values ranges from 0-1.11mg/l in Beldanga and 0-1.33 in Nabagram and in low As areas the ranges are 0.5-4.23 mg/L in Nabagram and 0-0.043 mg/L in Kandi.(Fig. 41)

In irrigation wells in high As areas are 0-0.214 mg/L in Beldanga; 0-0.44 mg/L in Hariharpara and in both low As areas (Nabagram and Kandi) Mn concentration was totally absent. (Fig.39)

The distribution of As and Mn concentrations in groundwaters in high As (Fig.34&35) and low As areas (Fig. 36 & 37) are represented in the maps below.

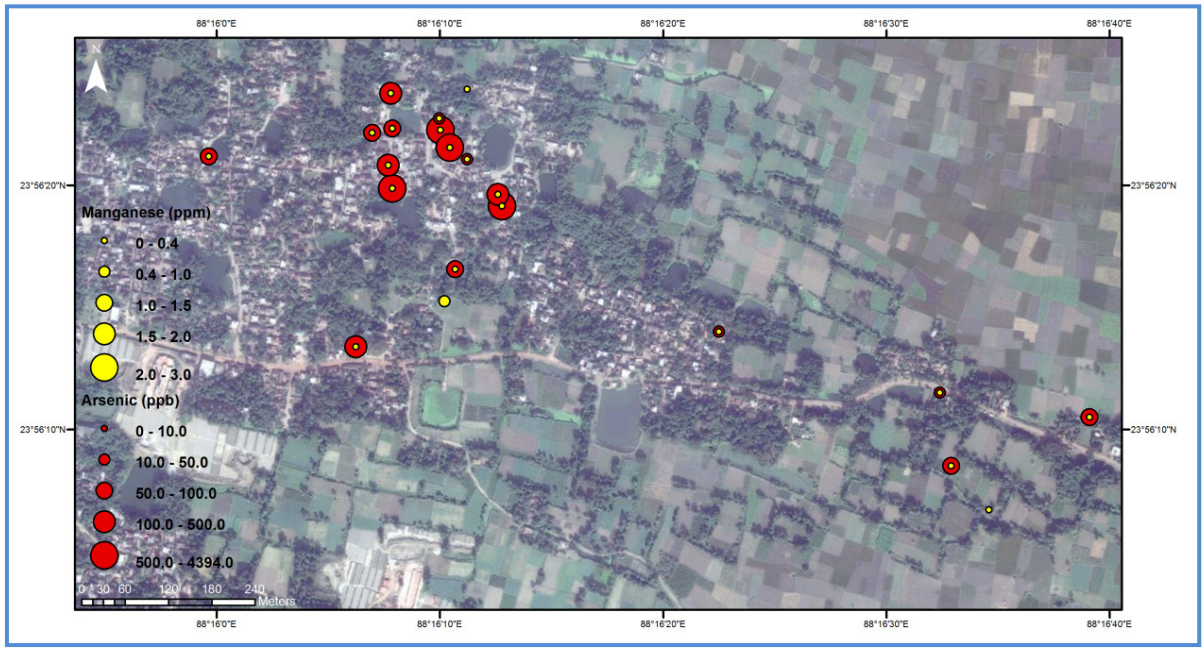


Figure 34: The map of Beldanga (high As area) showing the heterogeneity of lateral distribution of dissolved [As] in groundwater (shallow and deep tubewells) for the years 2009 through 2013. Arsenic concentrations (µg/L) are in red and Manganese concentration (mg/L) are in yellow. The [As] and [Mn] corresponds to size of the circle. [Mn] is only for the year 2012

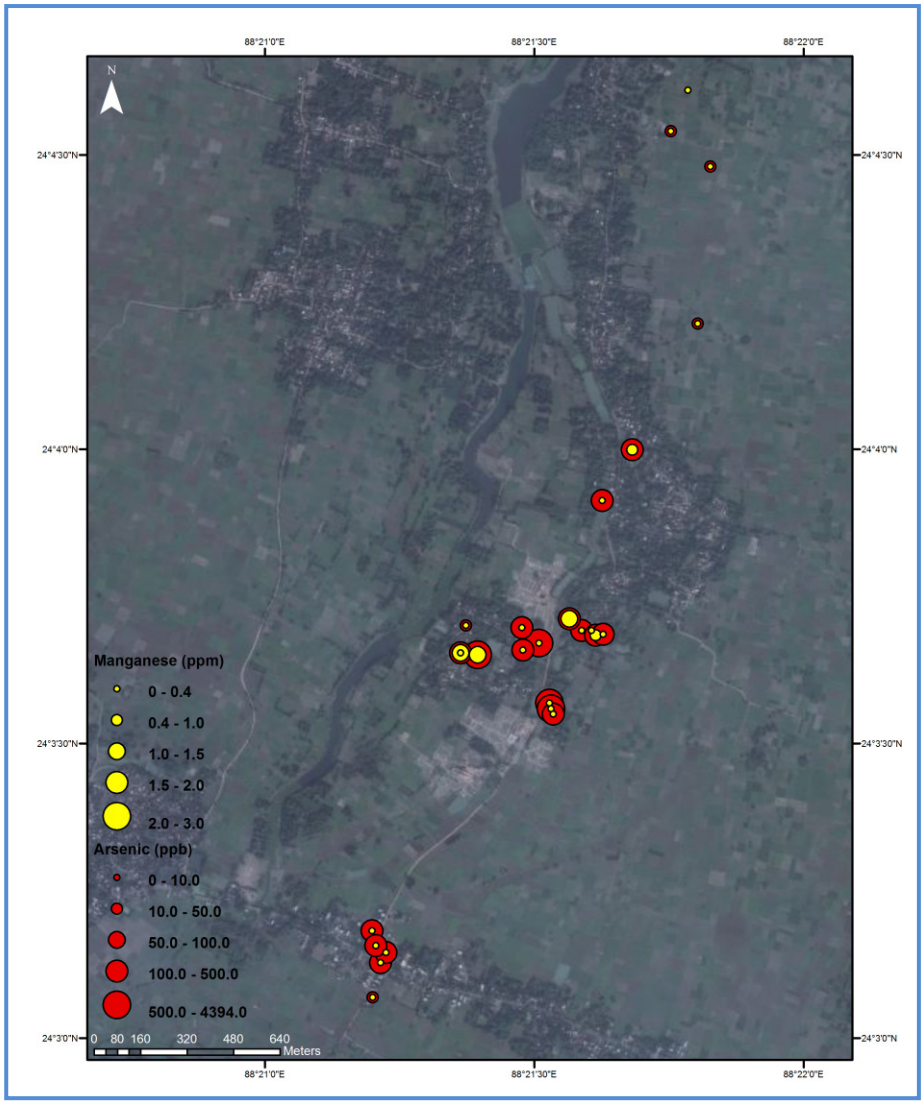


Figure 35: The map of Hariharpara (high As area) showing the heterogeneity of lateral distribution of dissolved [As] in groundwater (shallow and deep tubewells) for the years 2009 through 2013. Arsenic concentrations (µg/L) are in red and Manganese concentration (mg/L) are in yellow. The [As] and [Mn] corresponds to size of the circle. [Mn] is only for the year 2012

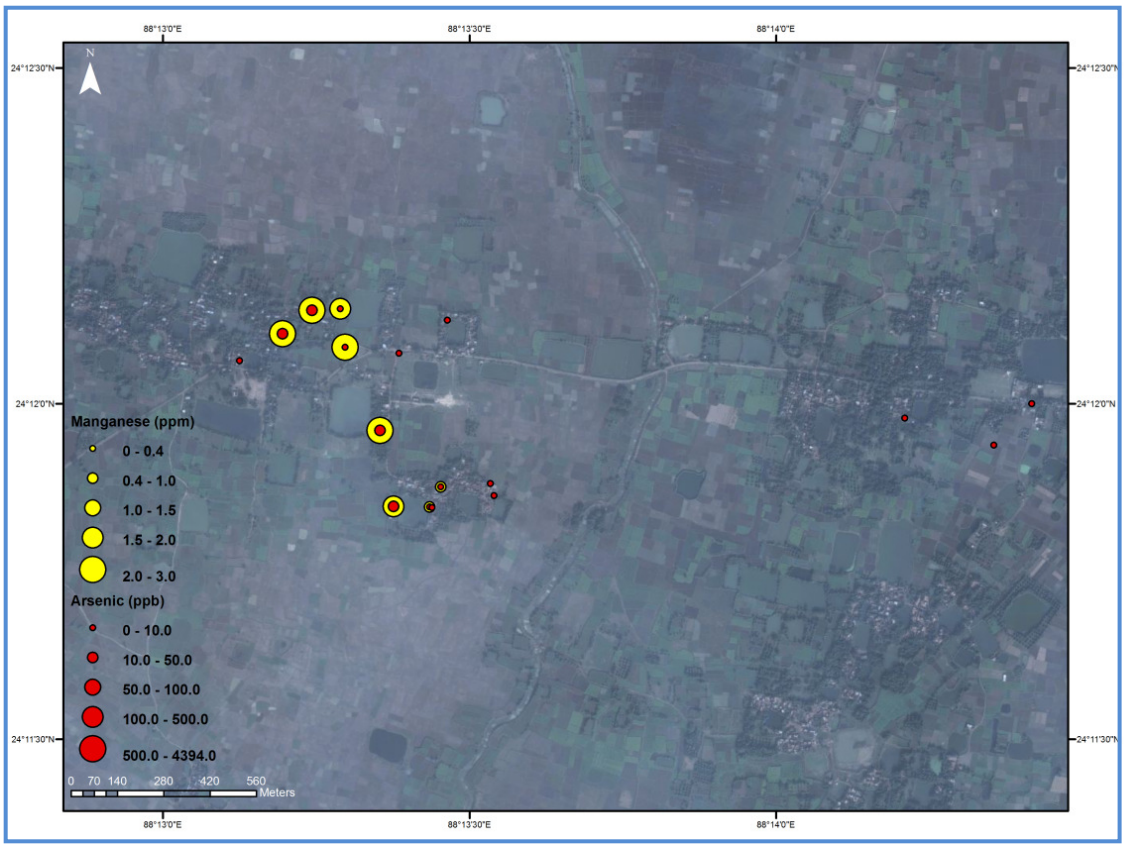


Figure 36: The map of Nabagram (low As area) showing the heterogeneity of lateral distribution of dissolved [As] in groundwater (shallow and deep tubewells) for the years 2009 through 2013. Arsenic concentrations (µg/L) are in red and Manganese concentration (mg/L) are in yellow. The [As] and [Mn] corresponds to size of the circle. [Mn] is only for the year 2012

Figure 37: The map of Kandi (low As area) showing the heterogeneity of lateral distribution of dissolved [As] in groundwater (shallow and deep tubewells) for the years 2010 through 2013. Arsenic concentrations (µg/L) are in red and Manganese concentration (mg/L) are in yellow. The [As] and [Mn] corresponds to size of the circle. [Mn] is only for the year 2012

The concentration of various cations in ponds; tube wells (both shallow and deep) and irrigation wells are represented in the Table-8. Single numbers means one sample been analyzed. Abbreviations BDL & 0 means below detection limit

Cations for 2012	Samples	High As area		Low As area	
		Beldanga	Hariharpara	Nabagram	Kandi
Fe (t) mg/L	Pond	0-70.85	0-0.02	0-0.15	BDL
	Tubewell	0-13.6	0-7.2	0.012	0-0.074
	Irrigation well	0.6-0.7	0-7.2	BDL	BDL
	Pond	44.02-55.48	12.97-22	6.5-37.1	35.4-40.86
	Tubewell	0-3.3	1.2-79.8	0-1.12	0-1.97

K mg/L	Irrigation well	0.3-1.6	1.92-3.14	0.84	0-1.98
Na mg/L	Pond	71.79-124.98	20.78-32.91	5.63-33.06	52.5-80.3
	Tubewell	0-36.5	14.4-36.4	0-1.12	0-1.97
	Irrigation well	36.5-40.44	21.5-27.7	38.3	150.79-300.7
Mg mg/L	Pond	26.3-31.2	13.3-19.6	2.4-19.9	13.6-19.4
	Tubewell	22.6-39.1	24.1-51.7	16.7-33.74	2.3-9.8
	Irrigation well	25.8-40.6	29.1-40.1	35.8	9.2-15.9
Ca mg/L	Pond	35.4-110.4	40.7-60.4	15.5-32.1	16.1-29.03
	Tubewell	0-123.05	94.24-174.94	52.95-112.8	20.98-34.34
	Irrigation well	105.2-116.3	94.2-121.75	102.5	28.12-62.3
Fe 2+	Pond	0.03mg	0.15	No analyses	No analyses
	Tubewell	0.01-0.06	0.04-0.11	0.06	0.04-0.06
	Irrigation well	0.03-0.04	0.03	No analysis	0.01

Table 8: Generalized table for various cation concentration for Murshidabad waters for the year 2012

For the data analysis (for all the diagrams) the best data is chosen. For most of the water 3 types of data are generated and best data is chosen to create all diagrams. If the value is below detection limit in the lab analysis then field data is chosen (kit data or spectrophotometer data) for those sample points.

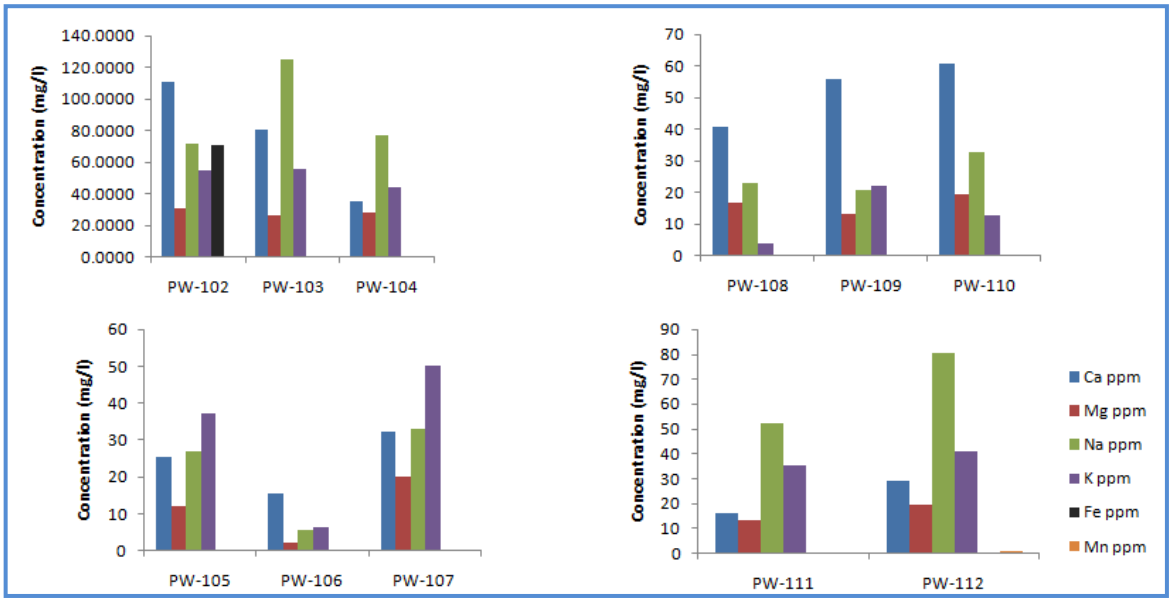


Figure 38: Bar diagram showing the concentration of various cations in pond water (surface) in high As areas like Beldanga (top left); Hariharpara (top right) and low As areas like Nabagram (bottom left); Kandi (bottom right). The plots are prepared from ICP-OES and HR ICP MS data

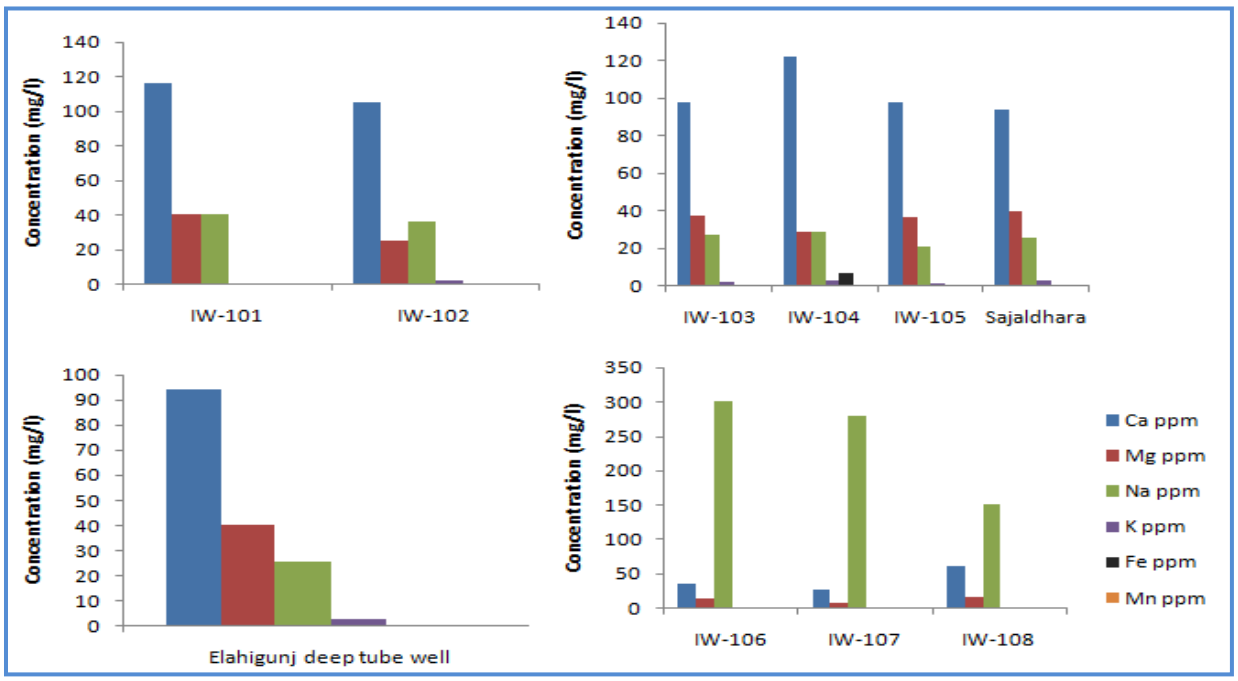


Figure 39: Bar diagram showing the concentration of various cations in Irrigation wells in high As areas like Beldanga (top left); Hariharpara (top right) and low As areas like Nabagram (bottom left); Kandi (bottom right). The plots are prepared from ICP-OES and HR- ICP MS data

Apart from these water samples, 2 rains water samples and one river water (Bhagirathi river) sample were analyzed for cations. The results are represented in Figure.40

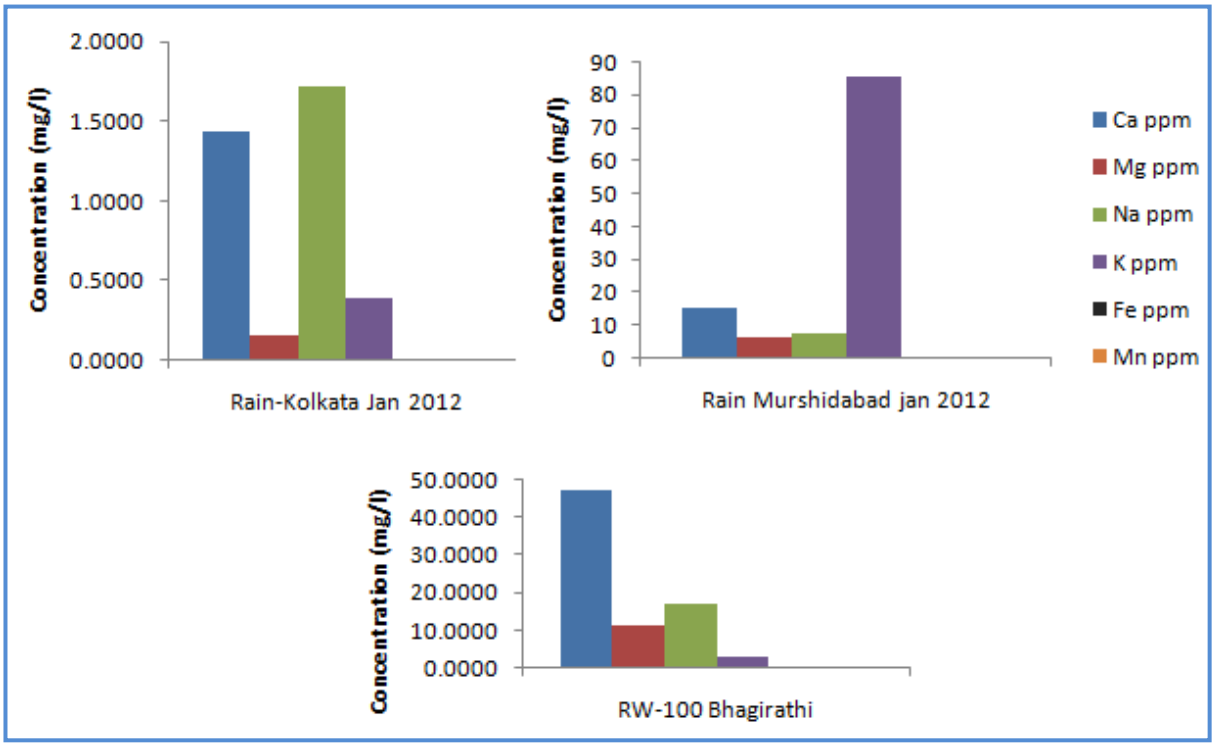


Figure 40: Bar diagram showing the concentration of various cations in Rain water (January 2012) from Kolkata (top left); Rain water from Murshidabad (January 2012) (top right) and River Bhagirathi water (bottom central). The plots are prepared from ICP-OES data.

The cations plots for tubewells (both shallow and deep) shown below (Fig.44) for Mn data sets from ICPS OES, HR ICP MS and Hatch test kits were taken. Fe(t) ICPS OES, HR ICP MS and spectrophotometer data were taken. For K, Na, Mg and Ca, ICPS OES, HR ICP MS were taken. The test kit data is taken for some of the water sample is because when these samples were analyzed later in lab no results were obtained. However when it was measured using test kits and spectrophotometer in field at the time of collection good results were obtained.

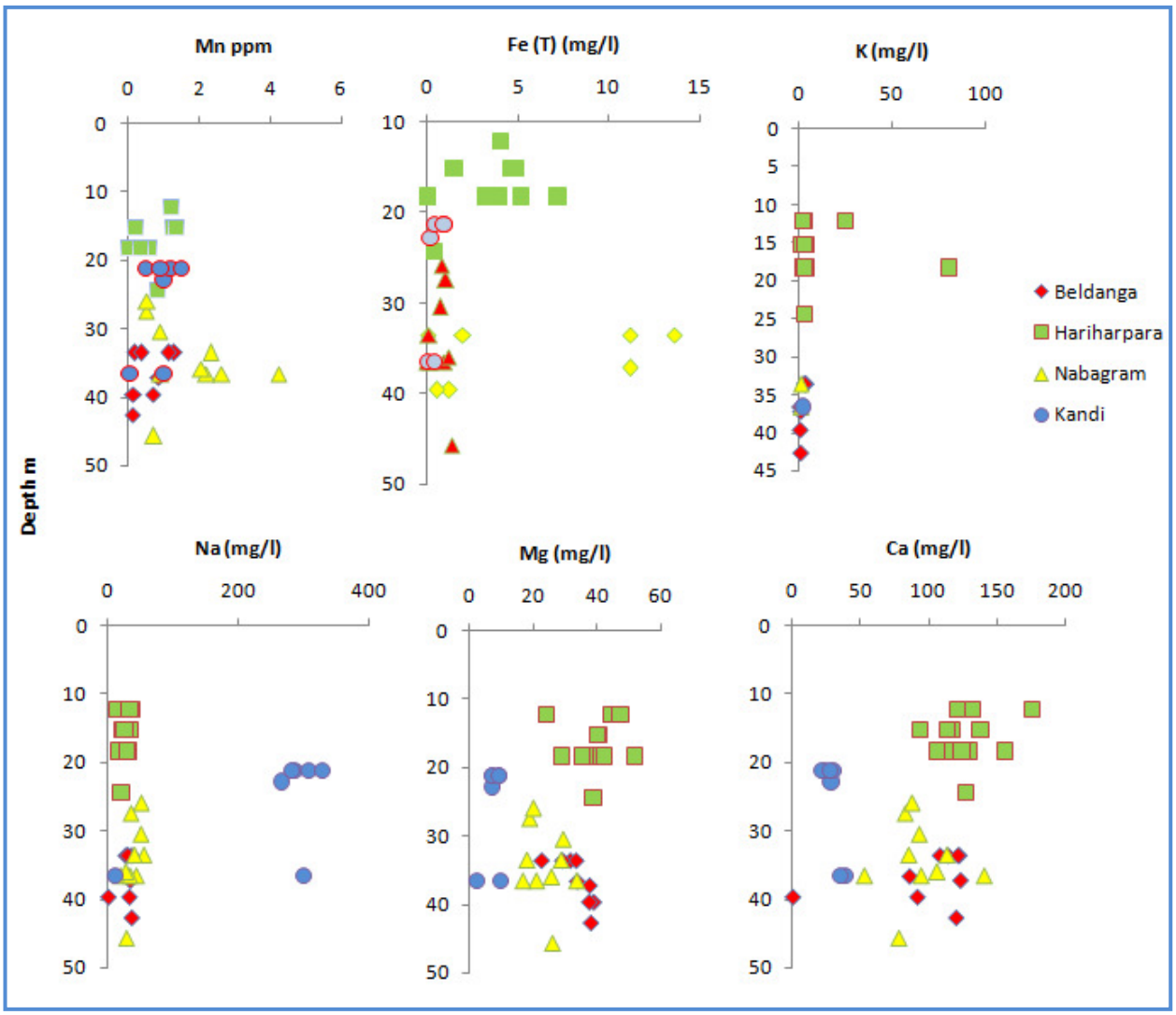


Figure 41: Concentration of cations vs. depth for tubewells (shallow and deep) at High As (Beldanga; Hariharpara) and Low As areas (Nabagram; Kandi) for the year 2012.

The details of cation concentration of Murshidabad waters are represented in Appendix-L

Anions

Chloride Results:

Chloride (Cl^-) concentration in pond water (surface) in high As areas range from 77.6-305.7 mg/L in Beldanga; 24.8-39.8 mg/L in Hariharpara and in low As areas the concentrations are 72.6 mg/L in Nabagram a and 75.8-105.8 mg/L in Kandi

In tubewells (shallow and deep) the concentrations are in high As areas ranges from 3.99-12.9 mg/L in Beldanga; 2.3-53.8 mg/L in Hariharpara and in low As areas the ranges are 29.09-103.4 mg/L in Nabagram and 24.1-180.2 mg/L in Kandi. (Fig. 42).

In irrigation wells the concentrations for the high As areas are 2.9-8.5 mg/L in Beldanga; 1.3-1.8 mg/L in Hariharpara and in low As areas the concentrations are 14.24 mg/L in Nabagram and 80.8-251.2 mg/L in Kandi.

Bromide (Br^-) results

Br^- concentration in pond waters ranges at high As areas ranges from 0.01-0.96 mg/L in Beldanga; <0.3-7.9 mg/L in Hariharpara and in low As areas the ranges from 12.58 mg/L in Nabagram and 5.9-7.8 mg/L in Kandi.

Br^- concentration in tubewells in high As areas ranges from 0.01-0.94 mg/L in Beldanga; <0.09-0.95 mg/L in Hariharpara and in low As areas the ranges are 0.01-1.48 and 0.01-1.38 mg/L in Kandi. (Fig.42)

Br^- concentration in irrigation wells in high As areas the ranges are 0.01 mg/L in Beldanga and Hariharpara in low As areas the ranges are 0.01 mg/L in Nabagram and 1.02-1.35 mg/L in Kandi.

Nitrate (NO_3^-) Results

In pond waters the nitrate concentration ranges from 0.24-1.08 mg/L in Beldanga; <0.3-7.9 mg/L in Hariharpara and in low As areas the ranges are 12.59 mg/L in Nabagram and 5.9-7.8 mg/L in Kandi.

The concentration of Nitrate in tubewells high As areas ranges from 0.02-0.67mg/L in Beldanga; 0.03-21.2 mg/L in Hariharpara and in low As areas the ranges are 0.2-13.8 mg/L in Nabagram and 0.04-0.69 mg/L in Kandi (Fig.42)

Irrigation wells the concentration of nitrates are 0.76-7.7 mg/L in Beldanga; 0.5 to 0.8 mg/L in Hariharpara and in low As areas the ranges are 0.66 mg/L in Nabagram and 0.01-0.92 mg/L in Kandi.

Phosphate (PO_4^{3-}) results

In pond waters the phosphate results ranges form 1.78-5.03 mg/L in Beldanga; 1.4-2.5 mg/L in Hariharpara and in low As areas the ranges are 2.2 mg/L in Nabagram and 1.54-1.9 mg/L in Kandi

In tubewells (both shallow and deep) the concentration of phosphate in high As areas are 0-1.2 mg/L in Beldanga; <0.06-2.2 mg/L in Hariharpara and in low As areas the concentration ranges are 0.3-2.5 mg/L in Nabagram and 0.08-2.23 mg/L in Kandi (Fig.42).

In the irrigation wells the phosphate concentration ranges are below detection limit (0.01)-1.3 mg/L in Beldanga; below detection limit (0.01)-1.3 mg/L in Hariharpara and 1.6 mg/L in Nabagram and 1.4-1.5mg/L in Kandi.

Sulfate (SO_4^{2-}) results

The sulfate concentration in pond waters at high As areas ranges from 5.58-24.2 mg/L in Beldanga; 6.3-9.4 mg/L in Hariharpara and in low As areas the concentrations are 11.05 mg/L in Nabagram and 6.4-6.5 mg/L in Kandi

Tubewells (shallow and deep) the concentration of sulfate in high As areas are <0.06-1.5mg/l in Beldanga; <0.09-35.8 mg/L in Hariharpara and in low As area the ranges are 14.6-33.8 mg/L in Nabagram and <0.1-6.69 mg/L in Kandi (Fig.42).

In irrigation wells the ranges in high As areas are 1.4-9.9mg/l in Beldanga; 1.5-2.9mg/l in Hariharpara and in low As areas the ranges are7.4mg/l in Nabagram and 1.4-1.5mg/l in Kandi.

Fluoride (F^-) results

The sulfate concentration in pond waters at high As areas ranges from 0.8-8.41 mg/L in Beldanga; <0.3-3.1 mg/L in Hariharpara and in low As areas the concentrations are 0.33 mg/L in Nabagram and <0.3-0.4 mg/L in Kandi

Tubewells (both shallow and deep) the concentration of sulfate in high As areas are 0.27-0.6 mg/L in Beldanga; <0.03-0.5 mg/L in Hariharpara and in low As area the ranges are 0.62-1.2 mg/L in Nabagram and below detection limit (0.01)- 1.76 mg/L in Kandi (Fig.42).

In irrigation wells the ranges in high As ranges from 1.4-9.9 mg/L in Beldanga; 1.5-2.9 mg/L in Hariharpara and in low As areas the ranges are 7.4 mg/L in Nabagram and 1.4-1.5 mg/L in Kandi.

Nitrite (NO_2^-) results

The nitrite concentration in pond waters at high As areas ranges from 0.83-8.14 mg/L in Beldanga; <0.3-3.1 mg/L Hariharpara and in low As areas are 0.33 mg/L in Nabagram and <0.3-0.4 mg/L in Kandi.

In tubewells (shallow and deep) the concentrations in high As areas are 0.01-<0.02 mg/L in Beldanga; 0.01-3.12 mg/L in Hariharpara and in low As areas the ranges are 0.01-1 mg/L in Nabagram and 0.01-0.3 mg/L in Kandi (Fig.42).

In irrigation wells the concentration in high As areas are 0.01 mg/L (below detection limit) in Beldanga; 0.01 (below detection limit)- 3.2 mg/L in Hariharpara and in low As areas the concentrations are 0.01 mg/L (below detection limit) in Nabagram and 0.01(below detection limit)- 0.4 mg/L in Kandi.

For the data analysis (for all the diagrams) the best data are chosen. For most of the water samples three types of data are generated and best are chosen to create all diagrams. If the value is below detection limit in the laboratory analysis then field data is chosen (kit data or spectrophotometer data) for those sample points. NH_4^+ plot is prepared from spectrophotometer data. Dissolved oxygen plot is prepared from field CHEMets® DO test kit. Plots for Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-} and NO_2^- are prepared from IC- data and spectrophotometer data.

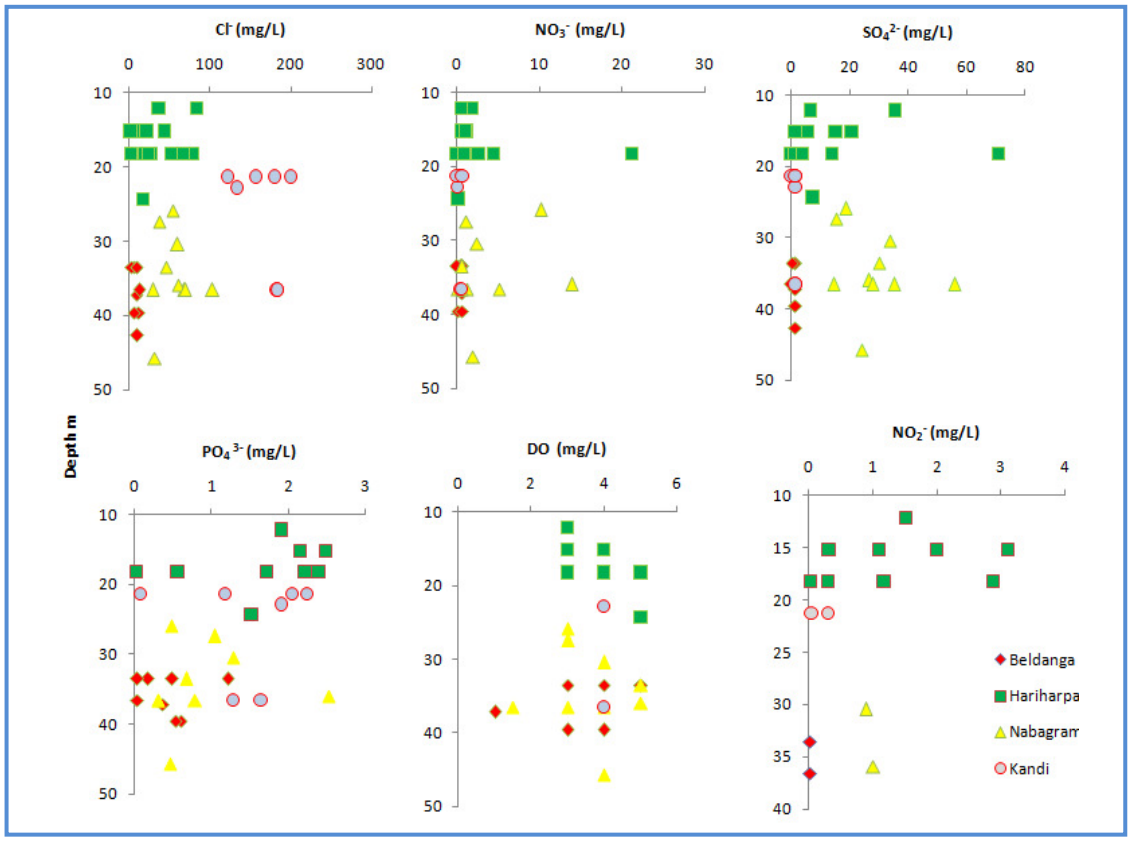


Figure 42: Concentration of anions vs. depth in High As (Beldanga; Hariharpara) and Low As areas (Nabagram; Kandi) for the year 2012.

The details of Anion data is represented in Appendix-M.

Chloride/Bromide ratio results

Cl^-/ Br^- ratio was calculated to study the effect of anthropogenic waste sources like pit latrines, septic tanks, highly contaminated ponds by various anthropogenic waste materials on shallow depth tube wells (McArthur et al., 2012, Xie et al., 2011) which is the major drinking water source in this area. To calculate the ratio (Cl/Br) the $[Cl^-]$ and $[Br^-]$ were converted to molar ratios. At first the concentrations in mg/l of both Cl^- and Br^- were converted from mg/L to moles per liter by dividing the concentration of element by molecular mass and 1000 to convert it in to moles per liter. Then the moles per liter value for both Cl^- and Br^- is converted to milli moles per litter by multiplying it with 1000. Then in the final step the Cl^- concentration in milli moles per liter is divided by Br^- concentration in milli-moles per liter to get the Cl^-/Br^- molar ratio.

Cl^-/Br^- ratio has been calculated for ponds, tubewells (both shallow and deep) and irrigation wells in high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi).

For the pond waters (surface) the Cl^-/Br^- ratio in high As areas are 714.89-32293.1 in Beldanga; 56.86-6381.99 in Hariharpara and in low As areas the ranges are 16368.99 in Nabagram and 170.69-271.59 in Kandi.

For the tubewells (shallow and deep) the Cl^-/Br^- ratio in high As areas are 28.9-2192.1 in Beldanga; 99.3-12122.2 in Hariharpara and in low As areas the ranges are 91.8-12340.3 in Nabagram and 280.6-561.2 in Kandi

Cl^-/Br^- ratio for the irrigation wells at high As areas are 729.1-1926.6 in Beldanga; 298.5-2358.9 in Hariharpara and in low As areas the ranges are 3211.5 in Nabagram and 177.8-420.92 in Kandi. The details of Cl^-/Br^- data is represented in appendix-N

Cl^-/Br^- ratio for the tubewells (shallow and deep) were plotted vs. As concentration and depth (Fig. 43 &.44) to study the effect of anthropogenic contaminants in these drinking waters. The tubewells are mainly used for Cl^-/Br^- ratio studies because they were the main drinking water sources of this area and the As data for the tubewells were more. During the field work number of samples collected from tubewells were many more compared to pond and irrigation wells. The data used for Cl^-/Br^- ratio calculations were from IC (ion chromatograph) data.

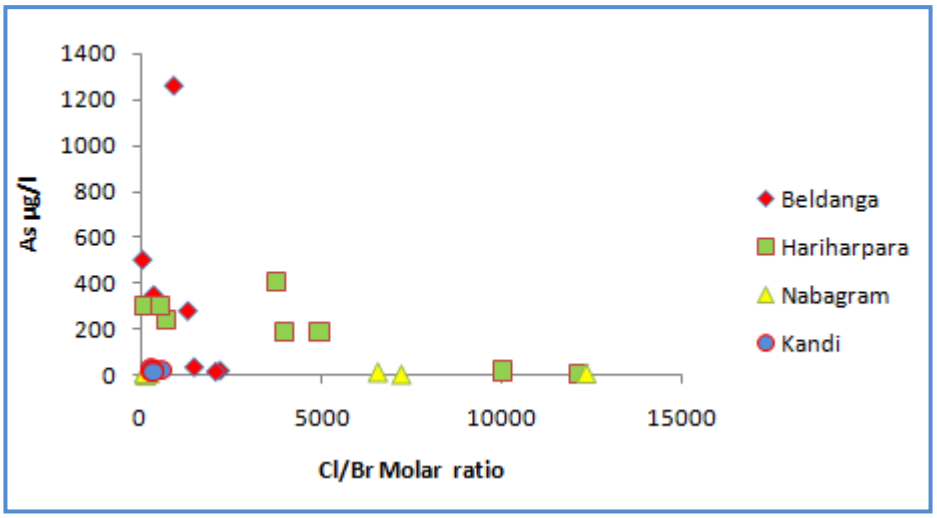


Figure 43: Plot showing Cl/Br molar ratio vs. As in Murshidabad tubewells

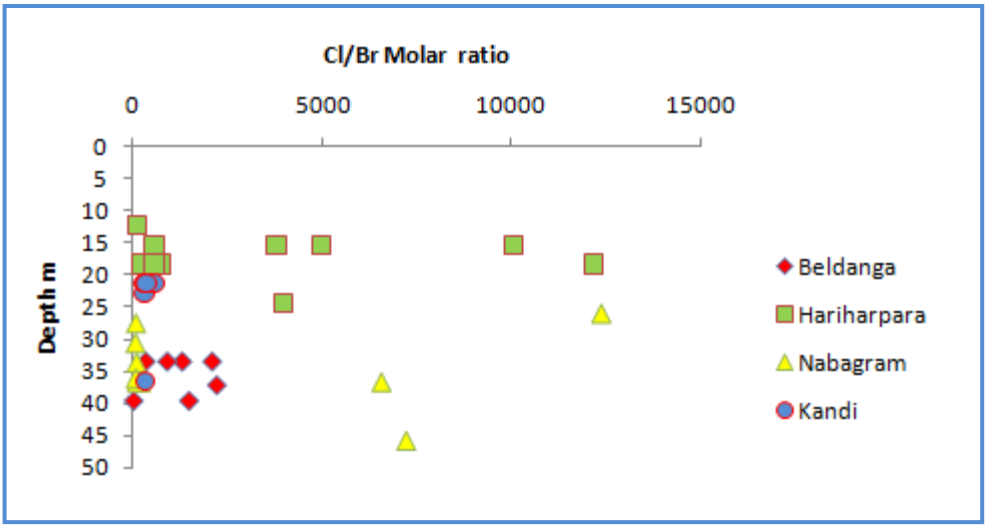


Figure 44: Cl/Br molar ratio vs. Depth in Murshidabad tubewells

δD and $\delta^{18}O$ results

Stable isotope vales were calculated for pond waters, tubewells (shallow and deep)and irrigation wells in Murshidabad in separate labs (Biology department , KSU and Isotec® lab, Illinois, USA). Data from both labs are used for plotting as they showed very good conformity.

Global meteoric water line ; GMWL ($\delta D = 8\delta^{18}O + 10$) has been plotted using the data from (Craig; 1961) and the local meteoric water line, LMWL ($\delta D = 7.2\ \delta^{18}O + 7.7$) was calculated from Mukherjee et al., 2007 to study the isotopic composition of Murshidabad waters for the year 2012. Values for δD and $\delta^{18}O$ for local wet season precipitation were -49‰, -64‰, and -46‰ for δD and -7.3‰, -9.3‰, and -6.7‰ for $\delta^{18}O$ (Mukherjee et al., 2007). Local dry season precipitation values for δD and $\delta^{18}O$ were -32‰, -31‰, -36‰ and -31‰ for δD and -5.1‰, -5.1‰, -4.7‰, and -4.7‰ for $\delta^{18}O$ (Mukherjee et al., 2007).For the current study pond waters (surface); tubewells (shallow & deep) and irrigation wells were selected from both high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi).

Ponds: The δD values (Y-axis) were plotted against the $\delta^{18}O$ values (X-axis) for pond waters in all the areas are represented in the Table-9. All the pond water samples falls below the GMWL and LMWL (Fig.49)

	High As area		Low As area	
	Beldanga	Hariharpara	Nabagram	Kandi
δD ‰	-30.1- - 28.2	-30.1 - -27‰	-42 - -31	-34.8 - -41

$\delta^{18}O$ ‰	-2.4 - -3.43	2.74 - -2.7	-4.24 - 1.81	-4.62- -3.55

Table 9: δD & $\delta^{18}O$ values for ponds in high and low As areas for the year January 2012

Tubewells : The δD values (Y-axis) were plotted against the $\delta^{18}O$ values (X-axis) for tubewells waters and ranges are represented in the Table-10.

	High As area		Low As area	
	Beldanga	Hariharpara	Nabagram	Kandi
δD ‰	-31.1 - -22	-31 - -25	-21 - -32.6	-26 -- 31.9
$\delta^{18}O$ ‰	-4.52- -3.1	-3.9- -4.8	-4.04 - -2.7	-3.9 - -4.45

Table 10: δD & $\delta^{18}O$ values for tubewells (shallow and deep) in high and low As areas for the year January 2012

Majority of the tubewells (shallow and deep) falls close to the LMWL. The Hariharpara water samples are falling in the LMWL. Beldanga and Kandi samples are just below the LMWL. Whereas the Nabagram samples are farthest from LMWL compared to other three. The overall isotopic composition of shallow depth tube wells are more enriched in heavier isotopes $\delta^{18}O$ like that of Ponds . But it more enriched in heavier isotopes of $\delta^{2}H$ compared to the ponds. Data sets for ponds and tubewells are showing parallel trend but not overlapping. One pond waters in Beldanga is almost overlapping with one tubewell waters in Beldanga; and this could be due to mixing of tubewell water in ponds (Fig.48)

Irrigation wells: The δD values (Y-axis) were plotted against the $\delta^{18}O$ values (X-axis) for deep tube well (irrigation wells) waters the values are in Table-11.

	High As area		Low As area	
	Beldanga	Hariharpara	Nabagram	Kandi
δD ‰	-32.4- -29.8	-28.2 - -24	No data	-27- -31.6
$\delta^{18}O$ ‰	4.56- -4.12	-3.4- -4.22	No data	4.1- -4.23

Table 11: δD & $\delta^{18}O$ values for irrigation wells in high and low As areas for the year January 2012

No Irrigation well samples were analyzed for Nabagram. The irrigation wells samples fall just below the LMWL. The plots for irrigation wells look similar to the tubewells and shows similar kind of trend and are overlapping each other (Fig.48&49). These samples contains

heavier values of $\delta^{18}O$ and lighter vales of δD. The irrigation wells (most of them were deeper depth) are coinciding with tubewell (shallow and deep) waters (Fig.47).

Figure-50 was made by plotting isotopic data for tubewells, pond waters and irrigation wells and reclassifying based on the As concentration . The classification are <50 µg/L As, 50-500 µg/L As and >500 µg/L As to study the relation between recharge mechanism and As distribution in Murshidabad waters. One of the pond water (Beldanga) with 50-500 µg/L As is overlapping with high As tubewell >500 µg/L (Beldanga). The location of both the tubewell and the pond are very near to each other (tubewell constructed on the bank of the pond) and similar isotopic ratios and high As concentration could be due to mixing of tubewell water with the pond.(Fig.50)

Plots were also prepared for the comparative study of ponds, tubewells, irrigation wells, dry season precipitation, wet season precipitation and river waters (Fig.48) by plotting them together and also plotting together by classifying each sample by area (Fig.49). Both dry and wet season precipitation were borrowed from Mukherjee et al., 2007 and river water datasets from Andy, 2010. The details of Isotopic data is for all samples were represented in Appendix-O.

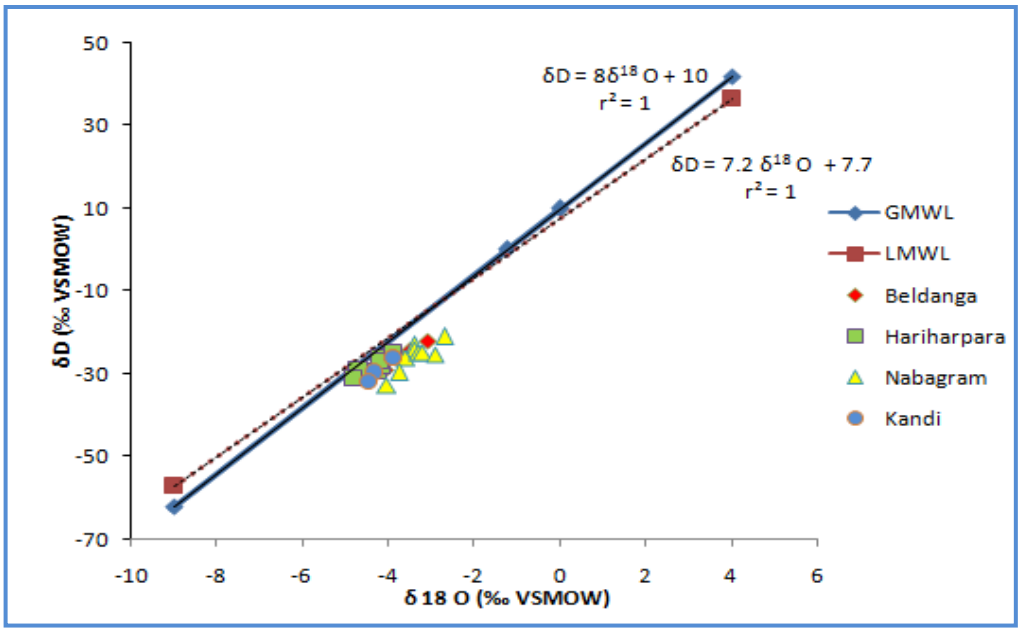


Figure 45: Stable isotope plots for δD and $\delta^{18}O$ calibrated to (Vienna-Standard Mean Ocean Water (V-SMOW) for tubewell waters (shallow depth 10-40m and deeper depth >40m) from high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi). Global meteoric water line (GMWL) and local meteoric water line (LMWL) are shown with their slope-intercept equations

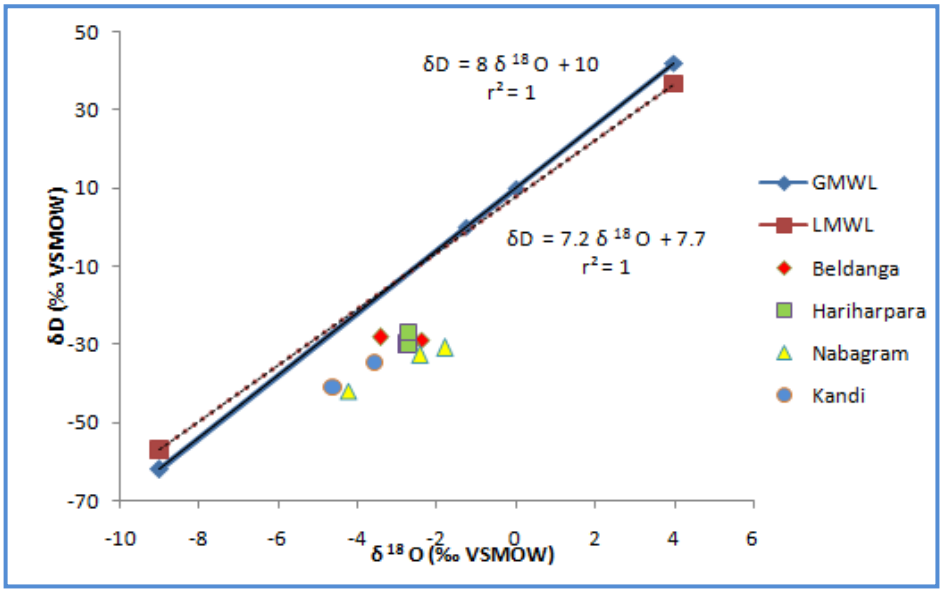


Figure 46: Stable isotope plots for δD and $\delta^{18}O$ calibrated to (Vienna-Standard Mean Ocean Water (V-SMOW) for pond waters (surface) from high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi). Global meteoric water line (GMWL) and local meteoric water line (LMWL) are shown with their slope-intercept equations

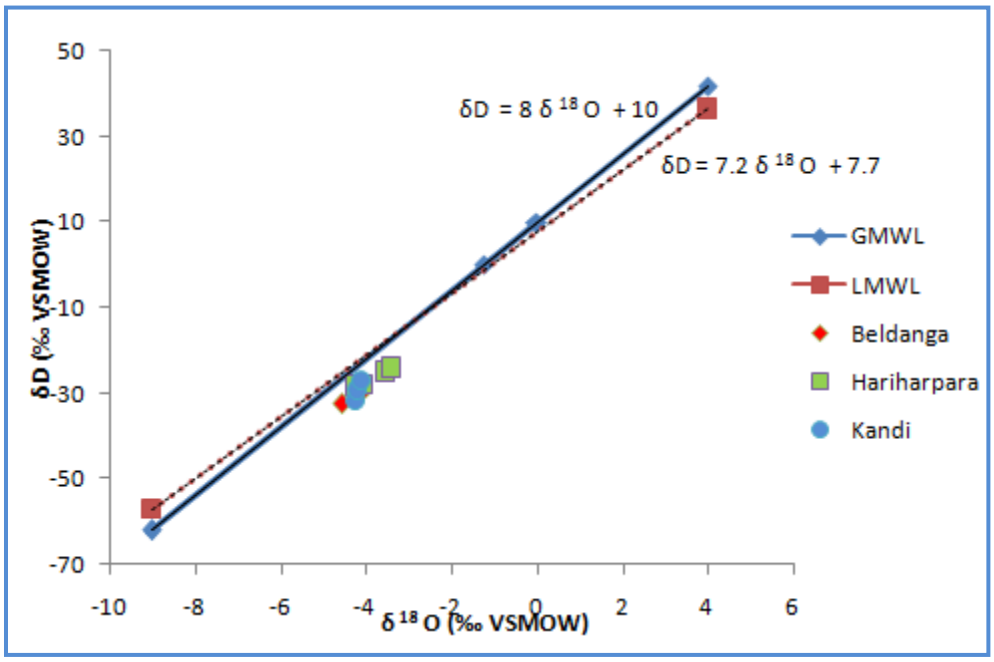


Figure 47: Stable isotope plots for δD and $\delta^{18}O$ calibrated to (Vienna-Standard Mean Ocean Water (V-SMOW) for irrigation wells (10-46m) (from high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi). Global meteoric water line (GMWL) and local meteoric water line (LMWL) are shown with their slope-intercept equations

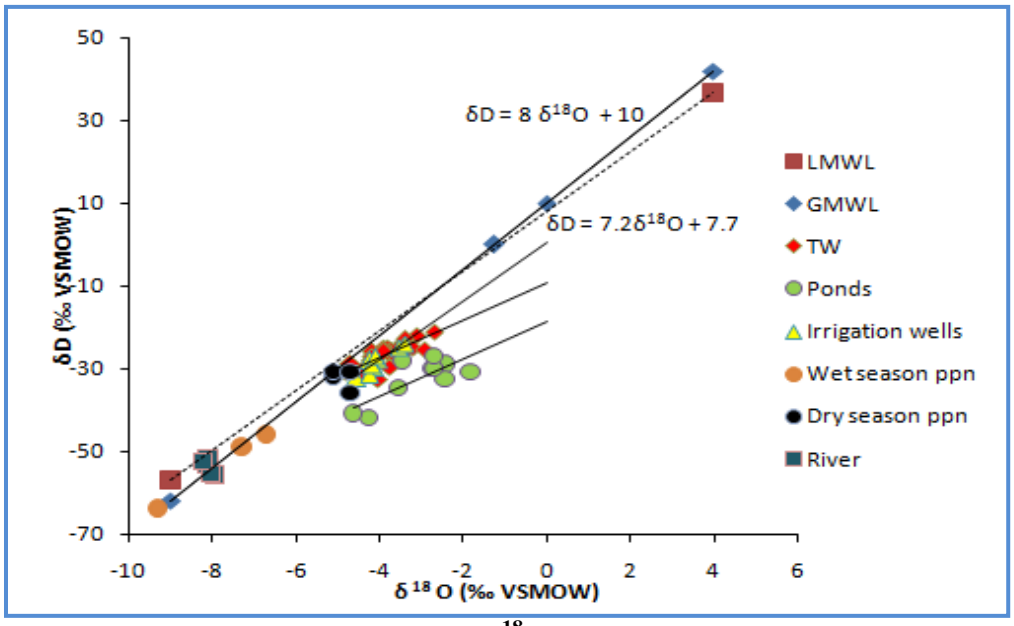


Figure 48: Stable isotope plots for δD and $\delta^{18}O$ calibrated to (Vienna-Standard Mean Ocean Water (V-SMOW)) tubewells (TW; shallow and deep), pond waters (ponds) and irrigation waters Murshidabad areas (both high and low As areas together) with trend lines drawn

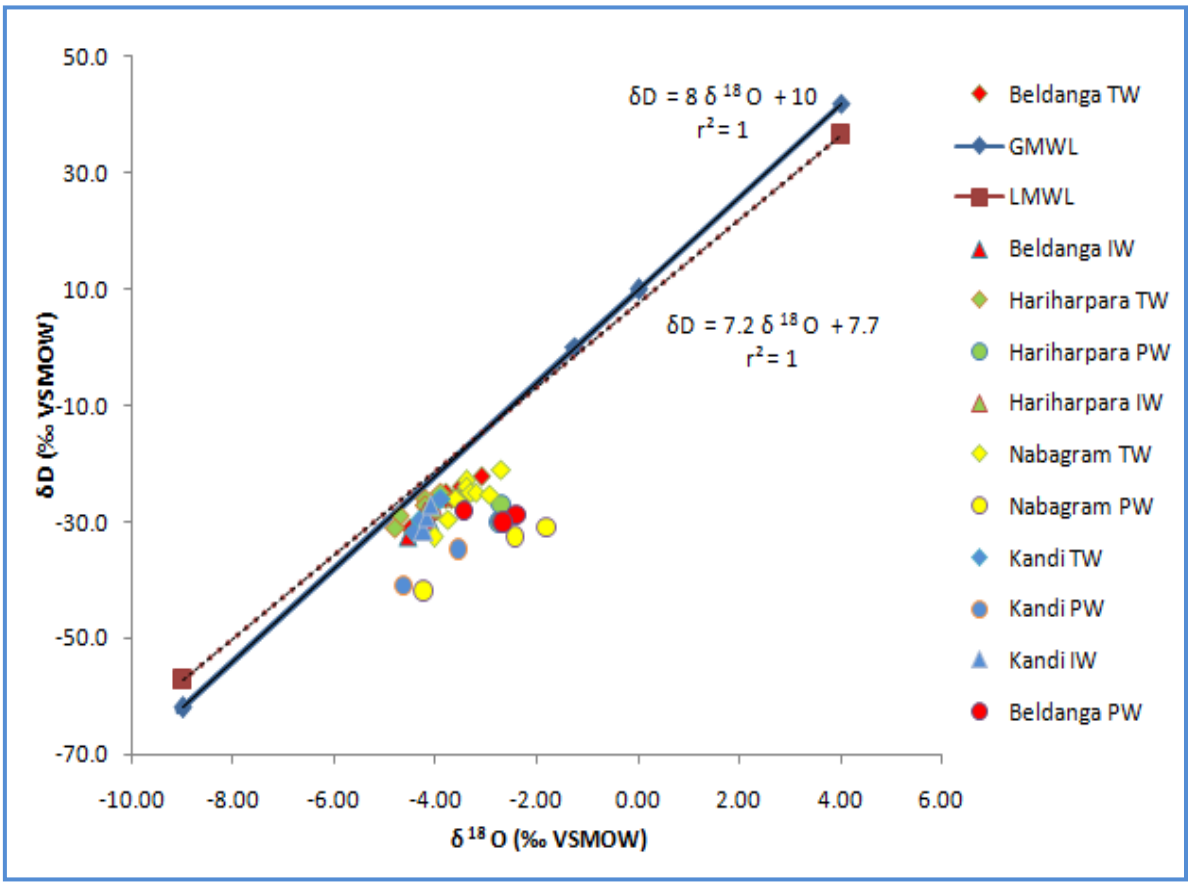


Figure 49: Stable isotope plots for δD and $\delta^{18}O$ calibrated to (Vienna-Standard Mean Ocean Water (V-SMOW) for tubewells (TW; sallow and deep), pond (PW) and irrigation well (IW) waters from high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi) in Murshidabad district. Global meteoric water line (GMWL) and local meteoric water line (LMWL) are shown with their slope-intercept equations

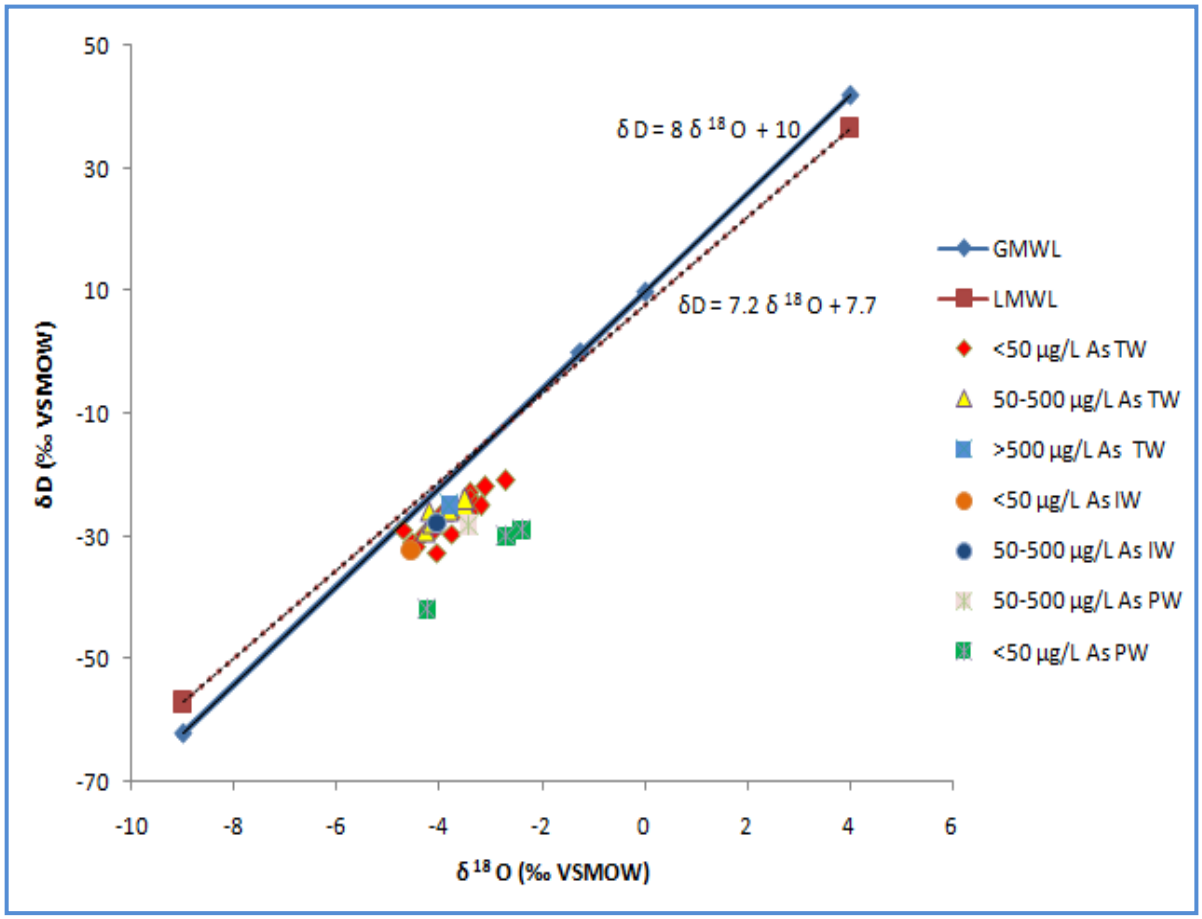


Figure 50: δD and $\delta^{18}O$ plots for tubewells (TW), irrigation wells (IW) and pond waters (PW) and subdivisions are based on dissolved As concentrations (µg/L) represented by different colored symbols

Dissolved Organic Carbon, Total Nitrogen and Fluorescence spectroscopic studies

DOC, TN, DON and C/N ratio results

Dissolved organic carbon (DOC) concentration , Total nitrogen concentration (TN) were measured and the dissolved organic nitrogen (DON) of high As areas and low As areas of Murshidabad district was been calculated for total nitrogen and other nitrogen species in water.

In ponds the concentration of DOC and TN ranges in high As areas are 9.6-13.5 mg/L and 2.6-8.43 mg/L in Beldanga; 2.64-8.43 mg/L and 0.74-2.54 mg/L in Hariharpara and in low

As areas the concentrations are 9.23-12.03 mg/L and 2.32-302.3 mg/L in Nabagram; 8.67-8.82 mg/L and 2.04-2.43 mg/L in Kandi.

The concentration of DOC and TN in tubewells (shallow and deep) at high As areas ranges from 1.303-2.404 mg/L and 0.11-2.2 mg/L in Beldanga; 0.88-3.3 mg/L and 0.234-5.64 mg/L in Hariharpara and in low As areas the ranges are 0.6-12.9 mg/L and 0.025-3.5 mg/L in Nabagram; 0.63-1.29 mg/L and 0.04-0.2 mg/L in Kandi.

In irrigation wells the concentration of DOC and TN for high As areas are 1.06-1.24 mg/L and 0.3-2.02 mg/L in Beldanga; 1.12-2.008 mg/L and 0.9-1.39 mg/L in Hariharpara and in low As areas the ranges are 0.8 mg/L and 0.6 mg/L in Nabagram and 0.9-9.6 mg/L and 0.1-0.49 mg/L in Kandi.

For the river water (Bhagirathi) the DOC is 1.2 mg/L and TN is 0.65 mg/L. Rain water (January 2012) for Murshidabad area and Kolkata city was also calculated for DOC and TN and the vales are 30.14 mg/L; 19.12 mg/L and 1.52 mg/L; 1.9 mg/L respectively. The rain water collected from Murshidabad was highly contaminated and it contains very much organic remains (plant remains- leafs) as it was collected from a local village house top which was totally covered with plant materials. Even after filtering the sample contains high organics. So the rain water data for DOC and TN from Murshidabad is not the actual value.

The dissolved organic nitrogen (DON) was calculated by subtracting various nitrogen species from the total nitrogen value. For the pond waters in high As areas DON values ranges from 0-0.92 mg/L in Beldanga; and the DON concentration in Hariharpara is totally absent. The DON values for Nabagram and Kandi were also absent.

For the tubewells (shallow and deep) the DON values ranges from 0.06-2.3 mg/L in Beldanga; 0.42- 2.94 mg/L in Hariharpara and in low As areas the ranges are 0-0.8 mg/L in Nabagram and 0.07 mg/L in Kandi. The results shows that there is positive correlation between DOC concentration and As concentration. When there is high DOC in water, then the concentration of As in that area was also high (Fig.51). In high As areas (Beldanga and Hariharpara) the concentration of DOC is high compared to low As areas (Nabagram) (Fig.52). The DON values also shows similar kind of relation in high and low As areas (Fig.51).

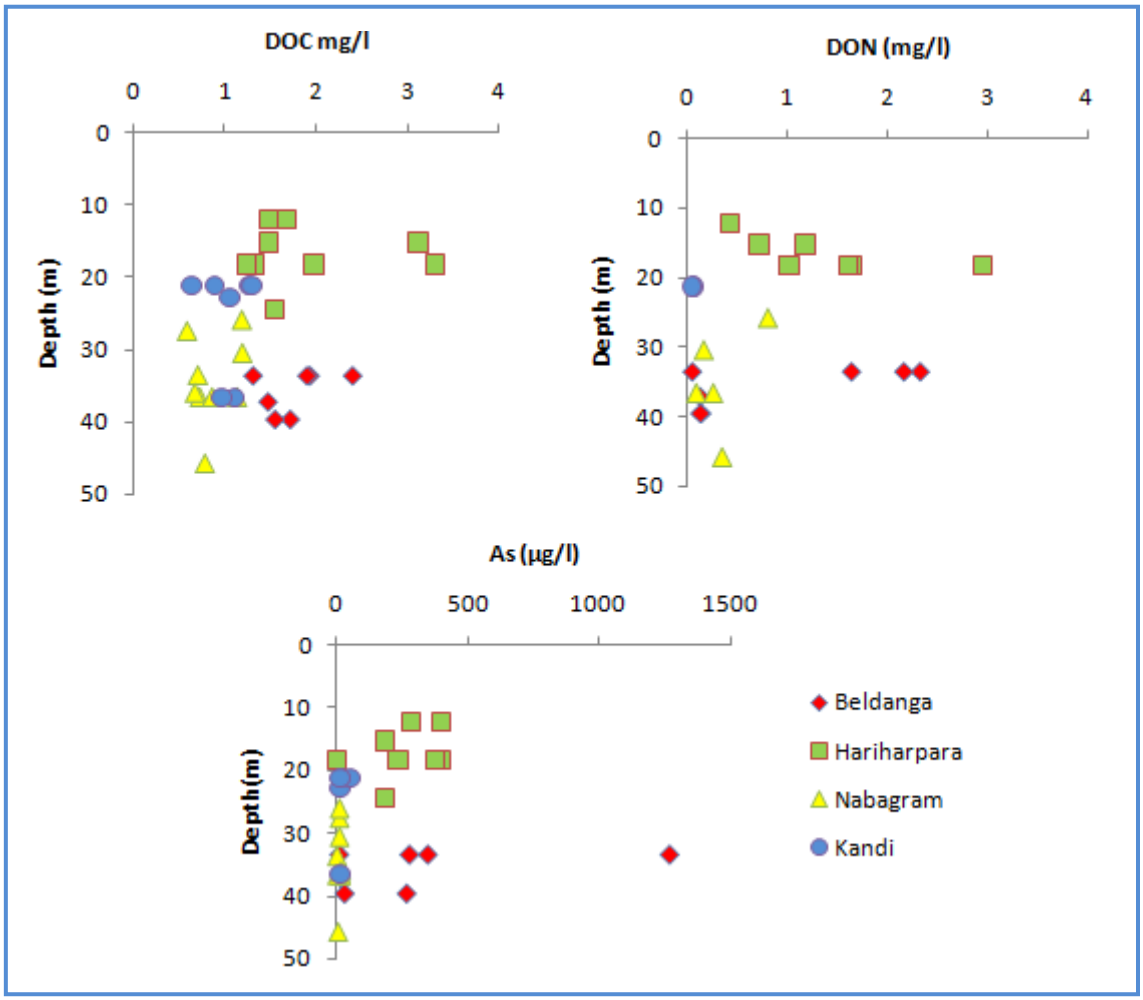


Figure 51: Concentration of DOC, DON and As with depth in High As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi) shallow depth tube wells

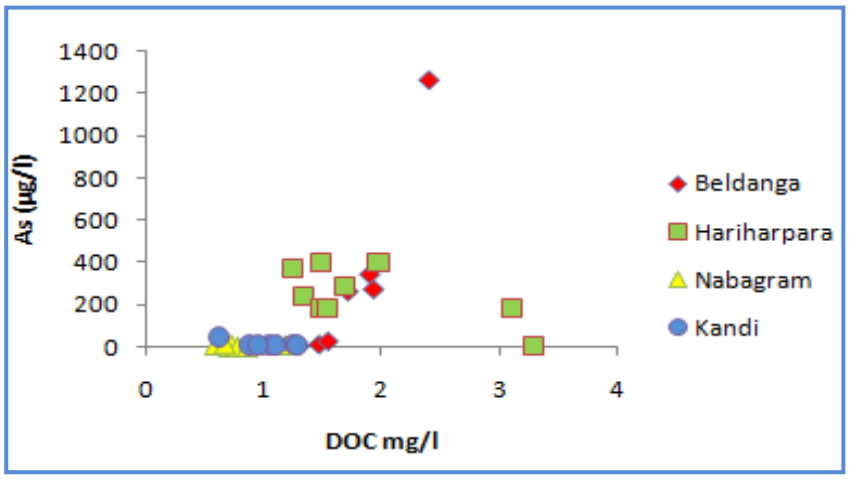


Figure 52: Plot showing the distribution of DOC and As in high (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi) shallow depth tube wells

C/N molar ratio calculations were done for tubewells (shallow and deep) to study the source of organic matter in sediments. For the calculation the DOC and DON values were converted from mg/L to moles per litter and then divided DOC by DON to get the C/N molar ratio. If the C/N molar ratio was >15 then it indicates terrestrial vascular plants (Bordowskiy, 1965; Sampei and Matsumoto, 2001). Most of our samples have very low C/N ratio (<4) which indicates reduction of nitrogen to inorganic ammonia (Muller, 1977) . Only 2 tubewell samples from Kandi, low As area (KHN-132 and 133; both 21m) have high C/N molar ratio and are 38.1 and 25.9 respectively. For the current study, C/N molar ratio of tubewells were used find the effect of C/N ratio with As distribution. In high As areas the C/N rations ranges for the tubewells are 0.97-27.34 in Beldanga; 1.31-5.13 in Hariharpara and in low As areas the ranges are 1.7-9.4 in Nabagram and 10.5-38.1 in Kandi. The results shows not much correlation between As and C/N ratio and As (Fig.53).

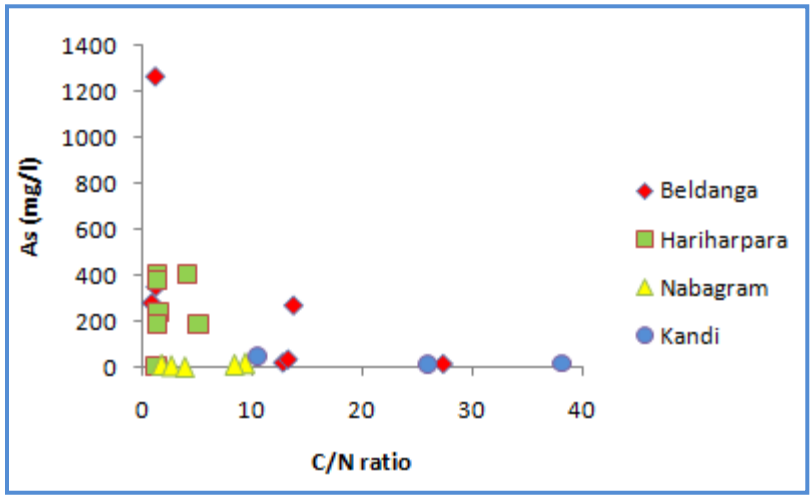


Figure 53: C/N ratio vs. As plot for high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi) for the shallow depth tube wells.

The distribution of C/N molar ratio vs. depth and DOC concentration in mol/L vs. depth for the tubewells; in high As (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi) do not showing any relationship. However the DON concentration in mol/L vs. depth plot shows that, in high As areas (Beldanga; Hariharpara) for most of the tubewells, the concentration of DON is higher compared to that of low As areas (Nabagram; Kandi) (Fig. 54).

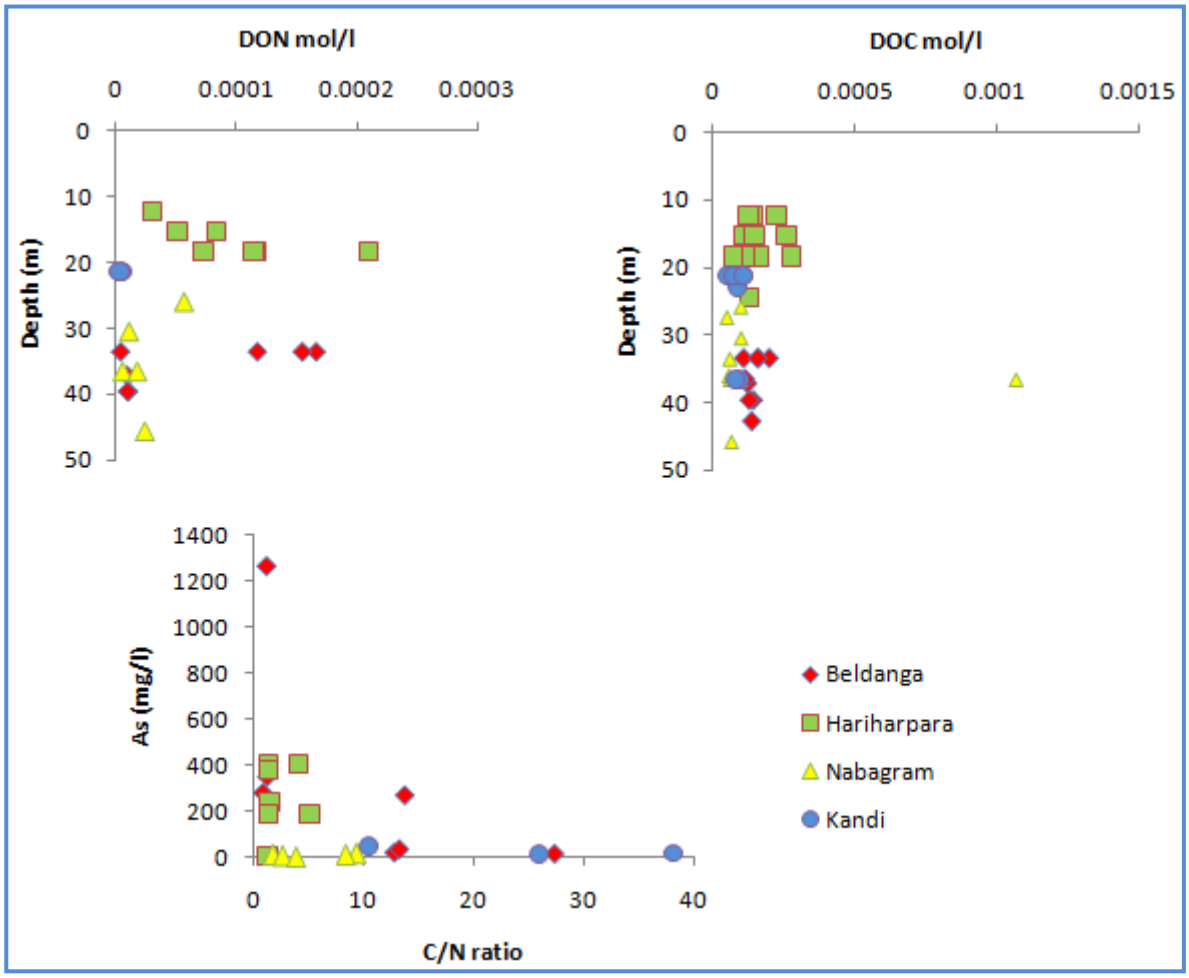


Figure 54: Distribution of DON (mol/L; top left) ; DOC (mol/L; top right) vs. depth and C/N ratio vs. As concentration in tubewell waters in high As (Beldanga; Hariharpara) and low As (Nabagram; Kandi) areas.

The details of C/N molar ratios for each of the tubewells are represented in Appendix-P

Fluorescence spectroscopic studies of the Murshidabad waters

All collected water samples of the present research was undertaken for organic matter characterization using florescence spectroscopic studies. The as per the fluorescence data, excitation emission matrix (EEM) the Murshidabad waters (both high and low As) contains 4 major DOC or DOM components. They were Humic component (A); humic component (C); Tyrosine like or protein like(B) and Tryptophane like or protein like or phenol like (T). Among them 'A' and 'C' are terrestrially derived components and 'B' and 'T' are bacterial protein components. To study the source of DOC, Fluorescence Index (FI) was calculated for each of the water samples. Freshness index (Fr.I) was calculated to study the contribution of recently

produced DOM or freshness of the DOM. To study the aromaticity or reactivity of DOC Specific Ultraviolet Absorbance (SUVA) is been calculated for each of the samples.

The for pond waters (surface) in high As areas fluorescence Index (FI) ; Freshness index (Fr.I) and SUVA for pond waters in high As areas are 1.55-1.69; 0.77-0.825 and 0.0024-0.003 in Beldanga; 1.56-1.67; 0.77-0.9 and 0.0023-0.003 in Hariharpara and in low As areas the ranges are 1.59-1.69; 0.72-0.82 and 0.0028-0.0033 in Nabagram and 1.61-1.62; 0.744-0.748 and 0.0029-0.0032 in Kandi.

For the tubewells (10-40 m and >40 m depth), in high As areas fluorescence Index (FI) ; Freshness index (Fr.I) and SUVA are 0.79-1.81; 0.14-0.779 and 2.4-3.4 in Beldanga; 1.56-1.79; 0.71-0.95 and 2.04-4.24 in Hariharpara and in low As areas the ranges are 1.58-2.72; 0.65-0.98 and 0.18-4.61 in Nabagram; 1.62-1.8; 0.95-1.1 and 1.74-4.66 in Kandi.

For the irrigation wells (10-46 m) the fluorescence Index (FI) ; Freshness index (Fr.I) and SUVA in high As areas are 1.76-1.8; 0.79-0.86 and 2.57-3.43 in Beldanga; 1.62-1.72; 0.69-0.764 and 1.88-2.96 in Hariharpara and 1.72; 0.78 and 3.86 in Nabagram and 1.62-1.67; 1.02-1.083 and 0.43-2.65 in Kandi

For the river water (Bhagirathi, the major river in this area) the fluorescence Index (FI) ; Freshness index (Fr.I) are 1.59 and 1.63.

Fluorescence Index (FI) ; Freshness index (Fr.I) The rain waters (January 2012) collected from both Kolkata city and Murshidabad are 1.49; 1.39 and 1.51; 1.58 respectively.

The 4 major types of DOC components in high and low As areas of Murshidabad waters and there ranges in ponds, tubewells and irrigation waters are calculated and their ranges are expresses below.

In pond waters the range for Tyrosine like (B) and Tryptophane like (T) Humic like (A) and Humic like (C) components in high As areas are 0.553-1.11; 0.83-1.67; 2.78-5.03 and 1.2-2.63 in Beldanga; 0.24-0.42; 0.33-0.68; 0.71-2.3 and 0.33-1.02 in Hariharpara and in low As areas the ranges area 0.21-0.61; 0.287-1.08; 0.89-4.08 and 0.46-1.9 in Nabagram; 0.38-0.42; 0.77-0.78; 3.23-3.996 and 1.42-1.73 in Kandi.

For the tubewell (shallow;10-40m & deep; >40 m depth) waters the range for Tyrosine like (B) and Tryptophane like (T) Humic like (A) and Humic like (C) components in high As areas are 0.07-0.23; 0.103-0.22; 0.47-2.11 and 0.296-0.99 in Beldanga; 0.054-0.23; 0.06-0.263; 0.32-1.5 and 0.206-0.69 in Hariharpara and in low As areas the ranges are 0.051-0.12; 0.0396-

0.065; 0.073-0.5 and 0.034-0.25 in Nabagram and 0.093-0.364; 0.12-0.596; 0.32-1.45 and 0.11-0.84 in Kandi.

Irrigation wells (10-46m) waters the range for Tyrosine like (B) and Tryptophane like (T) Humic like (A) and Humic like (C) components in high As areas are 0.14-0.16; 0.21-0.22; 0.48-1.02 and 0.24-0.498 in Beldanga; 0.1-0.13; 0.16-0.21; 0.93-1.2 and 0.43-0.54 in Hariharpara and in low As areas the ranges are 0.088; 0.064; 0.39 and 0.18 in Nabagram ; 0.11-0.27; 0.11-0.42; 0.2-1.11 and 0.08-0.395 in Kandi.

In high As areas the fluorescence EEM maps for the pond water contains Both humic components 'A' and 'C' and one of the bacterial protein 'B' (Fig.55).

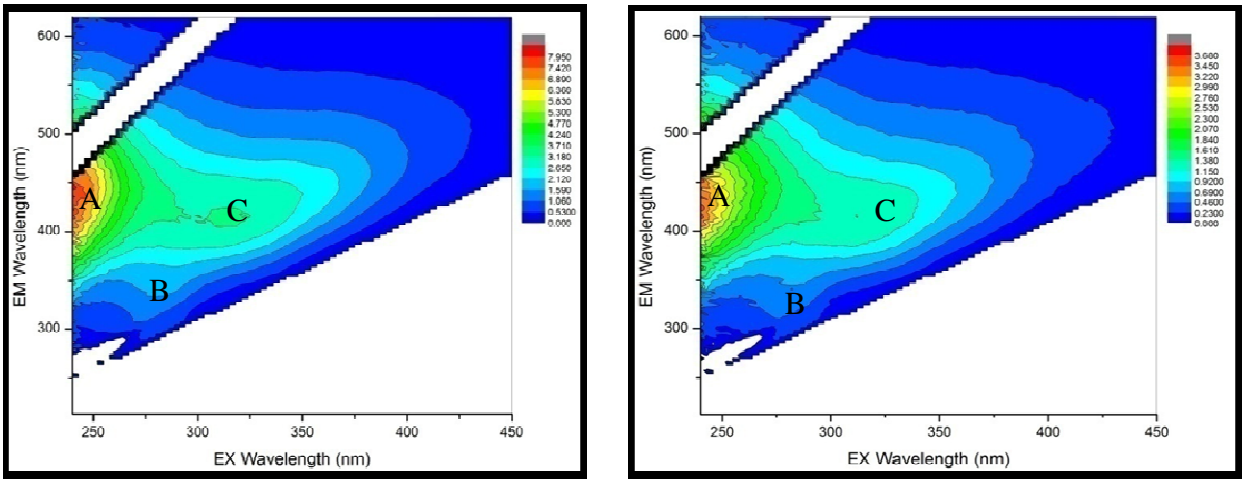


Figure 55: Excitation Emission Matrix (EEM) of pond water samples PW-102 BM (Left , Beldanga) and PW-109 HK (right, Hariharpara) showing presence of Humic components 'A', 'C' and a Bacterial component 'B'. As and Mn concentration for PW-102 BM is 110 µg/L and 0.47mg/L and PW-109 HK is 15.5 µg/L and 0.53 mg/L.

Most of the tubewell waters of high As areas also show Both humic components 'A' and 'C' and one of the bacterial protein 'B' (Fig.56)

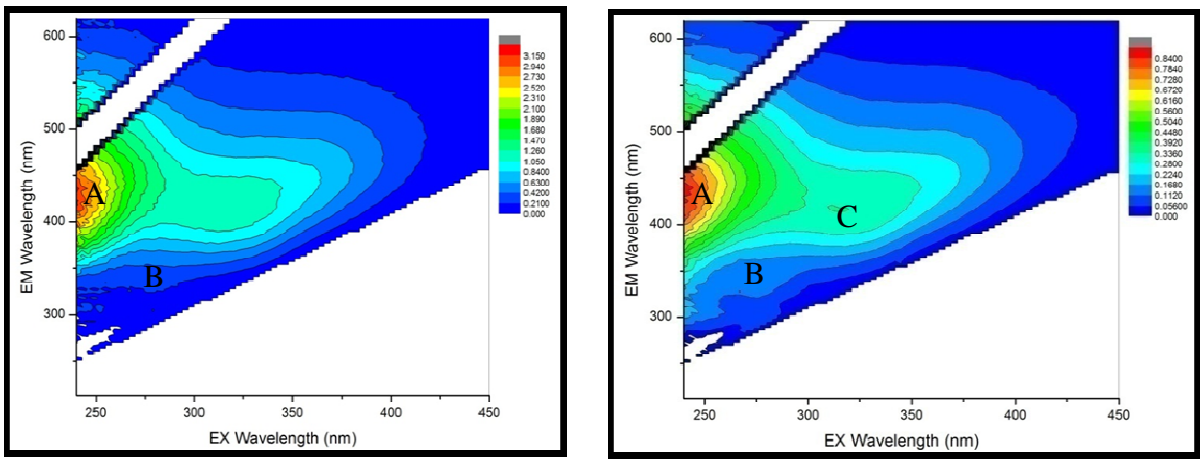


Figure 56: EEM for tubewell water samples TW-104 BM (Left , Beldanga) and TW-126 HK (right, Hariharpara) showing presence of Humic components 'A', 'C' and a Bacterial component 'B'. As and Mn concentration for TW-104 BM is 1263.73 µg/L and 1.29 mg/L and TW-126 HK is 185 µg/L and 0 mg/L

The EEM maps for irrigation wells in high As areas shows less humic component 'A' and 'C' but high amount of Bacterial component 'B' or 'T' (Fig.57)

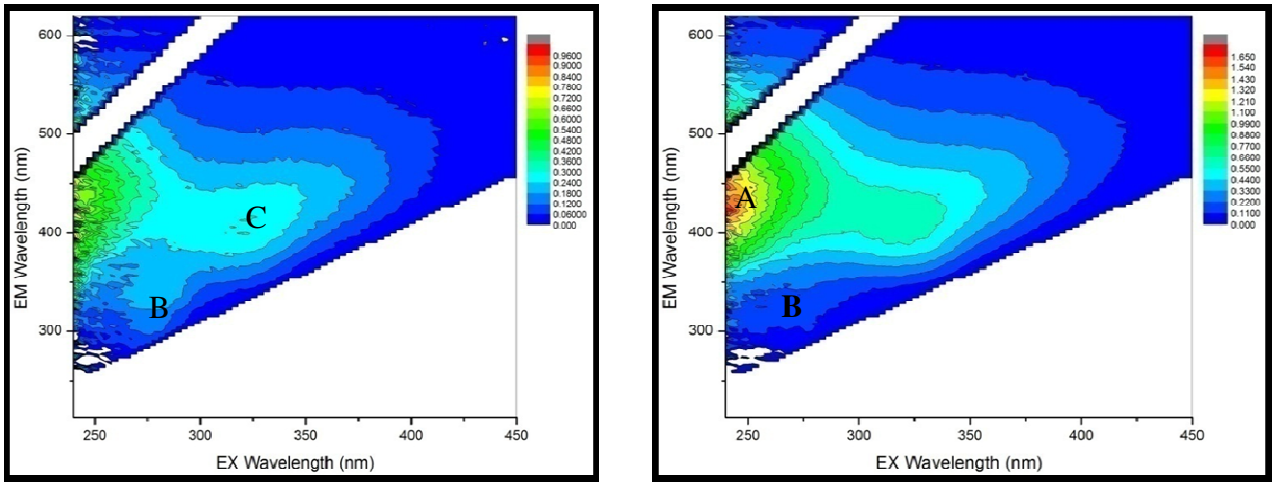


Figure 57: EEM for irrigation well water samples IW-102 BM (Left , Beldanga) and IW-104 HK (right, Hariharpara) showing presence of Humic components 'A', 'C' and are less compared to the Bacterial component 'B'. As and Mn concentration for 1W-102 BM is 42.9 µg/L and 0.21 mg/L and IW-104 HK is 433.02 µg/L and 0.44 mg/L.

EEM maps for pond waters in the low As areas shows similar kind of DOC components. The ponds in this areas contains both humic components 'A' and bacterial component 'B' as shown in the EEM maps below (Fig.58).

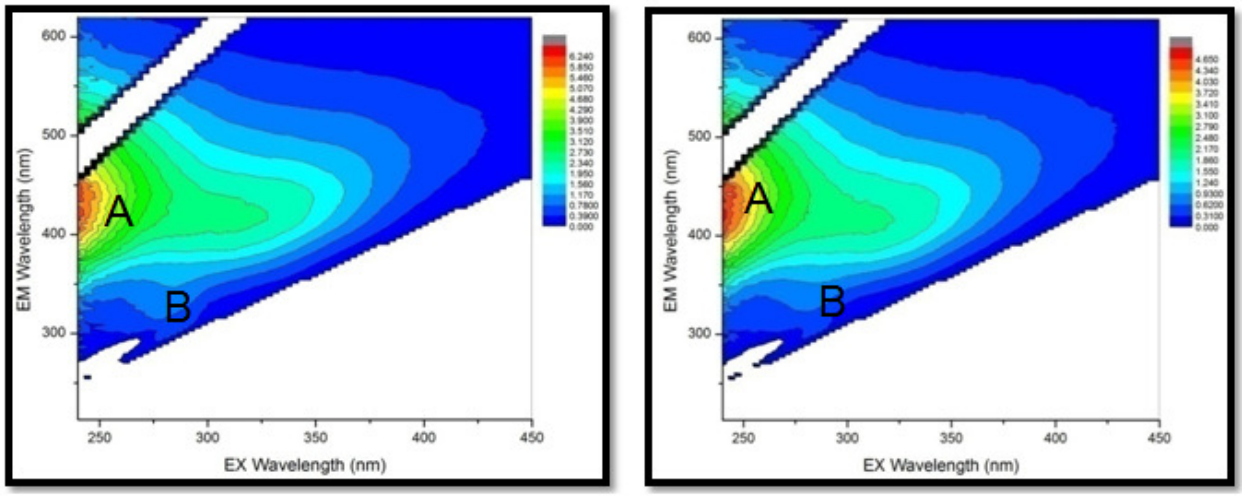


Figure 58: Excitation Emission Matrix (EEM) of pond water samples PW-107 NB (Left , Nabagram) and PW-111 KHN (right, Kandi) showing the presence of a Humic components 'A' and a Bacterial component 'B'.

Most of the EEM maps for the tubewells shows the humic components 'A' and 'C' and the bacterial component 'B' (Fig.59)

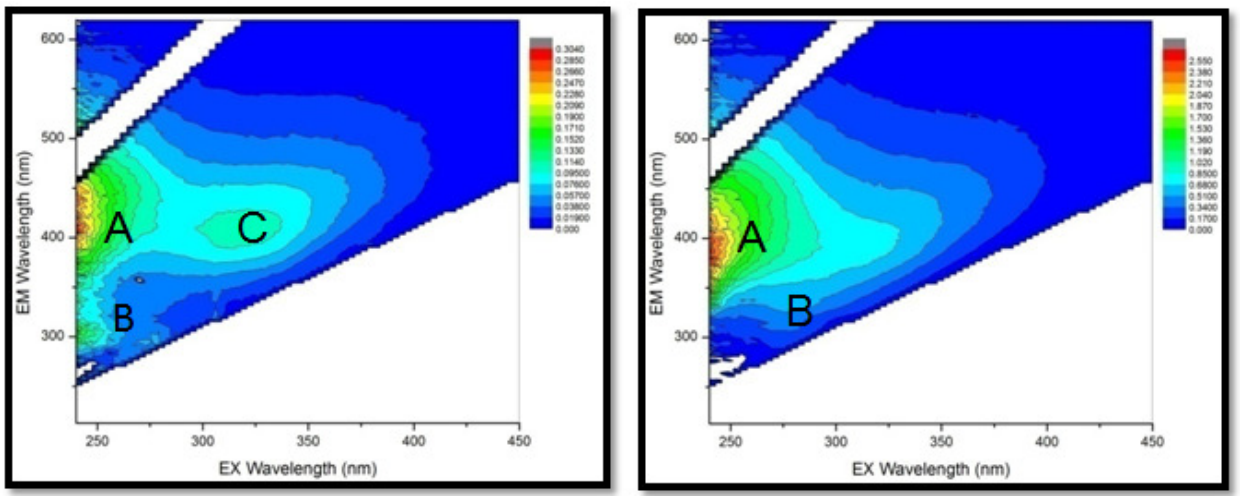


Figure 59: EEM for tubewell water samples TW-114 NB (Left , Nabagram) and TW-135 KHN (right, Kandi) showing the presence of Humic components 'A', 'C' and a Bacterial component 'B'. As and Mn concentration for TW-114 NB is 0.4 µg/L and 2.2 mg/L and TW-135 KHN is 10.2 µg/L and 0.04 mg/L.

The irrigation wells shows very less humic components 'A' and 'C' and high bacterial components, 'B' and 'T' compared to pond waters and shallow depth tube well waters. The DOC

concentration of irrigation wells are also less compared to ponds and tubewells (Fig.63) The DOC in groundwaters concentration decreases with increase in depth (Fig.60).

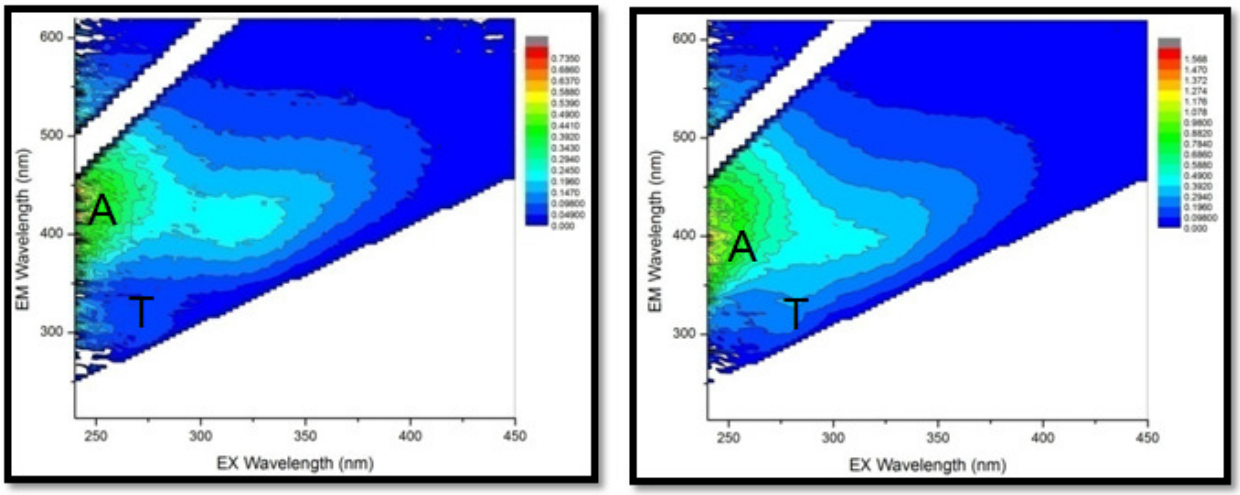


Figure 60: EEM for irrigation well water samples Elahigunj (Left , Nabagram) and IW-107KHN (right, Kandi) showing the presence of a Humic components 'A' and a bacterial component 'T'

There is an overall decrease in DOC concentration with depth. As the depth increases the humic component decreases and bacterial component increases (Fig. 61).

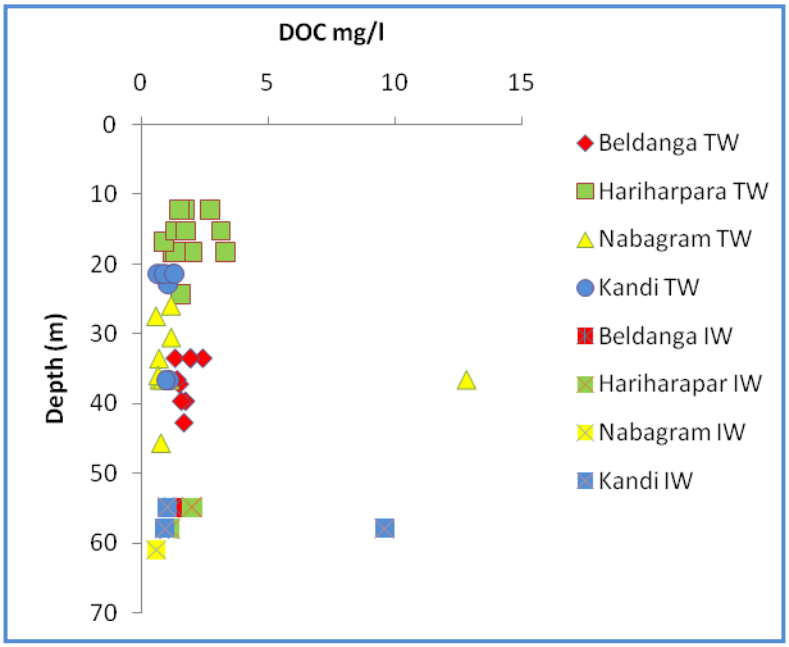


Figure 61: depth distribution of DOC (mg/L) in tubewells (10-40 m & >40m depth, TW); and irrigation wells (10-46 m) for high As (Beldanga; Hariharpara) and low As area (Nabagram; Kandi).

For all water samples (pond waters; tubewells; irrigation wells; river water and rain water) EEM maps and number matrix been generated. The details are represented in the appendix-Q.

Statistical analysis has been carried out to study the relationship of fluorescence data with various fluorescence components, cations and anions. For the classification purpose and better data processing , statistical comparison has been done between total tubewells, total pond waters, total irrigation waters vs. various fluorescence components, cations and anions. Again the tubewells are reclassified to high As tubewells and low As tubewells and did the same comparison with various fluorescence components, cations and anions. The main statistical components measured were the significance level (p value) by paired T test using SPSS® software (free trial version) and r^2 value (MS Windows®-XL plots) to study the statistical correlation. A total of 14 different statistical tables with numerous correlations were generated and among which the best possible relations (statistically significant) are presented in this research work to interpret the data. In order to normalize certain DOC parameters like **B**-Tyrosine- like, Protein like; **T**-Tryptophan-like, Protein like or Phenol Like; **A**- Humic like; **C**-Humic like, SUVA are divided by total DOC values. The concept of normalization calculations were done to reduce the overpowering nature of one of the above mentioned component. Total statistical tables generated and correlation data sets are attached in the appendix-R.

The selected statistical tables showing correlations were explained below. Abbreviations of the tables; **B**- Tyrosine- like, Protein like; **T**-Tryptophan-like, Protein like or Phenol Like; **A**-Humic like; **C**-Humic like; **DOC**- Dissolved organic carbon (mg/l);DON- Dissolved organic Nitrogen (mg/l); **SUVA**-Specific ultraviolet absorbance (L mg^{-1} m^{-1}) ; **As**- Arsenic (µg/l); **Mn**-Manganese (µg/L); **+ & -:** represent whether the relation is positive or negative; P- significance (if p value is >0.02 then there is no statistical significance between the data sets; if it is less than 0.02 then there is statistical significance between the data sets; if P is 0 then there is a very good statistical significance between data sets) ; **R**- correlation coefficient; **FI**- Fluorescence Index; **Fr I**- Freshness Index

	B	T	DOC	B/DOC	T/DOC	As
Fr I	P=0 r^2=0.369+	P=0 r^2=0.375+				
A			P=0.000 0024 r^2=0.4+			P=0.002 r^2=0.3+
C			P=0.000 0000001 r^2=0.3+			P=0.002 r^2=0.322+
DOC						P=0.002 r^2=0.2+
SUVA				P=0 r^2=0.2+	P=0 r^2=0.1+	

Table 12: Correlation matrix among the fluorescence parameters measured for the tubewell (shallow and deep) water samples (high As low As together)

Statistical comparison between the fluorescence components of total tubewell data revels that there is a very good statistical significance between fluorescence index (FI) and Freshness Index (Fr.I) data sets of tube wells with DOC humic component 'C' and both bacterial components' T 'and 'B'. The data sets also shows a small +ve correlation (r^2 value) between these components (FI & FrI vs. C, T& B). Fluorescence index (FI) shows good degree of significances with As data sets however the correlation(r^2=0.02) is very week and is positive. Bacterial components 'B' and 'T' of tubewells are showing good degree of significances with SUVA values (P=0) but their correlation(r^2=0.03 & 0.007) is very week and are positive. Both of the humic components 'A' and 'C' of shallow depth tube wells are showing very good degree of significances with DOC and As data sets of tubewells and shows comparatively good correlation. There is a good degree of significances between DOC and As data sets tubewells but the correlation is very week (r^2=0.2). SUVA data of tubewells are showing good statistical significance and week positive correlation with DOC normalized bacterial components 'B' and 'T (Table-12) .

	A	DOC
FI		
Fr I	P=0.003 r^2=0.656-	P=0.000064 r^2=0.547-
B		P= 0.000027

		r^2=0.594+
T		P= 0.000025 r^2=0.720+
A		P= 0.000022 r^2=0.742+
C		P= 0.00002 r^2=0.778+

Table 13: Correlation matrix among the fluorescence parameters measured for total pond water (high As low As together)

The statistical analysis of fluorescence data sets of pond waters shows there good degree of significance between the data sets of fluorescence index (FI) with bacterial derived proteins 'B' and 'T' (DOC components) however they show only a very weak positive correlation (r^2= 0.15;0.116). Freshness index (Fr.I) showed good degree of significance between one of the humic component of DOC 'A' and total DOC concentration data set. However both the relations negative correlation (r^2=0.656 and 0.547). All components of DOC (both humic and bacterial) 'A'; 'C'; 'T' and 'B' showed good degree of significance and positive correlation with DOC data sets (Table.13)

	B	**T**	**C**	**DOC**	**SUVA**	**B/DOC**	**T/DOC**	**A /DOC**	**C /DOC**
Fr I	P=0.0000009 r^2=0.383+	P=0.000004 r^2=0.203-	P=0.002 r^2=0.317-		P=0.0001 r^2=0.227-				P=0.0002 r^2=0.516-
B				P=0.0005 r^2= 0.489+	P=0.00001 r^2=0.377+				
T				P=0.0005 r^2= 0.664+	P=0.00002 r^2=0.595+				
DOC					P=0.006 r^2=0.719+	P=0.001 r^2=0.373-	P=0.001 r^2=0.324-	P=0.016 r^2=0.412-	P=0.001 r^2=0.41-
SUVA						P= 0.000008 r^2=0.402-	P= 0.000009 r^2=0.226-	P= 0.00002 r^2=0.548-	P= 0.000008 r^2=0.602-

Table 14: Correlation matrix among the fluorescence parameters measured for Total irrigation wells (high As low As together)

Freshness index (Fr.I) had good degree of significance with bacterial component 'B', 'T' and humic component 'C', SUVA and humic component 'C' normalized by dividing it with DOC. But all of them except Fr.I vs. B showed weak positive correlation (r^2=0.383) rest of them had weak negative correlations. The r^2 value for 'C 'normalized by DOC 0.516 and the relation was negative. Bacterial components 'B' and 'T' for irrigation wells showed good degree of significance and positive correlation with DOC and SUVA. The humic components 'A' and 'C' were also showed good significant relation with DOC and SUVA but are having very weak correlation. DOC value showed good significant relation and positive correlation with SUVA (r^2 =0.719). DOC and SUVA showed significant relation of data vs. B/DOC, T/DOC, A/DOC and C/DOC however their correlation were negative. However SUVA showed negative correlation with A/DOC and C/DOC (r^2=0.548 and 0.602) Table-14.

	DOC	**C /DOC**	**As**
FI		P= 0 r^2=0.304+	
Fr I	P= 0 r^2=0.216+	P= 0 r^2=0.213 -	
T	P= 0 r^2=0.368+		
A	P= 0 r^2=0.393+		P= 0.002 r^2=0.369+
C	P= 0 r^2=0.283+		P= 0.002 r^2=0.398+
SUVA		P= 0 r^2=0.244+	

Table 15: Correlation matrix among the fluorescence parameters measured for High As tubewells (Beldanga; Hariharpara)

The fluorescence index (FI) data sets of high As shallow depth tube wells have very good statistical significance with 'A' and 'C' normalized by dividing with DOC data (humic components); P=0 but they had very weak +ve correlation. freshness index data (Fr.I) showed good statistical significance (P=0) with DOC, SUVA, A/DOC and C/DOC and showing n weak negative correlation except with DOC (R^2=0.368). Bacterial component 'T' had good statistical significance (P=0) with DOC and SUVA data but its relation with DOC was positive (R^2=0.368)

and with SUVA relation was weak negative (R^2=0.061). Both humic components 'A' and 'C' data were having good statistical significance and positive correlation with DOC, SUVA and As data. SUVA showed good statistical significance with C/DOC (normalized) data and had a weak +ve correlation Table-15.

	B	**T**	**A**	**DOC**	**B/DOC**	**T/DOC**	**As**
Fr I	P= 0 r^2=0.42+	P= 0 r^2=0.386+	P= 0.001097 r^2=0.276+		P= 0 r^2=0.414+	P= 0 r^2=0.374+	
B				P= 0 r^2=0.311+			
T				P= 0 r^2=0.271+			
A				P= 0 r^2=0.292+			
SUVA							P= 0 r^2=0.37+

Table 16: Correlation matrix among the fluorescence parameters measured for low As tubewell (Nabagram; Kandi)

The freshness index data sets of low As tubewells showed significant relation with bacterial components ('B', 'T'); humic component 'A'; DOC data, B/DOC; T/DOC and As data sets and also indicated average positive correlation. r^2 value for Fr.I vs. DOC is 0.063.

Bacterial components 'B','T' and humic component 'A' showing significant relation with DOC data sets of low As tubewells and they showed average positive correlation. SUVA data is had significant relation with As data of low As tube wells and indicating positive correlation (r^2=0.37) Table-16.

	Ca^{2+} µg/L	Mg^{2+} µg/L	Na^{+} µg/L
FI	P= 0 r^2=0.274+		
Fr I	P= 0 r^2=0.246-	P= 0 r^2=0.391-	P= 0.001 r^2=0.429+
B	P= 0 r^2=0.478-	P= 0 r^2=0.451-	P= 0.001 r^2=0.306+
T	P= 0 r^2=0.497-	P= 0 r^2=0.545-	P= 0.001 r^2=0.336+
A	P= 0 r^2=0.537-	P= 0 r^2=0.549-	P= 0.001 r^2=0.298+
C	P= 0 r^2=0.504-	P= 0 r^2=0.453-	P= 0.001 r^2=0.316+
B/DOC	P=0.001 r^2=0.393-	P=0.001 r^2=0.512-	
T/DOC	P=0.001 r^2=0.435-	P=0.0001 r^2=0.643-	
A/DOC	P=0.001 r^2=0.47-	p=0.0001 r^2=0.616-	
C/DOC	P=0.001 r^2=0.324-	P=0.0001 r^2=0.323-	

Table 17: Correlation matrix among the fluorescence parameters and cations measured for low As Tubewells (Nabagram; Kandi)

The fluorescence index (FI); freshness index; (Fr.I); bacterial components 'B' and 'T'; humic components 'A' and 'C'; B/DOC; T/DOC; A/DOC and C/DOC data sets showed good significant relation with cations Ca^{2+} and Mg^{2+} and indicated negative correlations. Ca, Mg and Na were converted in to µg/L to compared with DOC concentration in µg/ L. For But FI was not having any significant relation with Mg^{2+} and Na^{+} ions. But (Fr.I); bacterial components 'B' and 'T'; humic components 'A' and 'C'; B/DOC and T/DOC data sets showed good statistical significance with Na^{+} and showed a very weak positive correlation, Table-17.

High As tube wells were not showing any good significant relations with cations.

	Ca^{2+} µg/L	Mg^{2+} µg/L	Na^{+} µg/L	K^{+} µg/L
FrI				P= 0.000362 r^2=0.483-
B	P= 0.001382 r^2=0.545+	P= 0.000022 r^2=0.625+	P= 0.000425 r^2=0.265+	P= 0.000362 r^2= 0.468+
T	P= 0.001382 ^{2}=0.379+	P= 0.000022 r^2= 0.511+	P= 0.000425 r^2=0.313+	P= 0.000362 r^2=0.622+
A		P= 0.000022 r^2=0.305+	P= 0.000425 r^2=0.452+	P= 0.000362 r^2=0.754+
C		P= 0.000022 r^2=0.341+	P= 0.000425 r^2=0.387+	P= 0.000362 r^2=0.746+
DOC				P= 0.000781 r^2=0.885+
A /DOC			P= 0.0008 r^2=0.464+	P= 0.001 r^2=0.394+
C /DOC			P= 0.0008 r^2=0.416+	P= 0.001 r^2=0.473+

Table 18: Correlation matrix among the fluorescence parameters and cations measured for total pond water samples

Freshness index (FrI) data showed good statistical significance with K^+ ion data and showed a negative correlation (r^2=0.483) . The bacterial components 'B' and 'T' are showing good statistical significance with Ca^{2+}, Mg^{2+}, Na^+ and K^+ cations and showed comparatively good positive correlation. The humic components 'A' and 'C' showed good statistical significance with Mg^{2+}, Na^+ and K^+ data sets and positive correlation. DOC data showed very good correlation (r^2=0.885) and statistical significance with K^+ data sets. A/DOC and C/DOC data sets had statistical significance with Na^+ and K^+ data sets and are also showed average positive correlation.Table-18.

	Ca^{2+} µg/L	Mg^{2+} µg/L
FI	P= 0 r^2= 0.258+	P= 0 r^2=0.305+
Fr I	P= 0 r^2=0.698-	P= 0 r^2=0.78-
B	P= 0 r^2=0.535-	P= 0 r^2=0.367-
B/DOC	P=0.0004 r^2=0.617-	P=0.0006 r^2=0.514-
T/DOC	P=0.0004 r^2=0.364-	P=0.0006 r^2=0.336-
C/DOC		P=0.0006 r^2=0.407+

Table 19: Correlation matrix among the fluorescence parameters and cations measured for Irrigation wells

Fluorescence index (FI); freshness index (Fr.I), bacterial component 'B'; B/DOC, T/DOC and C/DOC data sets showed good statistical significance with Mg^{2+} data sets. However FI and C/DOC showed positive correlation with Mg^{2+} data sets. Whereas FrI; B; B/DOC and T/DOC showed negative correlation. Fluorescence index (FI); freshness index (FrI), bacterial component 'B'; B/DOC and T/DOC had good statistical significance with Ca^{2+} datasets. FrI; B; B/DOC and T/DOC showed strong negative correlation with Ca^{2+}ion. But FI showed weak positive correlation with Ca^{2+}ion (Table.19)

	Cl µg/L	PO_4 µg/L	SO_4 µg/L
FrI	P= 0 r^2=0.704+	P= 0.001 r^2= 0.463+	P= 0.001 r^2=0.503-
B	P= 0 r^2=0.657+		P= 0.001 r^2=0.461-
T	P= 0 r^2=0.712+		P= 0.001 r^2=0.483-
A	P= 0 r^2=0.634+		P= 0.001 r^2=0.425-
C	P= 0 r^2=0.383+		P= 0.001 r^2=0.455-

Table 20: Correlation matrix among the fluorescence parameters and anions measured for low As tubewell waters

Freshness index (Fr.I); bacterial components 'B' and 'T'; humic components 'A' and 'C' datasets of low As tubewells were having very significant relation (P=0) with Cl^- and SO_4^{2-} anions. But the correlation of these fluorescence components showed strong positive for Cl^- and average negative for SO_4^{2-}. Freshness index (Fr I) data showed good statistical significance and good positive correlation with PO_4^{3-}(r^2=0.463) (Table-20).

	PO_4^{3-} µg/l
B	P= 0 R^2= 0.843+
T	P= 0 R^2= 0.795+
A	P= 0 R^2= 0.458+
C	P= 0 R^2= 0.586+
DOC	P= 0 R^2= 0.575+

Table 21: Correlation matrix among the fluorescence parameters and anions measured for ponds waters

Statistical correlation table for pond water showed a good significant relation (P=0) between bacterial component 'B' and 'T'; humic component 'A' and 'C' and DOC data sets of pond waters with PO_4^{3-} and were having positive correlation. Rest of the anions were not having any relationship with fluorescence data. (Table-21)

	Br^- µg/L	**PO_4^{3-}µg/L**
FI	P= 0.001 r^2=0.32-	
SUVA		P= 0.006 r^2= 0.482+

Table 22: Correlation matrix among the fluorescence parameters and anions measured for irrigation wells

Statistical correlation of fluorescence index and SUVA data of irrigation wells showed statistical significance with Br^- and PO_4^{3-} data sets. However FI showed a low negative correlation with Br^- and SUVA showed moderate positive correlation with PO_4^{3-} data. (Table-22).

A standard mean , median and standard deviation data table for the fluorescence data sets were created for each high As tubewells, Low As tubewells, ponds and irrigation wells to study the overall nature of each fluorescence parameters present in the waters samples of tubewells (high and low As areas), ponds and irrigation wells (Table.23).

	FI	**Fr.I**	**B**	**T**	**A**	**C**	**DOC µg/L**	**DON µg/L**
High As Tube wells	M=1.73 MD=1.75 SD=0.062 N=17	M=0.77 MD=0.76 SD=0.065 N=17	M=0.13 MD=0.11 SD=0.05 N=17	M=0.18 MD=0.15 SD=0.06 N=17	M=1.01 MD=0.83 SD=0.46 N=17	M=0.50 MD=0.45 SD=0.21 N=17	M=1808.89 MD=1546 SD=604.38 N=17	M=1095..51 MD=941 SD=1302.33 N=17
Low As Tube wells	M=1.73 MD=1.74 SD=0.096 N=11	M=0.96 MD=0.99 SD=0.14 N=11	M=0.18 MD=0.11 SD=0.12 N=11	M=0.26 MD=0.16 SD=0.21 N=11	M=0.67 MD=0.50 SD=0.51 N=11	M=0.30 MD=0.25 SD=0.24 N=11	M=989.43 M=1045 SD=233.69 N=11	M=415.31 MD=98.22 SD=802.22 N=11
Ponds	M=1.61 MD=1.61 SD=0.05 N=8	M=0.79 MD=0.77 SD=0.06 N=8	M=0.51 MD=0.42 SD=0.27 N=8	M=0.82 MD=0.77 SD=0.41 N=8	M=2.97 MD=3.003 SD=1.42 N=8	M=1.37 MD=1.3 SD=0.72 N=8	M=8741 MD=8742.5 SD=3333 N=8	M=1767.61 MD=1893 SD=689.68 N=8
Irrigation wells	M=1.69 MD=1.7 SD=0.07 N=7	M=0.85 MD=0.79 SD=0.15 N=7	M=0.14 MD=0.13 SD=0.05 N=7	M=0.20 MD=0.21 SD=0.05 N=7	M=0.81 MD=0.93 SD=0.36 N=7	M=0.36 MD=0.43 SD=0.17 N=7	M=1330.4 MD=1120 SD=464.51 N=7	M=706.7 MD=318.2 SD=716.16 N=7

Table 23: Mean, median and standard deviation of the DOC fluorescence parameter data for Murshidabad waters, 2012

Over all Fluorescence index (FI) of the high and low As tubewells were 1.73 and that for ponds and irrigation wells were 1.61 and 1.69 respectively. The freshness index (Fr.I) for the high As tube wells were low compared to low As tubewells, ponds and irrigation wells. For high As tube wells the freshness index was 0.77 and for low As tubewells, ponds and irrigation wells the freshness index (Fr.I) were 0.96; 0.79 and 0.85 respectively. The DOC concentration was low in low As tubewells 989.43 and it is high for high As tubewells and pond waters and the values were 1808.89 µg/L and 8741µg/L. For irrigation wells the average DOC concentration was 1330.4 µg/L.(Table-23)

Freshness index (Fr.I) for high and low As tubewells, ponds and irrigation wells were plotted against the Cl/Br molar ratio to study the anthropogenic influence.

For better understanding of the variation of 3 data series plots were prepared separately for each area. Tubewells in Beldanga (high As area) the Cl/Br molar ratio and freshness index were following same trend and As was following different trend except for two tubewells (25% o total tubewells in Beldanga TW-102BM, TW-103BM). For rest of the tubewells in this area, where there was high Cl/Br ratio , then the As concentration was low and the freshness index was high and vice versa (Fig.62).

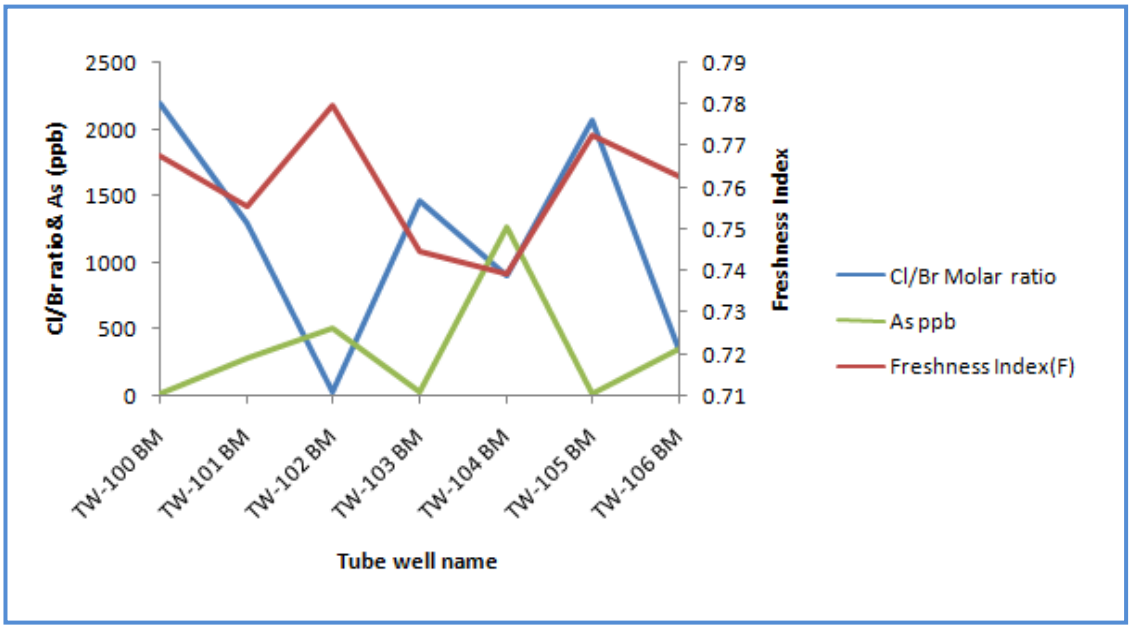


Figure 62: Cl/Br ratio and As (mg/L) vs. Freshness Index plot for tubewells in Beldanga (high As area)

For tubewells in Hariharpara (high As area) the freshness index was following same trend as that of Cl/Br ratio curve except for one tubewell (8.3% of total tubewells in Hariharpara, TW-126 HK). The As concentration showed opposite trend as the freshness index and Cl/Br ratio curve (Fig.63).

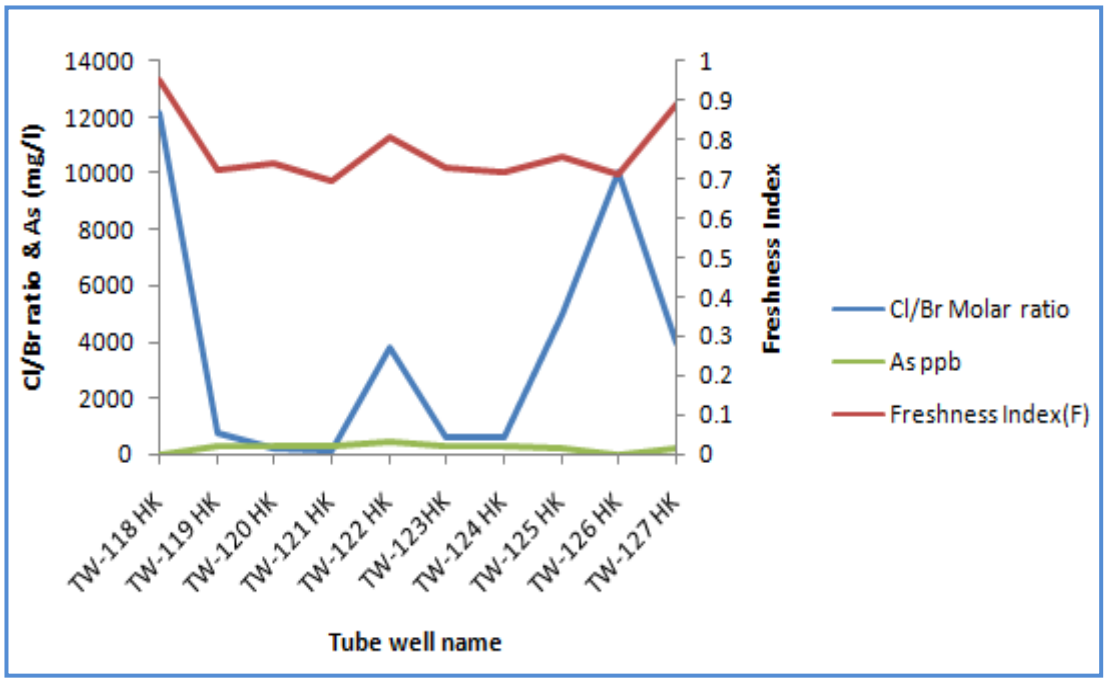


Figure 63: Cl/Br ratio and As (mg/L) vs. Freshness Index plot for tubewells in Hariharpara (high As area)

Tubewells in Nabagram (low As area), the As concentration is very low. But the freshness index and Cl/Br ratios are showing exactly opposite trends. But overall the freshness index was high compared to the high As tubewells. The data sets showed that the Cl/Br ratios and As concentrations were inversely correlated. As concentration curve in this plot showed no trend (flat) because the As concentration in these areas were very low.(Fig.64)

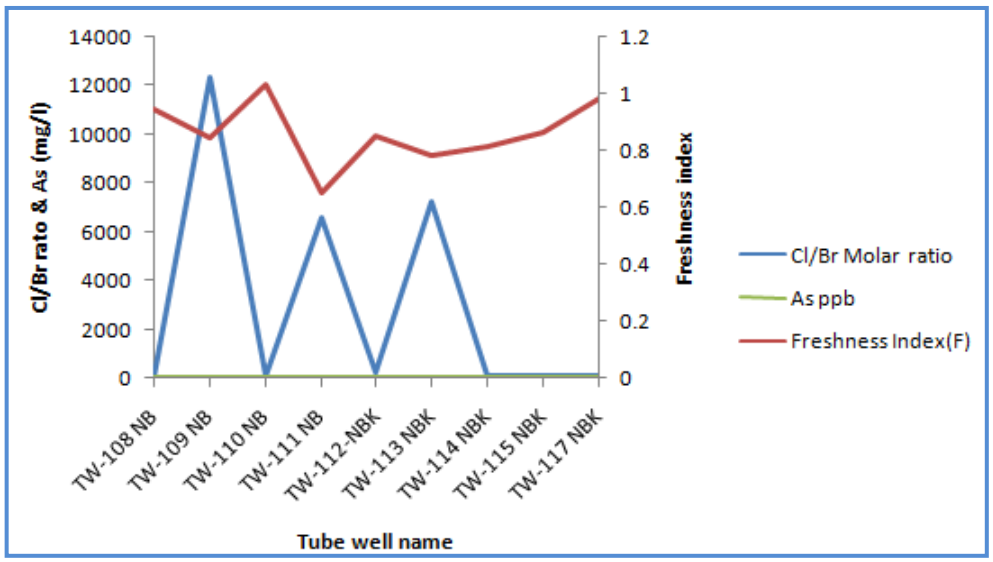


Figure 64: Cl/Br ratio and As (mg/L) vs. Freshness Index plot for tubewells in Nabagram (low As area)

Tubewells in Kandi area (low As area) the Cl/Br ratio and freshness index area showed opposite trends as similar to the Nabagram area (low As area) except for one tubewell (14.3% of total tubewells in Kandi, TW-131 KHN). For all tubewells with high Cl/Br ratio showed low As concentration (Fig.65).

Over all the tubewells in low As areas (Nabagram; Kandi) were having high freshness index, low As concentration compared to tubewells in high As areas (Beldanga; Hariharpara). The Cl/Br molar ratio showed inverse relation with As concentration in the low As areas.

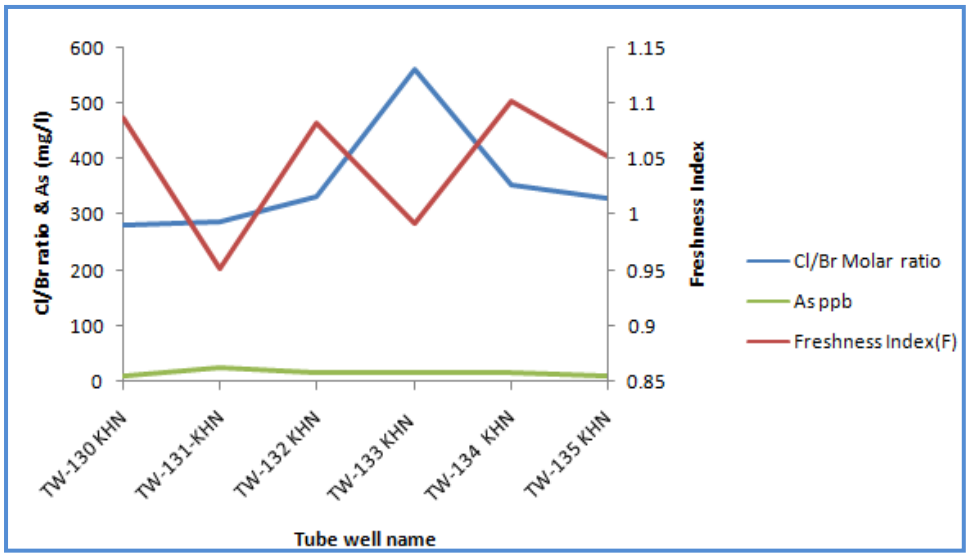


Figure 65: Cl/Br ratio and As (mg/L) vs. Freshness Index plot for shallow depth tube wells in Kandi (low As area)

Pond waters in high As areas (Beldanga, Hariharpara) and low As areas (Nabagram; Kandi) were plotted together because of the small number of data points. The Cl/Br ratio and freshness index were not compared with As concentration because there was not much As concentration data is available for pond waters. The Cl/Br molar ratio vs. freshness index plot for pond waters (Fig.66) showedthat the freshness index of low As area pond were low (Nabagram; Kandi) compared to the freshness index of high As area ponds (Beldanga; Hariharpara). While Cl/ Br molar ratio for Kandi area was very less compared to the Cl/Br molar ratios of most of the pond waters in high As areas (Beldanga, Hariharpara). The pond water in Nabagram (one pond water) had high Cl/ Br molar ratio.

Irrigation wells in high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi) were also plotted together because of the lesser number of data points. The data sets were also not compared with As data because not much As concentration data was available for irrigation waters. The Cl/Br molar ratio vs. freshness index plot showed that in Kandi (low As area) irrigation wells had low Cl/Br molar ratio and high freshness index compared to high As irrigation wells. Irrigation well in Nabagram (50% of total irrigation well in Nabagram, one data point) showed low freshness index and high Cl/Br molar ratio (Fig.67)

The maximum Cl/ Br molar ratio were observed in tubewells in high As areas and low Cl/Br molar ratio were observed in the irrigation wells

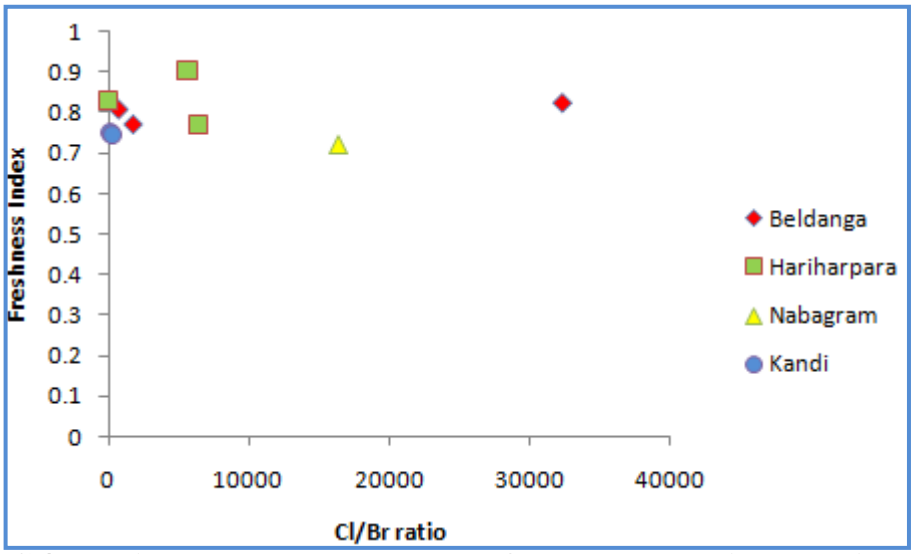


Figure 66: Cl/Br ratio vs. Freshness Index plot for pond waters in Murshidabad area for the year (2012)

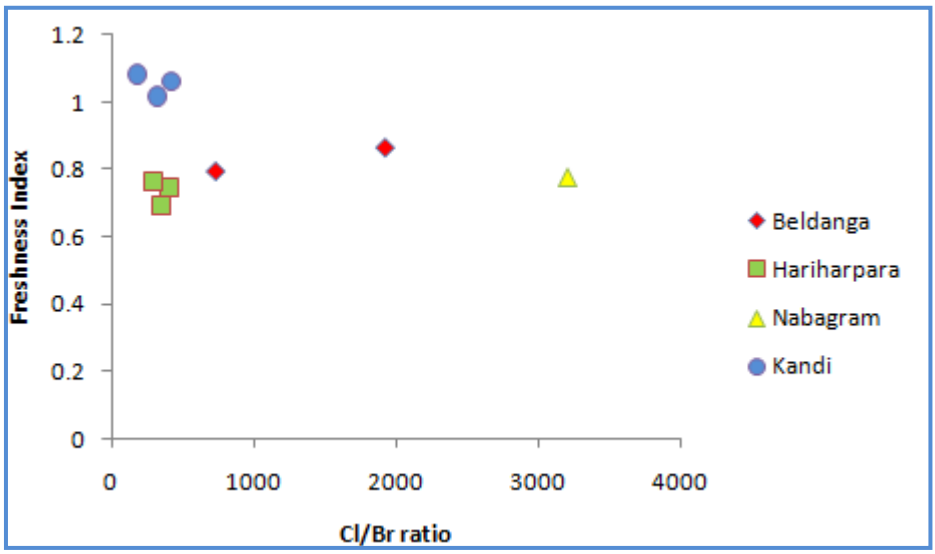


Figure 67: Cl/Br ratio vs. Freshness Index plot for irrigation well waters in Murshidabad area for the year (2012)

Over all statistical evaluation of fluorescence parameters did not reveal much information in this research work. However some of the tables were included in the text have got some information regarding the fluorescence parameters. All statistical tables were included in the appendix-R.

Chapter 6 - Discussions

Sediments

Sedimentary facies and major physical characters

Murshidabad area (south central portion of Bengal Basin) was comprised of sediments deposited by major Himalayan river systems like Ganges- Brahmaputra-Meghna where river Bhagirathi is a major tributary system in this area. The sediment core log analysis revealed that, a generalized fining upward sequence (fining of grain size towards top) of sediments. Fining upward sequence is a classic example of meandering river channel facies. Organic rich clay/fine sand beds without mud cracks also indicate presence of abandoned oxbow lake facies. Both meandering rivers and oxbow lake deposits are the major sedimentary facies that exist in this area.

Color of sediments is a major distinguishing physical property that separate sediments of high As areas (Beldanga and Hariharpara) from low As areas (Nabagram and Kandi). West of the Bhagirathi river is occupied by Pleistocene sediments where the concentration of dissolved As in ground water is less or absent (Nabagram and Kandi) and the orange -red brown sediments are oxidized. Whereas to the east of the river Bhagirathi is occupied by Holocene sediments and the concentration of dissolved As in groundwater is high and considerably greyish to dark grey sediments occur throughout the entire depth of 130ft. Color of the fine grained sediments are defined by the two main parameters and they are ratio of Fe^{3+} to Fe^{2+} and the percentage of organic carbon in the sediments (Wilde and Quinby-Hunt, 2010). The color of the sediments changes from greyish to reddish as the Fe^{2+} progressively oxidized to Fe^{3+} and increasing amount of organic content in the sediments darken the fine sediments from gray color to black (Wilde and Quinby-Hunt, 2010). Visual estimates revealed that most of the fine grained sediments were enriched in organic matter as compared to coarse grained sediments.

SEM analysis revealed that majority of sediments constitute clayey minerals with quartz grains spread throughout. The SEM analyses revealed that As is present quite sporadically within sediments and is not uniform. As per the SEM results the overall concentrations of As (wt%) within sediments is more in Nabagram (low As concentration in groundwater) compared to Beldanga (high As concentration in groundwater). The SEM-EDX analyses showed that the elements Fe and Mn are in close association in most cases. The SEM mapping by superposing

total Fe over Mn also indicates coexistence. The single elemental map of As also showed that As was distributed throughout the sediments even if it was very minute in concentration.

Total Digestion of Aquifer Sediment Cores

Total digestion of aquifer sediments by microwave digestion revealed that the concentration of As was almost equal in quantity both in high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi). The concentrations of As in sediments changed with depth and lithology of the sediments. Overall analyses revealed that As concentration was more in clay-rich sediments than in the sandy sediments. Fine grained sediments constitutes greater volume per unit area than the coarse grained sediments. Arsenic being associated with sediments, its concentration in unit area in fine grained sediments would be more compared to that of coarse grained sediments in both high As (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi). Fe and Mn concentrations within sediments also changed in the same fashion as that of As. However in Beldanga, dark-grey medium grained sandy sections at 27-34m depth, the concentration of Mn and Fe were higher compared to the clay beds above. This could be due to the high proportion of clay and organic matter in the sediments and As could be associated with those fractions (Sharma et al., 2011). The total digestion results thus indicated that mineralogically similar fractions of the sediments house the As, but favorable subsurface redox conditions only favor the release of As from the high As areas. In all areas (both high and low As) wherever there was a change in concentration of As, Mn and Fe(t) concentration will also change. As and Fe(t) and Fe(t) and Mn are positively correlated both in high As and low As sediments. This could be due to the adsorption of As within Fe and Mn oxyhydroxides (Rüde et al., 1997; Harvey et al., 2002; Sahai et al., 2007; Gasparatos, 2013). During sediment- water interaction, the microbial mediated reductive dissolution of FeOOH(s) mechanism caused the sediment (<50m depth) bound arsenic to release into groundwater in the Bengal Basin (McArthur et al., 2001 & 2004; Dowling et al., 2002).

Sequential extractions of Aquifer sediments

Sequential extraction results indicated the amount of As in various sediment fractions of the aquifer sediments in Murshidabad area. Sequential extraction experiments were performed on sediment cores from all the high (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi). In both high and low As areas the concentration of As in nonspecifically sorbed phases were mostly absent for all depths, except shallow depths (0-12m) and intermediate depths (37m) of

Hariharpara only. The concentration of As in the easily exchangeable phase at these depths in Hariharpara were very less (<3%) and could very easily get dissolved into the circulating groundwater. Whereas in other areas Beldanga (high); Nabagram and Kandi (low) As concentration in the easily exchangeable phase was undetectable.

In these areas at almost all depths the As concentration was present in specifically sorbed phases (Beldanga10-30%; Hariharpara 25-40% ; Nabagram 5-30%; Kandi 20-35%). Some of the minerals colud be goethite (Keon et al., 2001). As adsorbed in this phase can interact with percolating groundwater by the competitive ion exchange with PO_4^{3-} and enter into the groundwater system as dissolved As (Acharyya et al., 1999; Welch et al., 2000; Sharma and Kappler, 2011).

Bulk of the As, Mn and Fe in Beldanga and Hariharpara (high As areas) are present in the following order, residual phases; amorphous and poorly crystalline hydrous oxides of Fe and Al and then in the well crystalline hydrous oxides of Fe and Al phases. The sediments in high As areas are greyish (black) in color and are highly reducing in nature, evident by high concentration NH_4^+ions and Fe^{2+} within the sediments extracts (Anawar et al., 2003; Hagiwaraa et al., 2011). The existing reducing conditions can facilitates breakdown of Fe and Mn oxyhydroxides and can release the structurally bound As into the groundwaters in the presence of Fe(III) reducing bacteria (Cummings et al., 1999; van Geen et al., 2004).

In Beldanga a considerable amount of Mn was present in the easily exchangeable phases at all depths. The Mn bound to the easily exchange phase can interact with circulating groundwater and get into a dissolved phase.

In Nabagram bulk of As is present in residual phases (40-60%). The rest of As concentration is present in amorphous and poorly crystalline hydrous oxides of Fe and Al and well crystalline hydrous oxides of Fe and Al phases and overall there is an increase of As concentration with depth in these fractions. Whereas Mn in Nabagram is mostly present in the easily exchangeable phase (10-50%) at all depths and that can easily go in to solution by reacting with percolating groundwater. This was evident by the presence of high concentration of dissolved Mn in groundwaters of Nabagram. Rest of the Mn is distributed in all other phases at all depths at various concentrations along with As and Fe. The sediments in the shallow depths were oxidizing in nature but with depth the reducing conditions persists and cause the release of adsorbed As from the breakdown of Fe and Mn oxyhydroxides (Cummings et al., 1999; van

Geen et al., 2004; Akai et al., 2004). In Nabagram most of the Fe(t) is present in residual phases (40-60%) rest of the Fe (apart from residual phases) were present in well crystalline hydrous oxides of Fe and Al phases (40-60%) and amorphous and poorly crystalline hydrous oxides of Fe and Al phases (5-10%). Lesser concentration (<2%) of Fe was present in specifically sorbed phases in the intermediate and deeper depths.

In Kandi bulk of As attached to the well crystalline hydrous oxides of Fe and Al phases, Fe and Mn concentrations were also present in this phase throughout all the depths. Bulk of Mn was attached to amorphous and poorly crystalline hydrous oxides of Fe and Al phase along with minor amount of As and Fe. Bulk of the Fe was present in the residual phases along with considerable amount of As (5-40%) and Mn (30-40%). Shallow depths sediments were oxidized in Kandi and was represented by the reddish color however the deeper sediments were reducing in nature and can cause the release of As into ground water by the dissociation of Fe and Mn oxyhydroxides. High concentration of As, Mn and Fe in residual phases in all areas could be due to the release of organic matter bound As, Mn and Fe while digesting with H_2O_2. So part of the As Mn and Fe concentration in residual phases could be from OM (organic matter) also.

As per sequential extraction results it was quite evident that the main As releasing mechanism persisting in this area are 1. Competitive ion exchange process by which As in the specifically sorbed phases are replaced by PO_4^{3-}(phosphate) present in the circulating groundwater(Acharyya et al., 1999; McArthur et al., 2001). 2. Dissolution of Fe and Mn oxyhydroxides and thus releasing their adsorbed As onto the groundwater due to high reducing conditions present in the subsurface, this process can be enhanced by the presence of iron reducing bacteria (Cummings et al., 1999; Dowling et al., 2002; McArthur et al., 2001 & 2004; van Geen et al., 2004; Akai et al., 2004). In Beldanga As concentration in specifically sorbed phases were more and which was evident by higher concentration of dissolved As in groundwater at these depths. So both of these processes could act together and thus causing high concentration of dissolved As in these areas.

Organic matter Extraction results of Aquifer Sediments

Organic matter (OM) extractions revealed that there is a close association of As and organic matter in sediments. The OM digestion was carried out to find the amount of As attached with organic matter in aquifer sediments. The concept behind this extraction was, that while digesting the sediment bound OM (at various depths), the As, Mn and Fe attached to the OM

would come in solution along with OM. By measuring the concentration of As, Mn, Fe and DOM in the extractant would give an idea about the relationship of OM bound metals at various depths in Murshidabad sediments. To reconfirm the amount of OM, total amount of OM at each depth (in sediments) were also measured. Depth wise digestion of Murshidabad sediments revealed that As concentration totally depend upon the concentration of organic matter. While the Mn and Fe(t) did not follow always the same trend as As except at Beldanga (high As area).

In Beldanga the concentration of As, Mn and Fe(t) were dependent on with organic matter. In Beldanga the highest concentration of As, Mn, Fe and OM (both extractable and total) were present at 15-20 m depth and the concentrations are 0.18 mg/kg; 15.2 mg/kg; 604.6 mg/kg and 171.4 mg/kg (extractable) and 4.34% (total). Loss on ignition test also conforms highest concentration of organic matter at 15m depth in Beldanga (20%). Then the concentration of all the above said elements and OM remains almost same after 30m.

In Hariharpara As concentration is almost same (~0.07 mg/kg) from the surface till 20m depth and then the concentration of As decreases to undetectable levels at 30 m depth and then increases towards deeper levels (0.06 mg/kg). The OM concentration (both extractable and total) in Hariharpara follows the same trend as that of As. But the Mn and Fe are following diametrically opposite trend as that of As and OM. The total OM present in high As areas (Beldanga; Hariharpara) are high compared to the low As areas (Nabagram; Kandi).

In Nabagram (low As area) the total OM was very less (0.2-0.3 %) compared to all other areas . The OM bound As and Mn could be very less here. This could be the reason why the concentration of trace metals (As and Mn) are undetectable at all depths. Fe(t)was only detectable during the OM extraction because Fe(t) being the major element in sediments. The Fe(t) trend varies according the OM (total and dissolved).

In Kandi (low As area) both As and OM (extractable and total) show similar kind of trends. At the shallow depths the As concentration is undetectable and the OM concentration was about 119 mg/kg. Then the concentration of OM and As gradually increased towards the bottom to a maximum of 122.4 mg/kg and 0.19 mg/kg respectively at 31m depth. But Mn and Fe concentration is maximum (9 mg/kg and 30 mg/kg) at 30m depths.

The organic matter rich sediments sequester more metallic ions like As, Mn and Fe compared to the sediments with less organic matter (Hettiarachchi et al., 2003). Bengal Basin sediments were mostly enriched in organic matter (McArthur et al., 2004). As per the present

study the high As areas (Beldanga; Hariharpara) got high organic matter concentration than that of the low As areas (Nabagram; Kandi). In Bengal Basin sediments most of the As and Mn were attached to the FeOOH phase as grain coatings and a part of the As, Mn and Fe (minor concentration) could be attached to the solid organic matter present in the sediments. Up on digestion, these elements (minor concentration) could have come in to the solution. McArthur et al., 2004 reveled the existence of small peat layers in the adjoining areas of Murshidabad (Barasat, Barasat-1 and north 24-paraganas). Similarly this study also revealed the existence of organic rich layers in Murshidabad sediments. Studies by Qian et al., 1999 ; Morel and Price, 2003; Lloyd and Oremland, 2006; had shown that phytoplankton can uptake trace metals. The paleo environment of Murshidabad sediment being meandering river and oxbow lake facies the phytoplankton and algal species existed at that time could have absorbed much dissolved As in their cell structure. The organic matter rich layers with some trace metal concentration could represent the disintegrated phytoplankton and algal species once existed. So the trace metal concentration derived from OM digestion could be the trace metals absorbed by the past phytoplankton and algal species present in this area. This might be an idea to explore further.

For the current research work the maximum depth of sediments collected was 45m by drilling from all the 4 areas. LOT test and OM extraction results revealed that, there was an overall decrease in concentration of OM with depth (0-45m). However the OM data beyond 45m is not available to commend more about the OM concentration of deeper sediments.

Synchrotron beam line study of Aquifer Sediments (XANES and EXAFS)

Three separate beam lines were used to study various As (X27A and X11A) and sulfate (X15B) species in aquifer sediments in high As areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi). XANES results from X27A revealed that the majority of As species present in Beldanga sediments were As^{5+} represented by XANES peak value11874eV (Polizzotto et al., 2006). Whereas bulk XANES results showed coexistence of both As^{3+} and As^{5+} by showing a broad peak covering 11871eV for As^{3+} and 11874for As^{5+} (Polizzotto et al., 2006). The samples used in this beam line were not that much exposed to atmosphere (wet samples and not dried) but flushed with N_2 gas. The correlation plots for the high energy spots obtained by X ray mapping was carried out on this sample by X27A beam line revealed that there is a good correlation of As and Mn with Fe in sediments. This again confirmed the coexistence of As, Mn and Fe. As and Mn are adsorbed on FeOOH grain coatings in the aquifer

sediments of Murshidabad (McArthur et al., 2001 & 2004; Dowling et al., 2002; Smedley& Kinniburgh, 2002; Datta et al., 2012). The presence of As^{3+} in sediments indicate reducing environment. The dissociation of Fe^{3+} oxyhydroxides (FeOOH) reduction by anaerobic bacteria in the presence of organic matter can cause the reduction of FeOOH bound As^{5+} to As^{3+}, which is more mobile and get in to the circulating groundwater system and thus causing arsenic toxicity (Nickson et al., 2000; Smedley and Kinniburgh 2002; Goldberg, 2002; van Geen et al., 2004; McArthur et al., 2004; Lloyd and Oremland, 2006).

The sulfur speciation was carried out in X15B beam line and sediments in low As areas (Nabagram and Kandi) of Murshidabad basin showed that the major sulfur species present in the sediments were sulfate (SO_4^{2-}) represented by the peak value 2482 eV (Prietzel et al., 2006). There could be due to the sediments in the low As areas (Nabagram and Kandi) being more oxidized in nature, majority of sulfur species present in the low As areas could be sulfate.

Summary of Aquifer Sediment Chemistry

The fining upwards sediments present in high As areas (Beldanga; Hariharpara) and in the low As areas (Nabagram; Kandi) of Murshidabad district (part of Bengal Basin) represent meandering and oxbow lake depositional environments. The sediments are rich in organic matter (OM). The organic matter content is low in low As areas (Nabagram and Kandi) compared to the high As areas (Beldanga and Hariharpara). Sediments in high As areas (Beldanga and Hariharpara) were reducing in nature and which is evident by the coexistence of As^{3+} and As^{5+} species in sediments (XANES). Whereas the sediments in low As areas (Nabagram and Kandi) are oxidized in nature evident by the presence of Sulfate (SO_4^{2-}) being the major sulfur species in the low As sediments (XANES). As and Mn are present in almost equal quantities in both high As areas and low As area sediments. But the presence of high organic matter content and reducing environment were ideal condition for the dissociation by reduction of Fe^{3+} oxyhydroxides (FeOOH) by anaerobic Fe reducing bacteria in presence of organic matter in sediments of high As areas. Thus releasing the FeOOH bound As^{5+} into the water as As^{3+} and it is more mobile and forms water soluble complexes with dissolved organic matter present in the circulating groundwater. Organic matter in sediments are energy source (electrons) for bacteria (McArthur et al., 2004; Lloyd and Oremland, 2006). So sediments do not have much control in the dissolved As concentration in groundwater instead it is the process which control the

dissolved As concentration. Another mechanism which release As in to the groundwater is by competitive ion exchange between PO_4^{3-} derived from sediment bound organic matter and As adsorbed in the various mineral phases like FeOOH (in grain coatings). Microwave extractable (total digestion) As and Mn in both areas were correlating with Fe(t) indicating close association of As, Mn and Fe. Good correlation of As and Mn with Fe of high energy spots (XRF maps) also indicate close association of As, Mn and Fe.

Water

Studies show that commercially available As field test kits are a reliable means to measure As concentrations in water (Rahman et al., 2002 ; vanGeen et al., 2005; Steinmaus et al., 2006; Mukherjee et al., 2005; Spear et al., 2006). As per the studies of vanGeen et al., 2005 stated that 88% of the 799 tubewells measured for As using commercially available field test kits were right and inconsistencies arise while measuring the As range of 50-100 µg/L in Bangladesh part of Bengal Basin. This problem can be avoided by increasing the reaction time of the test from 20 minutes to 40 minutes (vanGeen et al., 2005). Rahman et al., 2002 stated that As test kits are very reliable for measuring the high range As concentrations i.e. >50 µg/L. Hence in this research we mostly used test kit values for As wherever applicable.

In this work the author has purposefully defined the depths of the tubewells as follows

a. Shallow depth tubewell -10-40m

b. Deep depth tubewell->40m

c. Irrigation wells 10-46m

d. Ponds (surface)

This classification was maintained throughout this work and interpretation. Both shallow and deep depth tubewells were considered together as the number of deeper tubewells were very few. Irrigations wells were shallow and deep both but the position of the irrigation wells were far away from the contamination sources like villages, ponds and pit latrines. Irrigation wells in this area draw out huge amount of groundwater from aquifers at various depths. The shallow and deep tubewells are usually used for drinking water purpose this was another reason to combine them together.

General groundwater quality and ionic constituents

There is a considerable difference in groundwater quality parameters in high areas (Beldanga; Hariharpara) and low As areas (Nabagram; Kandi). Salinity is very high in high As areas (7.21-12.02 ppt.) compared to low As areas and were (5.91-0.47ppt). High salinity in high As areas (Beldanga; Hariharpara) could be due to the high groundwater exploitation in these areas (Lamban and Aragon, 2004). Total dissolved solid (TDS) concentration is high in low As areas could be due to the presence of high concentration of Cl^- present in this area. Conductivity values varies from tubewell to tube well in high As and low As areas and are 2.6-155.5 µS/cm in Beldanga; 12.68-990 µS/cm in Hariharpara; 7.21-950 µS/cm in Nabagram and 912-988 µS/cm in Kandi. This could be due to the varying degree of flushing at various tube wells. pH of the Murshidabad groundwater ranges from 6.59-8.27 and this could be due to the presence of various mild organic acids derived from the disintegration of organic matter in sediments near each of those tubewells sampled.

Cl^- content was found to be very high in low As areas (Nabagram; Kandi, 38-103mg/L; 122-200mg/L) compared to the high As areas (Beldanga; Hariharpara; 5.7-12mg/L; 2.4-83mg/L). The presence of high chloride could be due to high evaporation rate or by anthropogenic inputs (McArthur et al., 2012, Xie et al., 2012). Chloride can either percolate from surface water sources or from pit latrines and both are very common in these areas (Neumann et al., 2010; McArthur et al., 2012). The surface water (ponds) in these regions are highly contaminated due various anthropogenic inputs and Cl^- concentration in ponds were very high (24.5-306 mg/L)

Nitrate concentrations in groundwaters from the high As areas of Beldanga and Hariharpara are typically lower than those measured in groundwaters from the low As regions of Nabagram and Kandi. For example, NO_3^- only attains concentrations up to 4.4 mg/L in groundwaters from these high As areas, but reaches 14 mg/L at Nabagram. These differences could reflect generally more reducing conditions that characterize the high As Holocene aquifers (Datta et al., 2011; Neal et al., 2011; Sankar et al., 2012). High concentration of nitrate in low As areas can suppress As reduction. When the nitrate concentration is high then microbes would not utilize oxidized species of Fe/Mn and As as electron acceptors (Yuan and Ponnamperuma, 1966; Oremland and Stolz, 2003)

Phosphate concentrations of groundwaters from the high As (i.e., Beldanga, Hariharpara) and low As sites showed similar ranges (0.4 –2.2 mg/L). Since the Bengal Basin is part of the

highly cultivated Indo-Gangetic alluvial plains, PO_4^{3-} in local groundwaters could be due to extensive use of phosphate fertilizers. For example, the presence of dissolved PO_4^{3-} in groundwater can cause replacement of As sorbed onto FeOOH (Acharya et al., 2000). Alternatively, sorbed PO_4^{3-} could be released during disintegration of organic rich peat layers (McArthur et al., 2001). The second hypothesis is relevant to the present study because during our field work, shallow drilling operations were conducted to recover aquifer sediments. The sediment analysis revealed the presence of several layers of organic rich clays and sands. Hence, oxidation of this organic matter contained within the clay and sand layers could contribute phosphate to the groundwaters in this region. Phosphate was present in all ponds waters (1.5-5 mg/L)

The concentration of NH_4^+ is similar in all surveyed wells (high and low As areas) in Murshidabad. The ranges are, 0-0.02 mg/L (Beldanga), 0-0.01mg/L (Hariharpara), 0.01-0.04 mg/L (Nabagram) and 0-0.06 mg/L (Kandi). High NH_4^+ indicates microbial activity (Dowling et al., 2002), however it was difficult to predict such high microbial activity or extent of microbial activity just from NH_4^+ data.

Sulfate (SO_4^{2-})in groundwater is variable in all areas (both high and low As) and maximum sulfate SO_4^{2-} was observed in Nabagram (low As). The ranges in the low As areas were 14.6-56mg/L in Nabagram; 0.1-1.5mg/L in Kandi, and the ranges in high As areas were 0.06-1.5 mg/L in Beldanga and 0.1-71mg/L in Hariharpara. SO_4^{2-} content in groundwater could come from multiple sources. Sulfur is a major element in plant tissue. When the plants decompose the sulfur in them (sulfur containing amino acids)get oxidized to sulfate. Most part of Murshidabad being used as agricultural land. Ponds in all these areas were all loaded with various kinds of phytoplankton and algae. Other surface source could be sulfur based fertilizer. Another source of SO_4^{2-} would be sea. West Bengal close to the sea (bay of Bengal) and the sea water mist could bring $CaSO_4$ (seal salt sulfate) and upon dissociation could lead to the increased concentration of SO_4^{2-}. Over all sulfate was low in all high and low As areas.

The HCO_3^- ranges are 270-540mg/L in Beldanga; 324-482mg/L in Hariharpara; 320-486 mg/L in Nabagram and 370-545mg/L in Kandi. The other source of HCO_3^- could be various carbonates. Sulfate concentration of the surface waters (ponds) were also high (6-24mg/L)

Both Na and Cl are showing very good positive correlation and indicates dissociation of NaCl (halite dissolution). Both Na and Cl for the pond waters were really high and were 6-124

mg/L and 25-305 mg/L. But the chloride concentration is less in deep tube wells. The content of Ca and Mg in the groundwaters and surface waters of high As areas were high compared to the low As areas. The content of Ca and Mg is less in surface waters compared to the groundwater owing to the formation by the disintegration of various mafic minerals or by silicate weathering (feldspars).

The concentration of Fe (t) was also high in groundwaters with high As concentrations (Beldanga; $0.09 \leq$ Fe (t) ≤ 13.6 mg/L; Hariharpara; $0.04 \leq$ Fe (t) ≤ 7.2 mg/L) compared to the low As areas like Nabagram (0.007-1.2mg/L) and Kandi (0.07-1.03 mg/L) .There is a weak positive correlation between Fe (t) and dissolved As. This could indicate release of As from the reductive dissolution of FeOOH present in the aquifer (Nickson et al., 1998, McArthur et al., 2001 & 2004, Dowling et al., 2002, Datta et al., 2011).

Chloride/Bromide ratio and As concentration

The Cl/Br molar ratio for the groundwaters from some tubewells surveyed in Murshidabad area has a ratio (>1561) similar to wastewater values as also stated in McArthur et al., 2012. In Beldanga (high As area) two of the tubewells and in Hariharpara 5 of the tubewells had a Cl/Br ratio more than 1561 and the As concentration in those wells were comparatively less. High Cl/Br ratio in these tubewells indicate sewage influence. In Nabagram (low As area) three tubewells have Cl/Br ratio greater than 1561 indicating possible sewage influence. However rest of the tubewells in Nabagram and all tubewells in Kandi (low As area) have low Cl/Br ratio indicating less sewage influence compared to high As areas. It is interesting to point out that some tubewells with high Cl/Br ratios even in high As areas show comparatively low As concentrations. This observation is consistent with the suppressed As releasing mechanism (bacterial mediated reductive dissolution of FeOOH) in those tubewells due to waste water influence derived from pit latrines, septic tanks, highly contaminated ponds with various anthropogenic waste materials. High Cl/ Br molar ratios can suppress As release mechanism (McArthur et al., 2012). van Geen et al., 2011 stated that As polluted groundwaters had low lower counts of coliform bacteria than that of As free groundwaters of Araihazar and Matlab area in Bangladesh part of Bengal Basin. The majority of tubewells from Beldanga and Hariharpara that produce groundwaters with high Cl/Br ratios and relatively low As concentrations are constructed close to pit latrines as well as ponds. Because excess water from local tubewells drain into the local ponds, these ponds are also subject to an influx of

anthropogenic organic matter. The variation of the Cl/Br ratios could be due to the position of tubewells close to and away from anthropogenic waste sources.

Hydrogen and Oxygen isotope relation to aquifer recharge

Isotopic signatures of Murshidabad waters are similar to the study by Mukherjee et al., 2007. All the water samples (pond, tubewells and irrigation wells) collected during January 2012 fall just below the local meteoric water line (LMWL) of Mukherjee et al., 2007 and trending parallel to the LMWL and global meteoric water line of Craig et al., 1961. The results indicate that rain water is the major source of recharge to the groundwaters (within a depth of 50m) of Murshidabad. The data showed that both shallow and deep ground waters of the areas were occurring together indicating rainwater as the major source.

Isotopic data (values) of ponds waters were well below the isotopic values tubewell waters indicating evaporative enrichment of heavier isotopes of δ D and $\delta\ ^{18}O$. One Pond (PW-102) in Beldanga showed almost similar kind of isotopic signatures like that of groundwaters of Beldanga. This could be due to the mixing of pond waters and groundwaters in this region. The As concentration in PW-102 was 110.27µg/L also indicate possible mixing of high As groundwaters (>1263 µg/L) of this region. But pond waters in rest of the regions (Hariharpara, Nabagram and Kandi) are falling much below the LMWL and showing heavier isotopic enrichment due to evaporation. The trend line of pond water samples are not intersecting the trend lines of tubewells and irrigation wells indicating ponds are not the major source of water to the aquifers in this region. Datta et al., 2011 also studied the effect of ponds on recharging the groundwaters of this region and came out with same conclusion.

The groundwater in this region were depleted with heavier isotopes and enriched in lighter isotopes (tubewells and irrigation wells). Hariharpara samples being more closer and parallel to the LMWL and Nabagram being the farthest from the LMWL. The ranges of δD and $\delta^{18}O$ for tubewell samples were -31.1--22‰ and -3.1--4.52‰ in Beldanga; -26--31‰ and -3.9--4.7‰ in Hariharpara; -32.6--25‰ and -4.04 -2.7‰ in Nabagram; -31.9--26‰ and -4.45--3.9‰ in Kandi. For the irrigation wells samples the δD and $\delta\ ^{18}O$ ranges were -32.4--29.8‰ and -4.56--4.12‰ in Beldanga; -28.2--24‰ and -4.22--3.4‰ in Hariharpara; -31.6--27 ‰ and -4.23--4.1 ‰ in Kandi. The similarity in isotopic signatures of groundwaters in the all the 4 regions and their position close to LMWL indicated that monsoonal rain as the main recharge sourse to these

areas. So during the monsoon the rain water would percolate into the subsurface and recharge the aquifers.

The isotopic data derived for this study is well matching with the previous works by Mukherjee et al., 2007 and Datta et al., 2011 for the same area (Murshidabad). All the 3 research work indicate that the isotopic signatures (δD and $\delta^{18}O$) of groundwaters in this region were falling close to the local meteoric water line (LMWL) indicating that rainwater as the main recharging source in this area. All studies revealed that there was similarity of isotopic signatures (δD and $\delta^{18}O$) groundwaters of this region with LMWL thus indicating that groundwaters were the product of recent monsoonal rainfall. The current study showed that pond waters have separate isotopic signature (enriched in heavier isotopes) than that of groundwaters in this regions which was consistent with the studies by Datta et al., 2011 thus concluding that ponds were not the recharging source of groundwater.

Dissolved Organic Carbon, Total Nitrogen and Fluorescence spectroscopic studies

Dissolved organic carbon in waters and dissolved As concentration are positively correlated. Dissolved organic nitrogen is also positively correlated with dissolved As. DOC concentration in groundwaters decreases with depth in Murshidabad region. This could be one of the many possible reasons why low dissolved As in shallow depth groundwaters compared to the deeper groundwater.

Fluorescence index (FI) value for all water samples (pond, shallow depth and deep groundwaters) in this region are >1.5 indicating high microbial activity (Cory and McKnight, 2005). The mean FI value of high As shallow depth tube wells (Beldanga and Hariharpara) and for the low As tube wells were similar and it is 1.73 (in an average). For the ponds mean FI value is 1.61 and for irrigation wells was 1.69. The freshness index (Fr.I) indicates age of the DOC (recently derived or decomposed) (Parlanti et al., 2000; Wilson and Xenopoulos 2009). Freshness index of the high As area shallow depth tube wells are low and the value is 0.77 compared to low As tubewells where the value is 0.96 indicating older or decomposed DOM in high As areas (shallow depth ground waters) compared to the low As areas. The low FrI (Freshness index) in high As areas indicate older DOC in these regions. The FrI of ponds are 0.79 and indicating decomposed DOC. FrI of the irrigation waters is 0.85 indicating fresh DOC compared to high As shallow depth groundwaters. The SUVA values in low As areas were higher (3.52) than that of high As areas (2.84) which indicates more aromatic DOC (terrestrial

DOC/ Humic). Humic DOC was mostly derived from the vascular plants. Humic DOC is more aromatic than the bacterial DOC because lignin is an important component of the vascular plants and they are aromatic in nature (ring structure), compared to the bacterially derived aliphatic (chain structure) DOC (proteins). SUVA values for ponds were 2.78; and for the irrigation waters are 2.58 both of these values indicate high bacterial activity (Weishaar et al., 2003; Mladenov et al., 2010). DOM characterization studies indicated that amino acid like (bacterial sources) compounds (B and T) were the major components in the low As wells, whereas high As wells tend to have highest content of humic DOM (with greater peak A and C intensities). Pond in this region had high content of bacterial DOC (B and T) this could be due to the waste water/ sewage influx in to the ponds. The pond also show humic DOC (A and C) and this could be due to various terrestrial (leaching of plant materials) and groundwater inputs. Oxygen and hydrogen isotopic data suggested that ponds in Murshidabad region receives a lot of groundwater from tubewells (most of the tubewells were constructed very near to the ponds and while pumping groundwater overflows into the ponds).

The study of EEM (Excitation Emission Matrix) showed that there were 4 major DOC components in Murshidabad waters. They were 1. humic component 'A', 2. humic component 'C', 3. bacterial derived protein Tyrosine 'B', 4. bacterial derived protein Tryptophan 'T'. There was not much difference between the EEM maps of high As areas and low As areas. However there was a very clear change in DOC components with depth of the waters. The pond waters and shallow depth groundwaters in both high and low As areas contain both humic and bacterial peaks. But in the deep groundwaters of irrigation wells the humic components were very less or absent but the bacterial component of DOM was very prominent.

There was an inverse relation between Freshness Index and Cl/ Br molar ratio for the tubewells (shallow and deep groundwater) at low As areas (Nabagram, Kandi). But in the high As areas (Beldanga, Hariharpara) for tubewells (shallow and deep groundwater) there were no such relationship.

During field work it was observed that most of the villagers construct their tubewells in between their kitchen and pit latrines or sometimes they construct tube wells closer to the local ponds. During the rainy seasons the various anthropogenic wastes (pit latrines and other human waste) may enter the ponds. Waste water from the pit latrines can percolate into the shallow depth groundwaters (~50m the average depth of most of the tubewells in this region) and can

cause contamination. Terrestrially derived fresh and young DOM could be going into the aquifers though these pit latrines. This could be one of the reasons why the same DOC signatures were seen in both pond waters and shallow depth groundwaters. But for irrigation wells; most of them were deeper and were situated far away from the villages (inhabitants) and pit latrines. So it is very unlikely that the irrigation wells could get affected by these contaminating sources. The high bacterial activity groundwaters of high As areas confirms that bacterially mediated FeOOH reduction and thus releasing adsorbed As in to the groundwater. High DOC in the water keep the As in solution for longer periods of time.

Most of the tubewells surveyed show low Cl/Br ratio both in high As and low As areas indicating less terrestrial input. Thus the DOM in the groundwaters of Murshidabad region could most likely been derived from sediment bound organic matter. This DOM may be causing the As pollution in this region. Sediments in this region were organic rich in nature.

The florescence data of the current research work were matching with the studies by Mladenov et al., 2010 in Bangladesh part of Bengal Basin (Araihazar). The DOM of the shallow depth aquifers rich in As were more humic in nature was reduced (low FrI) compared to the surface waters which contains more of microbially derived organic matter. The DOM at depths could be derived from the leaching of sediment bound terrestrially derived organic matter over time. The Cl/Br ratio results are consistent with the studies by McArthur et al., 2012. The data suggest that those tubewells near to the pit latrines has got high Cl/Br ratio compared to the ones far away. The tubewells with high Cl/Br ratio tends to have low dissolved As even in high As areas. High Cl/Br tend to suppress As releasing mechanisms.

As distribution within Murshidabad district

Areas east of river Bhagirathi (Beldanga, Hariharpara) had high dissolved As in groundwater (15-1263 µg/L; 5-400 µg/L) and low Mn content (0.1-1.1 mg/L; 0.3-1.3 mg/L). The possible reason for high dissolved As in groundwaters in these regions could be mainly due to high redox conditions existing in this regions and presence of high amount of organic matter in the solid phase (0.4-4.3%; %; 0.2-0.8%)and in the dissolved form (1.4-2.4 mg/L; 1.2-3.2 mg/L). High reducing environment is evident by the presence of high Fe^{2+} (0.01-.06 mg/L; 0.04-0.1 mg/L)and NH^{4+} (0.01-0.02 mg/L; 0.01 mg/L) ions in groundwater. The microbial mediated reductive dissolution of Fe^{3+} oxyhydroxides (FeOOH) in the presence of organic carbon

(electron source for bacteria) can cause release of adsorbed As in to the groundwater. During the process of microbial reduction Fe^{3+} would be converted to Fe^{2+} and As^{5+}would be reduced to As^{3+}. As^{3+} is more mobile and toxic in nature (Harvey et al., 2005). In the solution As^{3+} can from water soluble complexes with dissolved organic matter (DOC) and stay in solution for a longer period of time (Bauer and Blodau, 2006; Reza et al., 2010; Hery et al., 2010; Kalbitz and Wennrich, 1998; Sharma et al., 2010). Aquifer sediments in the high As areas contains high % of organic carbon. Upon disintegration the organic matter in the solid phase can under go in to dissolved form. The presence of dissolved PO_4^{3-} concentration in groundwaters can cause ionic exchange with As in the sediments thus causing high dissolved As in groundwaters in these areas.

Whereas in the areas on the west of Bhagirathi river (Nabagram; Kandi) had low dissolved As (0.4-15µg/L; 10-30 µg/L) and high Mn (0.5-4.2 mg/L; 0.04-1.5 mg/L) concentration in groundwater. Even though the aquifer sediments contain same amount of As and Mn as the high As areas but the redox conditions present in the western side of the river was different; it was more oxidizing. The presence of low Fe^{2+}(0.06 mg/L; 0.04-0.06 mg/L) sulfate species in the aquifer sediments (XANES) indicate oxidizing conditions. The dissolved sulfate concentration in Kandi was very less (0.1-1.5 mg/L) however there was a high sulfate concentration (15-33 mg/L) in Nabagram area. The dissolved organic matter content in the groundwaters of these areas were very less 0.5-1.2 mg/L in Nabagram and 0.6-1.2 mg/L in Kandi. The organic matter in the aquifer sediments were also less in these areas 0.18-0.26% in Nabagram and 0.47-0.93% in Kandi. So the process bacterial FeOOH reduction in presence of organic carbon was less active these areas. The presence of less amount of As in groundwaters in these regions could be due to the ionic exchange between PO_4^{3-} concentration in groundwaters and As in the sediments.

As speciation studies conducted in two tube wells and one pond waters indicated that the major As species in groundwater and the surface waters in this region (both high and low As areas) were As^{3+}. Tubewells sampled were one from Beldanga (TW-102 BM; High As area);78% As^{3+}(total-265.2 µg/L), one from Nabagram (TW-112 NBK, low As area); 99% As^{3+} (total-15.5 µg/L) and one pond water from Hariharpara (PW-109 HK, low As area); 56% As^{3+}(total- 30 µg/L). As per the sampling protocol pond water samples were collected from center bottom of the pond. The presence of dissolved As in pond water could be because at the

center deep bottom of the ponds could be highly reducing compared to the shallow sides. So the reducing conditions existing at the lake bottom could cause microbial mediated FeOOH reduction reaction thus causing release of adsorbed As. The dissolved organic matter content of ponds were high; 8.4 mg/L. The mean As and Mn concentration in the groundwaters of high As areas and low As areas were 274.59 µg/L and 756.63 mg/L and 12.78 µg/L and 1031.18 mg/L.

Summary of Water Chemistry

Water Quality Parameters for the shallow depth tube wells were temperature (24°C-27°C), salinity (0.01ppt-12ppt), TDS (98 mg/L-10g m/L), conductivity (2.6µS/cm-990µS/cm), pH (6.6 to 8) and alkalinity (375 mg/L-630mg/L). The groundwater geochemical data revealed that regions where As concentrations were high such as Beldanga ($< 10 \leq As \leq 4622$ µg/L; ~35-45m depth) and Hariharpara ($5 \leq As \leq 695$µg/L; 6-37m depth), had Mn concentrations 182 - 1291µg/L (Beldanga) and 602.3-1232.3 µg/L (Hariharpara). In contrast, regions characterized by low groundwater As concentrations like Nabagram ($0 < As \leq 16$ µg/L; 20-45m depth) and Kandi ($5 \leq As \leq 50$ µg/L; 20-55m depth) groundwaters typically exhibit high Mn concentration (i.e., Nabagram: $75.6 \leq Mn \leq 2327$µg/L; Kandi: $Mn \leq 42.68$ µg/L) though Kandi sites were not fully explored (only one low Mn data was obtained). The concentration of NH_4^+ was similar in all surveyed wells (high and low As areas) in Murshidabad. The presence of high chloride in this region could be due to high evaporation rate or by anthropogenic inputs. The high Cl^- concentration in ponds (24.5-306 mg/L) indicated anthropogenic sources. The low concentration of nitrates in the high As Holocene aquifers indicate reducing conditions. Phosphate content in groundwaters in this regions could be derived from two sources and they are phosphate based fertilizers (minor) and decomposition of organic matter in the sediments. The sulfate concentration in Murshidabad waters could be derived from the degradation of surface plants. The HCO_3^- could be derived from the dissolution of various carbonates or from the microbial sulfate reductions. The high nitrate in low As areas can suppress As reduction mechanisms. The Cl/Br molar ratio for the groundwaters of most of tubewells surveyed in high As areas has a ratio (>1561) and indicates anthropogenic contaminations. High Cl/Br ratio cause the suppression of As releasing mechanism (microbial FeOOH reduction) operating in the high As areas. Oxygen isotopic data suggest that monsoonal rain is the major source of aquifer recharge (for shallow and deep) in these areas. Most of the ponds in this region are mostly mixed with groundwaters

either by humans (during agricultural practices) natural supply of groundwater to the ponds during the rainy season when water table is higher. The DOC concentration varies with depth and maximum DOC is observed at the shallow depths and at the deeper depths DOC concentration was low. DON is also following same depth wise trend as that of DOC. The EEM maps indicate 4 major DOC components in Murshidabad waters. they were 1. humic component 'A', 2. humic component 'C', 3. bacterial derived protein Tyrosine 'B', 4. bacterial derived protein Tryptophan 'T'. Ponds and shallow groundwaters shows almost similar EEM maps with both humic and bacterial components. The deep groundwaters shows mostly bacterial components 'B' or 'T'. The vertical stratification of DOC components in groundwaters of Murshidabad waters indicates less contamination by surface sources to the deep groundwater (most of the irrigation wells were deep). Whereas shallow groundwaters (tubewells near to pit latrines) were highly affected by the surface waters either by ponds or pit latrines. The dissolved As forms soluble complex with DOC and stays in water for longer period of time. DOM characterization studies indicate that humic DOC (A and C) were the major components of tubewells in high As areas (Beldanga,Hariharpara) where as bacterial DOC (B and T) were the major components in the tubewells of low As areas. Tubewells in these areas have mostly bacterially derived DOC and humic DOC components. The bacterial DOC signatures could be due to the high waste water/sewage influence in to the ponds in this area and the terrestrial DOC signatures imply leaching of various plant materials and groundwater influx (which contain humic DOC from sediment bound organic matter). Irrigation wells are rich in bacterial DOC than the terrestrial component. This could be due to the less amount of sediment bound organic matter at deeper depths.

Chapter 7 - Conclusions and Recommendations

The study reveals that there is As in both eastern and western sides of the river Bhagirathi. The groundwaters in the eastern side (Beldanga and Hariharpara) of the river Bhagirathi (within Holocene aquifers) contain high concentration of dissolved As (>10µg/L) compared to the western side (Nabagram and Kandi) which is occupied by Pleistocene sediments. The Holocene aquifers were reducing in nature whereas the older Pleistocene aquifers are oxidizing. The aquifer sediments do not have much control on the distribution of groundwater As. However it is the process and conditions that exists in these aquifers which control the dissolved As in groundwaters in this region. The main process that drives the As release to the groundwater from the aquifer sediments is bacterial mediated FeOOH reduction in presence of DOC, thus releasing adsorbed As onto the groundwater. FeOOH exists in aquifer sediments as grain coatings and also individual amorphous grains. Majority of the sediments being fine grained in nature thus having high surface area, hence more concentration of FeOOH in these sediments per unit volume thus as a result more adsorbed As. Once the As is released into the groundwater it forms complexes with DOC and stays in the groundwater. Under the reducing conditions existing in Bengal Basin aquifers, the As^{5+} species will converted to As^{3+}, which is more mobile and toxic in nature. As speciation results confirms that the major As species in the groundwaters of Murshidabad are As^{3+}. The presence of high PO_4^{3-} in the Murshidabad groundwaters can cause competitive ionic exchange between PO_4^{3-} in water and As adsorbed on the sediments. Both of these processes could be causing the dissolution of As in to the shallow groundwater (~50m) within high As areas. Monsoonal rainfall is the major recharging mechanism for the aquifers of Murshidabad region with minor contribution from ponds.

High bacterial activity (Fe Reducing Bacteria) in reducing medium to fine grained sediments rich in organic matter in high As areas can cause the reduction of FeOOH grain coatings and this was reflected in the high As groundwater in high As areas (as in Beldanga, Hariharpara) compared to the oxidizing aquifers with low As (Nabagram, Kandi). Based on the results of total digestion and sequential extraction results it was very clear that sediments in these regions (both high and low As areas) contains As and Mn in almost equal amounts. However most of the Mn is associated with the bioavailable sediments phase compared to As.

Maximum bioavailable Mn was observed in Nabagram sediments and groundwater in Nabagram was also enriched in dissolved Mn. As is mostly associated with specifically sorbed sediment phases and its release into groundwater could be attributed to bacterial mediated reducing process. The low Freshness Index in high As areas indicate older or decomposed DOC. Cl/Br molar ratios (>1561) indicated that external sewage influx nearby tubewells or presence of pit latrines may be causing anthropogenic contamination in some of the tubewells in high and low As areas. However the recent human induced organics maybe another source for fresh organic matter (terrestrially derived) to the shallow aquifers of these regions. Monsoonal rain is the main recharging mechanism in these aquifers. During these times (monsoon) various organic matter from the surface can get easily onto these aquifers (~50m). DOM characterization studies indicate that humic DOC (A and C) were the major components of tubewells in high As areas (Beldanga; Hariharpara) whereas bacterial DOC (B and T) were the major component in the tubewells of low As areas. Humic DOC were highly reactive than the bacterially derived DOC due to the aromatic nature.

The major conclusions from sediment and water chemistry were that the different variations in the types of OMs in the shallow aquifer sediments mostly control the release of oxyanions like As from the sediments. The DOC in shallow depth aquifers were derived from the leaching of sediment bound organic matter. Sediments in these areas were rich in organic matter. A major contribution of older existing organic matter in sediments and the fresh young organic matter added to sediments, were equally contributing to the significance of organic matter with in the sediments. The results of this work on organic matter are consistent with the studies by Mladenov et al., 2010. The shallow aquifers are more contaminated than deeper aquifer hence major water management control will promote sustainable availability from the deeper aquifers. From the overall trend of OM with depth, it was expected that control of organic matter from the deeper sediments are negligible which contribute to the fact that exploitation of deep aquifers can lead to safer drinking water in Murshidabad.

Recommendations for Future Research Work

1. Being in the fluvio-deltaic type of depositional environments, the subsurface stratigraphy and sediment architecture would be highly complex. I recommend that by drilling one deep bore hole (1000-2000m) one in Pleistocene aquifer and one in Holocene aquifer could lead to much more insights to the stratigraphy of the region and hence comparison can be made.

2. Most of the tube wells sampled for the current research seem to be affected by various anthropogenic sources. It would be better to drill some new wells far away from these anthropogenic sources and collect groundwater, pond waters and then studying the water chemistry including the fluorescence spectroscopy. These results can be compared with the data set of the current research, which could lead to new insight into the As releasing mechanisms and DOC components.

3. Ponds are very dynamic areas due to the high anthropogenic influences. In future they need to be better studied. A drill core at the center of the pond can lead to the insight on water mixing of ponds and groundwater; evidence on the types of OM that gets concentrated in the ponds and any necessary processes that could lead to the infiltration of these OM into the shallow aquifer sediments.

4. Constructing piezometer network in this region and adjacent well studied regions could be an important asset to study the temporal As variation in this region.

5. More research is needed to investigate the evolution of Mn and its relation with DOM in this region.

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Appendix A- Detailed Materials and Methods

Test Kits:

1. As test kits

a. HACH® As test kit (low range; cat no. 2800000): Fill 50mL water to be tested into the reaction bottle, (Cat No.28002-00) after that add one reagent#1 powder pillow (Cat No. 27978-99) to the bottle containing 50 mL water sample. Swirl to mix until the power dissolve. Then add reagent #2 powder pillow (Cat No: 27977-99) to the bottle containing sample and swirl to mix. At this point solution could be cloudy. After adding reagent#2 wait for 3 minutes. After waiting time is over add reagent#3 powder pillow (Cat. No. 27979-99) to the same bottle and swirl to mix until the reagent power dissolve. Wait for 2 minutes and swirl again. After this procedure add a scoop,~2gm (plastic scoop, cat no: 27998-00) of reagent #4 (Cat. No: 454-29) to the sample and swirl to mix until the reagent is dissolved. In the mean time insert a test strip (Cat. No. 28001-00) to the bottle cap pad so that it covers the small opening and then close the flap and press to secure. Then add reagent#5 (Cat. No: 27981-99) powder pillow to the same bottle containing sample. Immediately after this attach the cap containing test strip to the reaction bottle and swirl to mix. While swirling make sure that the bottle is not shaken or inverted or never allow the sample to get into the test strip. Then bottle is kept for 30-35 minutes for reaction time. Within this 30-35 minutes of reaction time swirl 2 times. Once the reaction time is over then remove the test strip and immediately compare the developed color to the chart on the test strip bottle. Compare the color code in shade and read the concentration of As in µg/l. After the test is complete, wash thoroughly the reaction bottle and the cap with water then wash 3 times with distilled water. Then wipe bottle and the cap with chemwipes and preserve the test strip inside a plastic bag.

b. HACH ®EZ Arsenic high range (0-500µg/l & 0-4000µg/l As) test kit (Cat No:2822800): (0-500µg/l As test): Insert a test strip to the cap of the reaction bottle(Cat No. 4934800) in such a way that the test strip completely covers the small opening. Then close the flap of the cap and secure. Fill the reaction bottle (Cat No. 2800200) to the 50mL line. Then add reagent#1 (Cat No.28229-99) and reagent#2 (Cat. No.28230-99) to the sample in the reaction bottle. Immediately after this step attach the cap containing the test strip to the reaction bottle. Swirl gently for 60 seconds. Then keep the bottle for 20minuits for the reaction to take place and

swirl twice in between the reaction time. Once the reaction time is over then remove the test strip and immediately compare the developed color to the chart on the test strip bottle and compare the color code in shade and read the concentration of As in µg/l. After the test is complete, wash thoroughly the reaction bottle and the cap with water then wash 3 times with distilled water. Then wipe bottle and the cap with chemwipes and preserve the test strip inside a plastic bag.

(0-4000µg/l As test): Insert a test strip to the cap of the reaction bottle(Cat No. 4934800) in such a way that the test strip completely covers the small opening. Then close the flap of the cap and secure. Fill the reaction bottle (Cat No. 2800200) with 9.6ml of water to be analyzed. Then add reagent#1 (Cat No. 28229-99)and reagent#2 (Cat. No. 28230-99) to the sample inside the reaction bottle. Immediately after this step attach the cap containing the test strip to the reaction bottle. Swirl gently for 60 seconds. Then keep the bottle for 20minuits for the reaction to take place and swirl twice in between the reaction time. Once the reaction time is over then remove the test strip and immediately compare the developed color to the chart on the test strip bottle and compare the color code(0-4000µg/L color code) in shade and read the concentration of As in µg/l. After the test is complete, wash thoroughly the reaction bottle and the cap with water then wash 3 times with distilled water. Then wipe bottle and the cap with chemwipes and preserve the test strip inside a plastic bag.

2. HACH® Manganese Test kit (Model MN-5, Cat. No: 1467-00): First fill the water sample to be analyzed in to the sample mixing bottle (Cat. No:493-06) add the contents of the buffer powder pillow for Manganese, periodate method (Cat. No. 983-99) to the mixing bottle containing sample. Then add contents of sodium periodate power pillow for manganese (Cat. No. 984-99) to the mixing bottle .Swirl to mix and then keep the sample undisturbed for two minutes for the f or the color development. If manganese is present then a pink color will develop. During this time fix the color comparator (Cat. No. 1732-00) by inserting lengthwise viewing adapter (Cat. No. 24122-00) inside the color comparator. Then place the color disc for manganese (Cat . No. 1739-00) in the proper slot inside the comparator and then close the color comparator. After two minutes of waiting period transfer 15mL of this sample to the color viewing tube (Cat. No. 1730-00). Place this color viewing tube containing the prepared sample to the opening comparator opening labeled “prepared sample" or in to top right opening. Then fill another color viewing tube (Cat. No. 1730-00) with same unprepared sample and insert it to the

left opening labeled "clear sample". Hold the comparator with the tube tops pointing to a light source and then view and compare both samples through two small opening in the comparator. During this process make sure that sample does not spill. Rotate the color disc for manganese until there is a color match between the two samples. Once the match is done read the concentration of manganese (mg/L) through the scale window. Once the experiment is done wash the tubes and bottles properly with water. Then wash again properly with distilled water. Then rinse the bottles and tubes with distilled water at least 3 times and then wipe with chemwipes. Store the prepared sample in the waste collection bottle.

3. Nitrate CHEMetrics® test kit (Cat. No. K-6909D): Fill 1.5mL of water sample to be tested in the reaction tube (Cat. No. A-0187). Then dilute the sample by adding distilled water to 15mL mark of the reaction tube. Add the contents of one cadmium foil pack (Cat. No. 7440-43-9) to the reaction tube containing water sample. Cap the reaction tube firmly and shake it for three minutes then keep it undisturbed for 2 minutes. Transfer 10mL of processed sample to the sample cup (Cat. No. A-0013) while doing this transfer make sure that no cadmium particles are going in to the sample cap. Then place the CHEMetrics ampoule (Cat. No.R-6904) to the sample cap containing processed sample. Snap the tip then the ampoule will fill itself leaving a bubble for mixing. Mix the ampoule several times and during this process the bubble should travel from end to end. Keep the ampoule undisturbed for 10 minutes for color development. After the color development compare the ampoule with nitrate color standard (Cat. No. C-6909 D) until best color match is found.

4. HACH® Sulfate Test kit (Model SF-1, Cat. No: 2251-00):Experiment starts with filling 25mL of water sample to be analyzed into the sample mixing bottle (24102-00). Add the contents of one Sulfa Ver® powder pillow(Cat. No. 12065-66) to the sample mixing bottle containing the water sample. Fix the cap of the sample mixing bottle tightly and shake the bottle for 15 seconds and make sure that the powder is dissolved. If sulfate is present in the water sample a white turbidity would appear. Then keep the sample undisturbed for five minutes. Then invert the bottle to mix if there is any solid left behind on the bottom. Then remove the cap and pour the contents to a clean 25mL graduate cylinder(Cat. No. 2172-40). Hold the graduate cylinder in a vertical position. While looking straight down in to the graduated cylinder containing water sample insert the sulfate measure dipstick (Cat. No.46814-00) into the graduated cylinder until the black dot disappears completely. While holding the dipstick at the

same position where the black dot disappears and reading the value (number on the dipstick scale that meets with the surface of the sample) on the dipstick through the non graduated portion of the cylinder. This number corresponds to mg/L of sulfate in the sample. If the black dot on the dipstick disappear before the first test mark (200mg/L) then the concentration of sulfate is greater than 200mg/L. If the black dot does not disappear after the dipstick is inserted to the cylinder bottom, the sulfate concentration is less than 50mg/L. Once the experiment is done wash the cylinder and bottle properly with water. Then wash again properly with distilled water. Then rinse the bottles and tubes with distilled water at least 3 times and then wipe with chemwipes. Store the prepared sample in the waste collection bottle.

5. HACH® Orthophosphate Test kit (Model PO-19, Cat. No: 2251-00): There are 3 different types of tests for Phosphate (PO_4^{3-}) they are 1. Low range phosphate concentration (0-1mg/L) test procedure. 2. Mid range phosphate concentration (0-5 mg/L) test procedure 3. High range phosphate concentration (0-50 mg/L) test procedure. Spectrophotometer test for phosphate concentration was conducted to determine the concentration of phosphate. Then based on concentration of phosphate measured from spectrophotometer, the test kit procedure was decided (low, mid or high range) to reconfirm the concentration

1. low range (0-1mg/L) phosphate: Fill 20mL water to be tested in a mixing bottle (Cat. No.232706). Add contents of one PhosVer® 3 phosphate reagent powder pillow (Cat. No. 220999) and swirl to mix then keep this bottle for 8 minutes. Mean while fix the color comparator box (Cat. No. 173200) by first inserting the long path viewing adapter (cat. no.2412200) and color disc for phosphate (Cat. No.2489800) to the right knob and close the color comparator box. After the 8 minute waiting period is over if phosphate is presnt in the water sample then blue color will develop. Fill the prepared sample in a glass color viewing tube (Cat. No. 173106) till the top mark. Fill another glass color viewing tube with unprepared water sample. Insert the glass color viewing tube with prepared sample into the right top opening of the comparator and the other glass color viewing tube with unprepared water sample to the top left opening of the comparator. Hold the comparator to the light source such a way that light source is above both tubes . Then slowly rotate the color disc until the color in the front windows match. Note down the reading in the scale window just below (left) the view window. Divide this number by 50 to obtain the mg/L phosphate. Then again divide the value by 3 to obtain the concentration of phosphorus in mg/L.

2. Mid range (0-5mg/L) phosphate: First fix the color comparator box for phosphate as mentioned for the low range test for phosphate. Fill two glass color viewing tubes to the first line (5mL) with the water sample to be analyzed. Add one PhosVer® 3 phosphate reagent powder pillow (Cat. No. 220999) to one of the glass color viewing tube and swirl to mix. Wait for 1 minute. In the mean time insert other glass color viewing tube with untreated sample to top left opening of the comparator. When the one minute wait time is over and if phosphate is presnt a blue color would develop. Insert this glass color viewing tube with the prepared sample to the top right opening of the comparator. Then hold the comparator to a light source in such a way that light source is directly behind the tubes. Rotate the color disc until the colors in the front windows match. Note down the reading from the scale window and divide this value by 10 to obtain the concentration of phosphate in mg/L. Again divide the phosphate value by 3 to obtain the concentration of phosphorous in mg/l.

3. High range (0-50mg/L) phosphate: Remove the long path viewing adaptor from the comparator box. Rinse the two glass color viewing tubes with deionized water. Then fill 5mL deionized water in one of the glass color viewing tubes. Insert this tube in to the left opening of the comparator box. With help of a dropper take out 0.5mL of the sample to be analyzed and pour this sample to the second glass color viewing tube. Then fill deionized water to this glass color viewing tube till 5mL line and swirl to mix. Stopper should be washed and rinsed several times with deionized water. Add contents of one PhosVer® 3 phosphate reagent powder pillow (Cat. No. 220999) to this glass color viewing tube containing the sample to be analyzed and swirl to mix. Waite for 1 minute and if phosphate is present then a blue color would develop. Insert this tube to the top right opening of the comparator. Then hold the comparator to a light source in such a way that light source is directly behind the tubes. Rotate the color disc until the colors in the front windows match. Note down the reading from the scale window and that is the concentration of phosphate in mg/L. Divide the phosphate value by 3 to obtain the concentration of phosphorous in mg/L.

1. The Manganese analyzed by HACH test kit (Cat. No. 1467-00) was again reconfirmed with HACH DR 2800 spectrophotometer periodate oxidation manganese method (method 8034). The experiment started with taking 10mL of sample to be analyzed in the DR 2800 cell (Cat. No. 2495402). Then Added contents of one citrate type for manganese powder pillow (Cat. No. 2107669) to the cell containing sample. Capped the cell and inverted to mix the

contents. After this process, contents of one sodium periodate powder pillow (Cat. No. 2107769) was added to the sample cell. Again cap the cell and inverted to mix. If manganese was present then a violet color will develop. In the mean time spectrophotometer (DR 2800) was switched on and the timer was set for 2 minute reaction time period. In The mean time the bank was prepared by adding 10mL untreated sample to a separate DR 2800 cell. Once the timer expires the blank was inserted to the cell holder of the DR 2800 spectrophotometer. Zero the instrument by pressing options on the screen of DR 2800 then display screen will show 0.0mg/L Mn. Within 8 minutes after the time expires insert the prepared sample to the cell holder and read the concentration of manganese in mg/L from the screen. Make sure that before inserting the cell to the spectrophotometer the sample cells should be wiped with chemwipes.

2. Nitrate (NO_3^-) was analyzed with Nitrate CHEMetrics® test kit (Cat. No. K-6909D) and was again reconfirmed with DR 2800 spectrophotometer cadmium reduction method for powder pillows (method:8039) in the field. The experiment starts with inserting adaptor (LZV584 C) to the DR 2800 spectrophotometer. Then filled 10 mL of sample to be analyzed t the sample cell (Cat. No. 2495402). Added contents of one NitraVer 5 nitrate reagent powder pillow (Cat. No. 2106169). The capped the cell and mix the contents by shaking. Then machine was started on and 1 minute reaction time was set. Once this reaction time was over, started the timer again and set reaction time for another 5 minutes. If nitrate was present in the sample then an amber color will develop. A blank was prepared by filling 10 mL fresh sample to another sample cell. Once the 5 minute reaction time was over, wipe the cell containing the blank and inserted in to cell holder of the machine. Zero the instrument and then display will show 0 mg/L nitrate concentration. Within one minute after the timer expires insert the cell containing the prepared sample and read the result of nitrate in mg/L. After the experiment wash the cell with normal water and then distilled water 3 times and wiped with chemwipes.

3. HACH® Iron total FerroVer method for powder pillow(method:10249): The analysis was indicated by filling 10mL of sample to be analyzed to the HACH DR 2800 spectrophotometer cell. The 2 drops of EDTA solution (Cat. No. 2241926) was added to the cell containing sample and swirled to mix. Then sample was inserted to the cell holder of the DR 2800 spectrophotometer and zero the instrument and read the display and it will show 0mg/L. After that the cell containing the sample was removed from the cell holder and contents of one FerroVer iron reagent powder pillow (Cat. No. 2105769) was added to the sample cell. Swirled

to mix. Then the instrument timer was set for 3 minute reaction time. If iron is present then an orange color will appear. When the timer expires the sample was inserted to the cell holder of DR 2800 and read the concentration of iron total in mg/L.

4. HACH® USEPA SulfaVer 4 Methods for Sulfate (SO_4^{2-}) concentration: 10mL of sample to be analyzed was added to the cell and inserted to the cell holder of DR 2800 and read the concentration from the display and it will show 0 mg/L sulfate. Then contents of one SulfaVer 4 reagent powder pillow (Cat. No. 2106769) was added to the sample cell. Swirled to mix. The sample will become cloudy if sulfate is present. The instrument timer was set for 5 minutes. When the timer beeps after 5 minutes reaction time, wipe the cell and inserted the prepared sample to the cell holder and read the concentration of sulfate in mg/L. Once the analysis is completed the cell was cleaned with soap water. Then wash and rinse 3 times with distilled water before analyzing next sample.

5. HACH ® USEPA PhosVer 3 (Ascorbic Acid) Method for Phosphate (PO_4^{3-}): Adaptor LZV584 (C) was inserted to the DR 2800 and 10mL of sample to be analyzed was filled to the cell. Contents of one PhosVer 3 phosphate powder pillow (Cat. No. 2106069)was added to the cell containing water sample and then capped the cell and shook it vigorously for 30 seconds. Instrument timer was set for 2 minute reaction period. A standard was prepared by filling 10 mL of unprepared sample to the cell. Once the 2 minute reaction period is over, wipe the cell containing the untreated sample (standard) and inserted to the cell holder. Zero the instrument and read the concentration of phosphate of standard as 0mg/L. Then the cell containing prepared sample was inserted to the cell holder and read the phosphate concentration in mg/L.

6. HACH®Salicylate Method for measuring Ammonia (NH_3-N) (method: 8155): 10mL of sample to be tested was filled to a spectrophotometer cell and contents of one Ammonia salicylate powder pillow (Cat. No. 2653299) was added to it . Prepare a blank by filling other cell with 10mL deionized water and then contents of one ammonia salicylate powder pillow was added to it. Both cells were capped and shock to dissolve the contents. The instrument timer was set for 15 minutes reaction period. Green color will develop if ammonia-nitrogen is present. Once the timer was expired, wipe the cell containing blank and inserted to the cell holder. Zero the instrument and read the concentration of the blank from displayer and it will show 0mg/L.

Then wipe the cell with processed sample and inserted it in to the sample holder. Read the concentration of NH_3-N in mg/L.

Scanning Electron Microscopy (SEM)

SEM analysis was performed to find out the concentration of various trace elements in the aquifers sediments. 3 samples (aquifer sediments) were chosen (Beldanga=2, Nabagram=1) for the study. Samples are taken from various depth in the aquifer (Beldanga 43m and 27m depth; Nabagram 24 m depth). Each sample was mounted on a separate aluminum SEM stub with a carbon coating. Then once the samples were magnified the area of interest was chosen and analysis was performed to find out the concentration of various elements especially As, Mn, Fe, Ca, C etc. Then grains of interest were also chosen and mapped to find concentration of various elements presnt in that particular grain. The concentration of elements were measured using intensity of peak in the spectrum . It depends on a number of factors, but primarily, on the probability of X-ray generation as a result of a given transition. The relative probability of generating X-rays at the various ionization energies from a given element depends on the value of the incident energy and the excitation cross section for the relevant shell. The intensity of a given line will depend on the ratio between the incident beam energy and the critical ionization energy for that line or transition. The detection is done by the secondary electrons emitted by atoms of various elements which has been exited by incident electron beam. In X-ray microanalysis it refers to the shell or level closest to the nucleus as the K shell. Electrons fill this level first. The next closest level is the L shell and then the M and then N shell etc. Since the K shell is closest to the nucleus, it requires the most energy to remove an electron from this shell. Therefore if a spectrum from an element contains K, L and M line, the K will be the highest in energy i.e. furthest towards the right of the spectrum if the scale is defined in units of energy.

Synchrotron beam line stud nies of Aquifer Sediments (XANES and EXAFS)

X27A bean line is specializes in X-ray fluorescence microprobe of soils and minerals with a spatial resolution of 15 (h) x 10 (v) microns utilizing KB mirrors. It is equipped with a 13-element Ge fluorescence detector. The X27A micro-focusing system consists of two, 20 cm long, dynamically bent rhodium-coated silicon mirrors arranged in Kirkpatrick-Baez (KB) geometry, which are housed within a helium-purged enclosure. The KB mirrors (10.2 meters from the source) focus a 1mm x 1mm beam down to about 10 μm [vertical] x 15 μm [horizontal] with an average flux of $5x10^9$ ph/sec. The demagnifications in the vertical and horizontal directions were

26:1 and 55:1 respectively, and the working distance was 9 cm. The monochromator consisted of two water-cooled channel-cut crystals [Si(111) and Si(311)], with a four-jaw motorized slit system located immediately upstream of this arrangement. The instrumentation consisted of radiation hutch. Vortex ME4 SDD Array or Canberra 13-element Germanium Array detectors with XIA XMAPS DXPs. It is also equipped with Ion chambers and photodiode detectors. The samples can be fixed on a XYZ-theta high-resolution motorized sample position stage inside the radiation hutch and which can be controlled by a motorized experimental table (6-degrees of freedom). Samples are analyzed using CCD-coupled optical microscopes. Beam line components were controlled by EPICS 3.14.7 running on a VME (VxWorks) and LINUX systems. In this beam line XRF mapping of a sample (Beldanga=1) is done to find out As hot spots. Then XANES, EXAFS and correlation plots for As with Mn and Fe for those two major hot spots in that particular sample were done. The standard operating procedures of this beam line are 1.Close the beam or shutters (by pressing the red button in the control box outside the radiation hutch); 2. Undo the interlock; 3. carefully fix the sample on mounting block inside the radiation hutch; 4. Engage the interlock; 5. Open the shutters; 6. Start the analysis. The configurations are Motor 1: Sam Hor X (mm), Motor name X27AA=m1, current position =52.2250, start (abs)=51.420, stop (abs)=53.0250, step=0.0140000, start (rel)=-0.80002, stop(rel)=0.800000,#points=115; Motor 2: Sam Vert Y (mm), motor name X27AA=m2, Current position=110.570, start (abs)=109.770, stop (abs)=111.370, step=0.014000, start (rel) =-0.800006, stop (rel)=0.800000,# points=115; map=12200 eV; XANES (As)=11750 eV and XRD=17479 eV.

X 15B beam: X15 B beam line is used to do sulfur speciation of Murshidabad samples and was optimized for spatially for energy x-ray absorption spectroscopy (XANES, EXAFS). Optics scheme was windowless (UHV) with adjustable-pitch collimating/harmonic-rejection mirror, double-crystal fixed-exit monochromator, toroidal focusing mirror. Accessible energy range was 1.2-8 keV, but optimized for 1.7-5 keV. Spatial resolution at the sample position was 0.2 mm to 1.0 mm. Sample environment inside the radiation hutch include He and UHV. Detection schemes include transmission (ion chambers and foils/grids) and fluorescence (Canberra ultra-low-energy Ge). The instrumentation of this beam line includes, Mirror 1: Cylindrical platinum coated Glidcop; 1m long; cooled; vertically collimating; incidence angle can be adjusted (0.2 deg. to 2.0 deg. range) to discriminate against harmonics; located 8 meters

from the source. Monochromator: Double flat crystal UHV monochromator with fixed-exit geometry; first crystal is cooled; Bragg angle range from 10 deg. to 80 deg.; located 10 meters from the source. Crystal pairs include Si(111), Ge(111), Si(311), InSb, Beryl. Energy resolution is determined by crystals. Energy repeatability is within 0.1 eV scan-to-scan and over 24+ hours. Mirror 2: 1:1 focusing platinum coated ULE (silica) toroid; 0.4 degree incidence angle; 1m long. Experimental apparatus includes a small hutch Box with He atmosphere and is equipped with a Ge fluorescence detector, ion chambers, and sample stage. Operating range is 1.2-8 keV. Whole system is operated by Windows MS-DOS operating system. Samples are at first pulverized to a fine powder using an agate mortar and packed inside a polyethylene cover (Fig.8). The operating procedure of the beam is 1. Shut the beam or shutters (by pressing the red button in the control box); 2.Undo the interlock and open the hutch; 3. Place the sample carefully inside the mounting plate inside the hutch using clips and polyethylene tapes (while doing this process fix the delicate door of the shutter to a clamp to avoid breakage and make sure that no dust go inside the hutch); 4. lock the hutch; 4.Swetch on n the beam (by pressing green button in the control box); 5.Purge Helium gas (by rotating the control knob and make sure that the once the pointer reaches 0.5 rotate 2.5 times and stop) ; 6. Waite till I0 (in the left top monitor) is below 0.4 (ideally it should be below 0.25) and close the valve of gas chamber; 7. target the samples with the beam using a standard fluorescence reference material; 8. check the I(t) if it is 0.0003 (if it is 0.0003 then the beam is on the sample); 9. check the fluorescence; 10. start the analysis. A total of 7 number of samples were analyzed in this beam (Beldanga=2; Hariharpara=1; Kandi=3 and Nabagram=1).

X11A beam is mainly used for As XANES and EXAFS of aquifer sediments. Beam line X11A is a typical x-ray absorption spectroscopy beam line with a double-crystal monochromator. Set-up includes three ion-chambers to measure the transmission of the sample and a reference foil, but it is also possible to measure the fluorescence with a 13-element Ge detector to separate contributions from different elements. Beam line uses double crystal monochromator using a Huber goniometer, Si (111) or Si (311) crystals as optical system. The experimental apparatus includes Solid state detector with digital electronics. 13-element Ge detector and radiation hutch. This beam line is controlled by using Mac OS 9, XDAC spectroscopy data acquisition software. Before the analysis the samples are dried (in a nitrogen glow bag) and pulverized to a fine powder using an agate motor. Latter the samples are fixed in

steel sample holder and covered with polyethylene tapes on either openings. The standard operation procedure include 1. close the beam. 2. fix the sample inside the radiation hutch; 3. place the filter in front of the sample; 4. close the hutch; 5. start the beam .6 start the analysis (configuration for beam is attached in appendix-2). Before starting the analysis for As, the beam line was normalized for As using a gold foil. A total of 10 samples were analyzed using this beam (Beldanga=3; Hariharpara=3; Kandi=3 and Nabagram=1).

Appendix B- Description of Sediment Cores

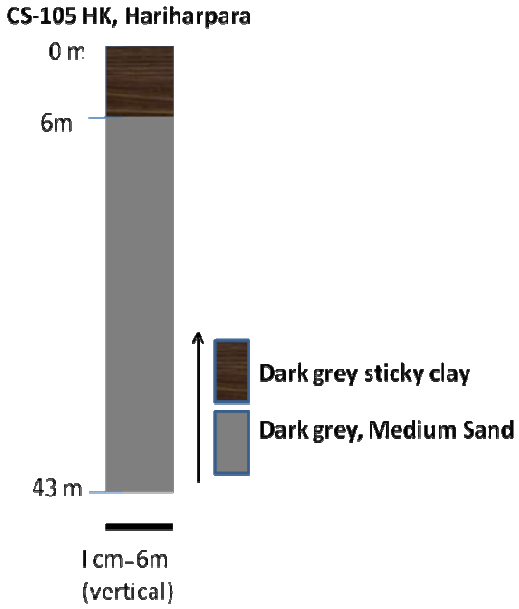


Figure A: Comprehensive litholog for Hariharpara core

CS-105 HK (High As area)- Borehole drilled on 01/06/2012: From the surface till 6m deep dark-grey sticky clay was encountered. From 6 m to 27m medium grained dark- greyish loose sand bed with abundant mica, organic matter (plant) and mafic mineral particles were encountered. This above mentioned sand bed also continued from 27m until 43m . In close observation while core logging was executed it was identified that the size of mice flakes (muscovite) are bigger compared to sand bed above; However the other characters were similar. This dark grey medium sand is the major aquifer in this region as similar to Beldanga.

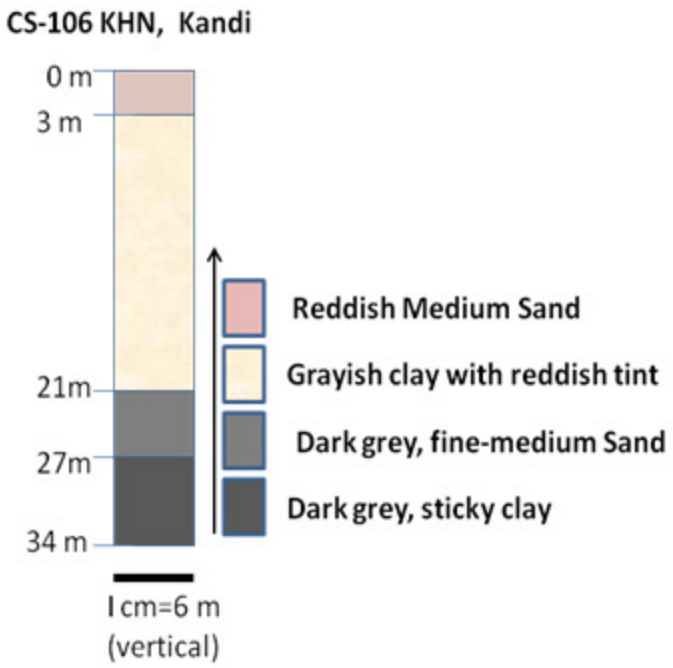


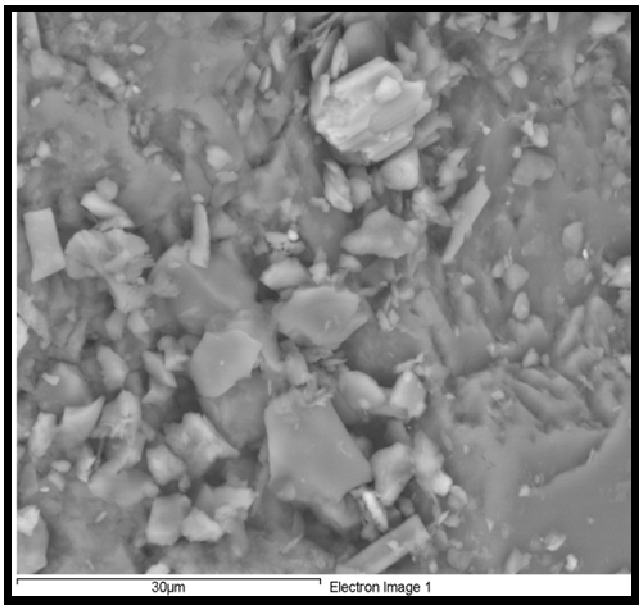
Figure B: Comprehensive litholog for Kandi core

CS-106 KHN (low As area): Borehole drilled on 01/07/2012: The first lithology encountered while drilling in Kandi was reddis- brown colored medium grained loose sand with muscovite flakes to a depth of 3m . From the base of the sand bed to a depth of 21m grayish colored clay bed with reddish tint is encountered. Later at the lower depths (19 m to 21 m) the reddish tint color in the clay bed is comparatively less. From the base of clay bed (21m) uptill 27 m there is dark grayish loose sand bed. It is composed of abundant muscovite mica and organic matter (plant matter) and some mafic minerals. Initially the sand bed (quartz) is fine grained in nature (21m-24 m) and later it changes to medium grained. Then from the base of sand bed (27m) to 37m depth dark gray with reddish tint colored sticky clay bed was encountered.

Appendix-C- Scanning Electron Micrographs and EDXs

Scanning Electron Microscopy (SEM)

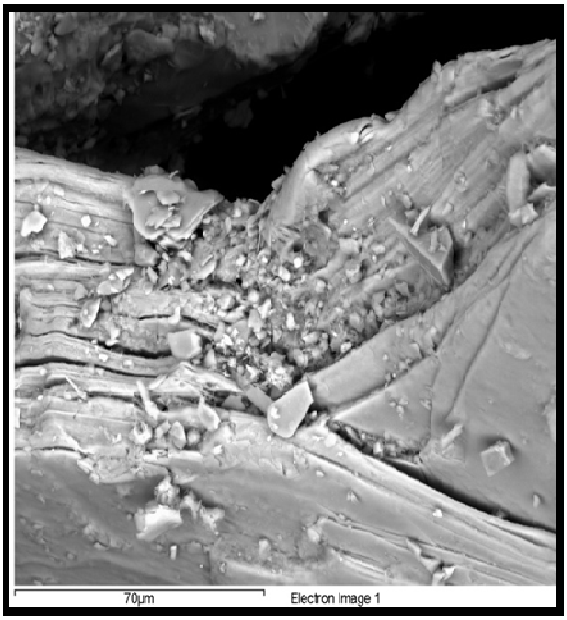
SEM analysis was performed to find out the concentration of various trace elements in the aquifers sediments. 3 samples (aquifer sediments) were chosen (Beldanga=2, Nabagram=1) for the study. Samples are taken from various depth in the aquifer (Beldanga 43m and 27m depth; Nabagram 24 m depth). Each sample was mounted on a separate aluminum SEM stub with a carbon coating. Then once the samples were magnified the area of interest was chosen and analysis was performed to find out the concentration of various elements especially As, Mn, Fe, Ca, C etc. Then grains of interest were also chosen and mapped to find concentration of various elements presnt in that particular grain. The concentration of elements were measured using intensity of peak in the spectrum . It depends on a number of factors, but primarily, on the probability of X-ray generation as a result of a given transition. The relative probability of generating X-rays at the various ionization energies from a given element depends on the value of the incident energy and the excitation cross section for the relevant shell. The intensity of a given line will depend on the ratio between the incident beam energy and the critical ionization energy for that line or transition. The detection is done by the secondary electrons emitted by atoms of various elements which has been exited by incident electron beam. In X-ray microanalysis it refers to the shell or level closest to the nucleus as the K shell. Electrons fill this level first. The next closest level is the L shell and then the M and then N shell etc. Since the K shell is closest to the nucleus, it requires the most energy to remove an electron from this shell. Therefore if a spectrum from an element contains K, L and M line, the K will be the highest in energy i.e. furthest towards the right of the spectrum if the scale is defined in units of energy.



Element	Weight %
O (K)	56.73
Si (K)	34.51
Al (K)	3.61
K (K)	1.01
Ti (K)	1.20
Fe (K)	1.62
As (L)	0.01

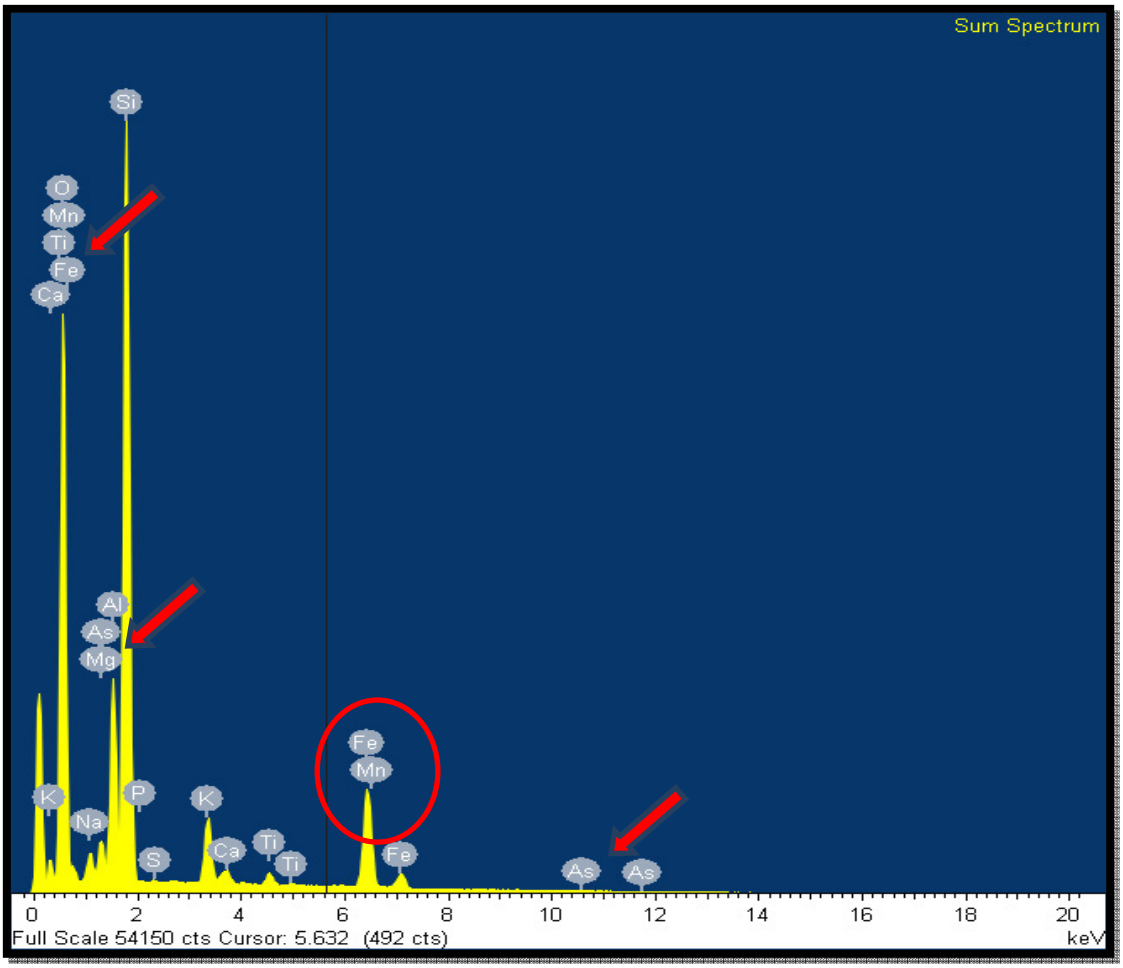
Figure A **Table A**

Figure A (left): SEM photomicrograph of selected area in sample BM-140 (high As area) clay; Table A to the right shows the major elements and their weight % in this selected area. The weight % is obtained from the ionization intensity peaks obtained from the major sub shells (represented inside the bracket) of a particular element.



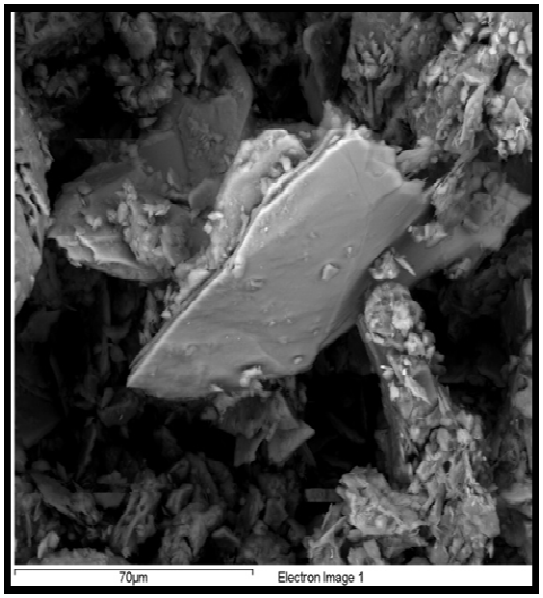
Element	Weight %
O (K)	50.77
Si (K)	23.21
Al (K)	5.88
K (K)	2.85
Ti (K)	0.80
Fe (K)	13.16
Mn (K0	0.10

Figure B **Table B**



Spectrum-B

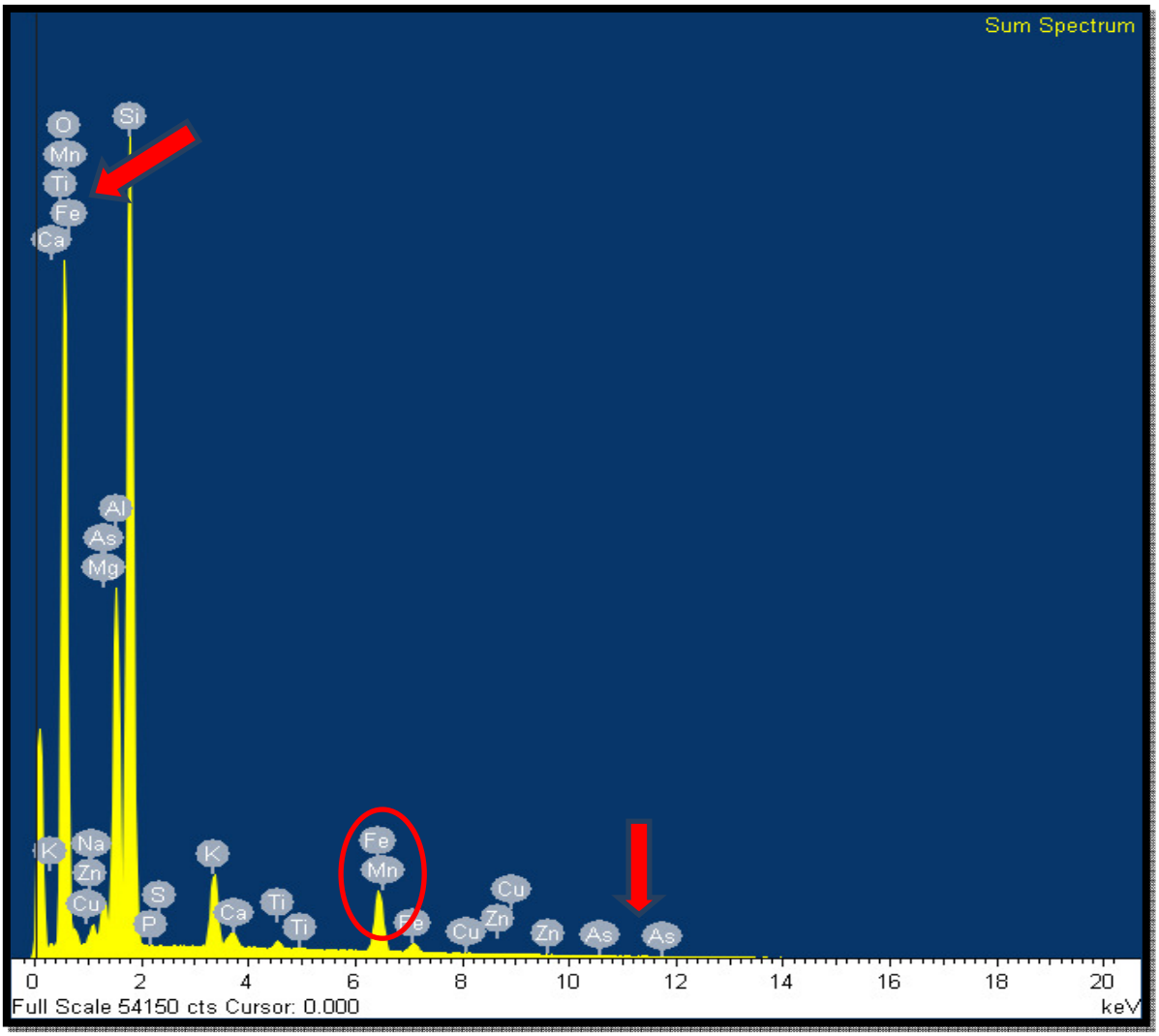
Figure B: (top left): SEM photomicrograph of selected area in BM-140 (high As area) clay. Table-B to the right shows the major elements and their weight % in this selected area. The weight % are obtained from the ionization intensity peaks obtained from the major sub shells (represented inside the bracket) of a particular element. Spectrum B: Spectra (bottom) showing elemental proportions. Arsenic is present as very minute concentration. Fe and Mn shows close association or overlap along the similar intensities (red circled area).



Element	Weight %
O (K)	55.14
Si (K)	22.44
Al (K)	9.11
K (K)	3.00
Ti (K)	0.50
Fe (K)	7.33
Mn (K)	0.06

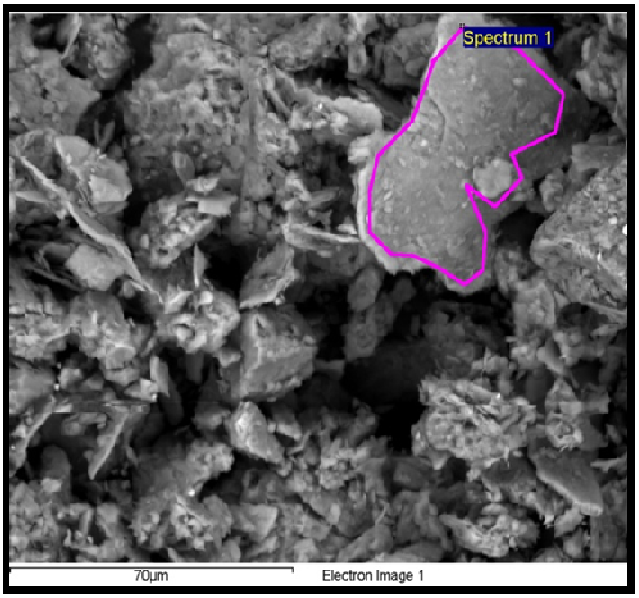
Figure C

Table C



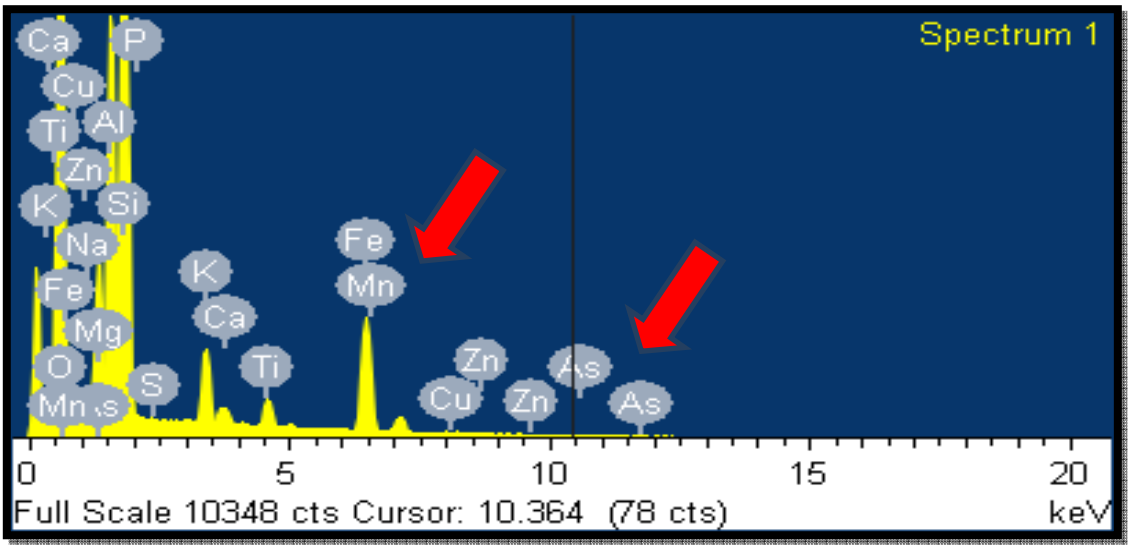
Spectrum C

Figure C: SEM photomicrograph (left) of selected area in sample no.BM-90 (high As area) , Table C: Represent (right) the major elements and their weight % in this selected area, clay. The weight % are obtained from the ionization intensity peaks obtained from the major sub shells (represented inside the bracket) of a particular element. Spectrum C: Spectra (bottom) showing elemental proportions. As is present as very minute concentration. Fe and Mn shows close association (red circled area)



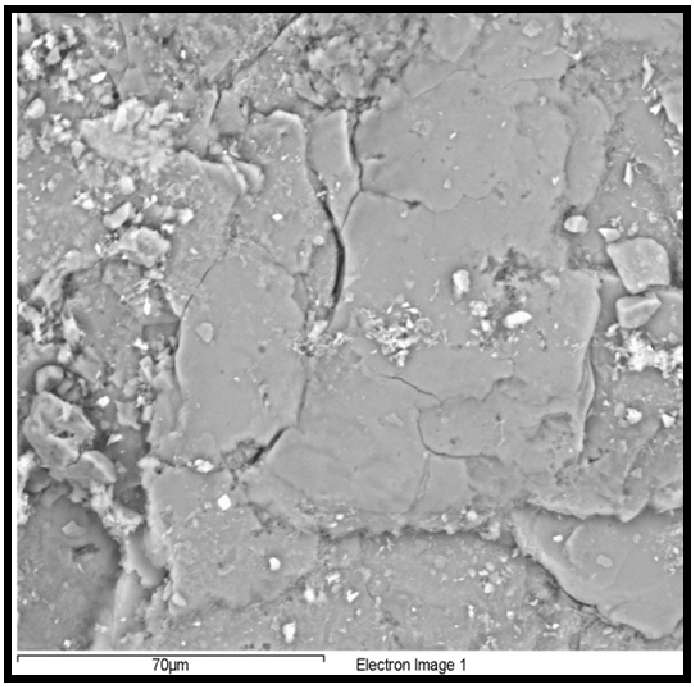
Element	Weight %
O (K)	54.33
Si (K)	17.04
Al (K)	9.5
K (K)	2.28
Fe (K)	10.61
Mn (K)	0.07
As (L)	0.03

Figure D **Table D**



Spectrum D

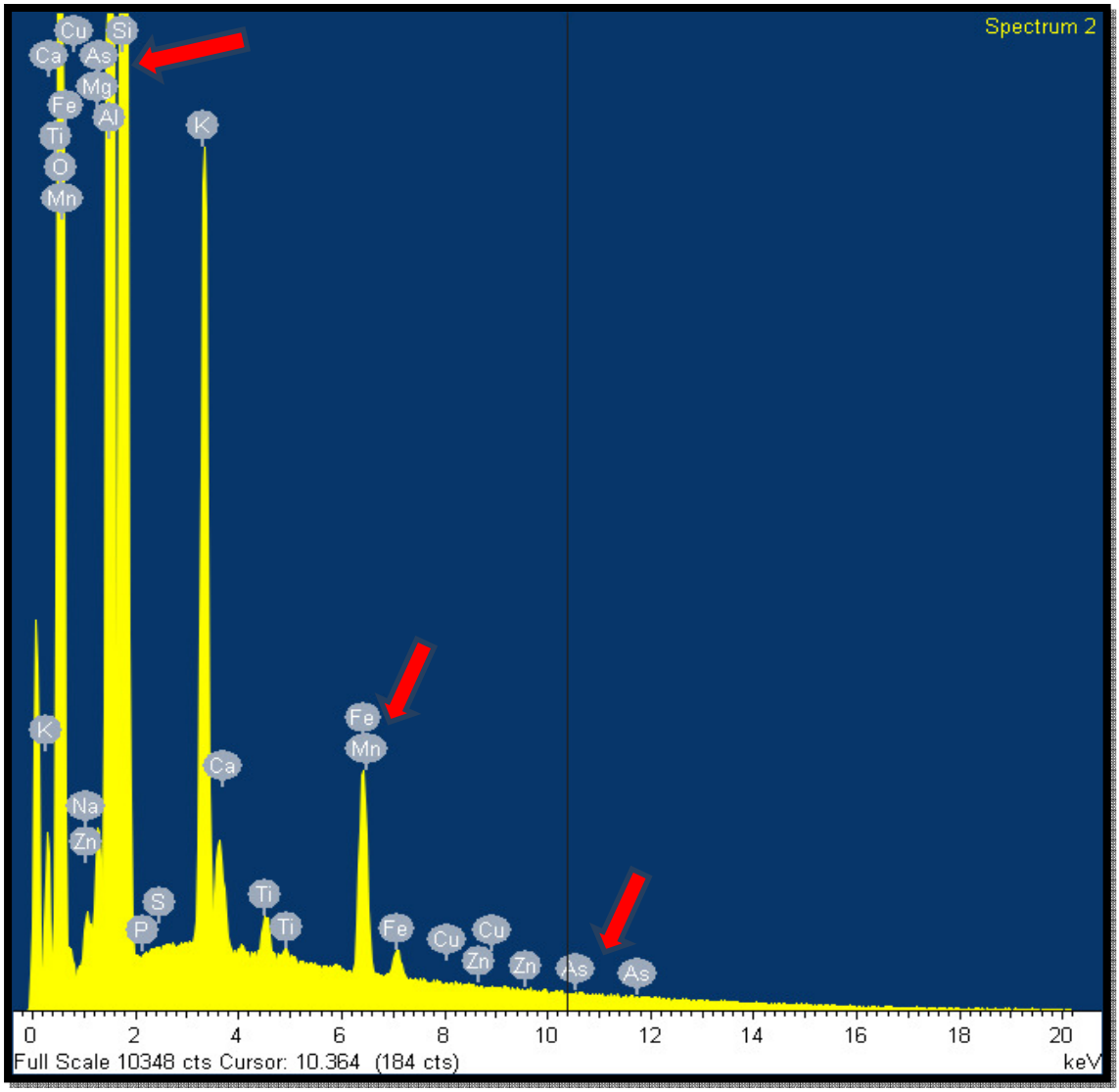
Figure D: SEM photomicrograph (left) of a selected grain in sample no.BM-90 (high As area) , Table D: Represent (right) major elements and their weight % in this selected area, clay. The weight % are obtained from the ionization intensity peaks obtained from the major sub shells (represented inside the bracket) of a particular element. Spectrum D: Spectra (bottom)showing elemental proportions. As is present as very minute concentration. Whereas Fe and Mn shows association.



Element	Weight %
O (K)	58.91
Si (K)	20.09
Al (K)	13.14
K (K)	4.13
Fe (K)	1.99
Mn (K)	0.04
As (L)	0.04

Figure E

Table E



Spectrum E

Figure E: SEM photomicrograph of a selected area in NB-80 (low As area) clay,. Table E: on the right shows the major elements and their weight % in this selected area. The weight % are obtained from the ionization intensity peaks obtained from the major sub shells (represented inside the bracket) of a particular element. Spectrum E: Spectra (bottom)showing elemental proportions. As is present as very minute concentration, But Fe and Mn show overlap.

Appendix-D- Total Digestion results (70% trace grade HNO_3 acid digestion by Microwave)

Sample ID	Depth (m)	Mn conc. (mg/kg)	As conc. (mg/kg)	Fe (t) conc. (mg/kg)	Sample Description
BM-10	3.048	628.5	18.06	32972	Core Sample (CS-103 BM) collected from Beldanga, date: January 2nd 2012. Coordinates: N 23 56.392 E 88 16.206
BM-30	9.144	196.4	9.96	14721	
BM-40	12.192	810.8	11.92	29626	
BM-50	15.24	225.5	18.09	28495	
BM-70	21.336	971.1	8.31	28443	
BM-90	27.432	1840.7	16.52	29229	
BM-100	30.48	151.4	9.71	13140	
BM-110	33.528	192.0	9.35	10689	
HK-10	3.048	533.0	12.78	26227	Core Sample (CS-105 HK) collected from Hariharpara, date: January 6th 2012. Coordinates: N 24 03.651 E 88 21.395
HK-20	6.096	1369.5	15.54	31731	
HK-30	9.144	147.2	7.37	11978	
HK-40	12.192	191.2	7.53	10337	
HK-50	15.24	154.6	8.30	10151	
HK-60	18.288	59.0	6.93	6871	
HK-70	21.336	116.0	8.17	9819	
HK-80	24.384	127.3	7.54	9777	
HK-90	27.432	136.6	6.03	7982	
HK-100	30.48	142.5	7.79	11082	
HK-110	33.528	132.0	7.69	11133	
HK-120	36.576	53.3	6.89	6427	
HK-130	39.624	76.2	6.40	7603	
HK-140	42.672	109.3	7.62	9941	
NB-10	3.048	332.8	10.42	25613	Core Sample (CS-104 NB) collected from Nabagram, date: January 4th 2012. Coordinates: N 24 12.156 E 88 13.492
NB-30	9.144	89.2	7.59	12962	
NB-40	12.192	90.1	6.80	10598	
NB-50	15.24	108.0	7.00	9989	
NB-60	18.288	69.4	5.48	9260	
NB-70	21.336	113.6	6.08	10166	
NB-90	27.432	116.3	6.75	8087	
NB-110	33.528	150.3	7.29	10104	
NB-130	39.624	73.9	6.05	6986	

NB-140	42.672	69.5	5.94	6927	
KHN-10	3.048	35.2	7.40	6463	Core Sample (CS-106 KHN) collected from Kandi, date: January 7th 2012. Coordinates: N 23 58.570 E 88 06.814
KHN-20	6.096	1070.3	14.12	33773	
KHN-30	9.144	328.7	11.23	35598	
KHN-40	12.192	224.2	15.67	25390	
KHN-50	15.24	106.5	14.03	28269	
KHN-60	18.288	446.7	11.44	35314	
KHN-70	21.336	981.9	11.04	36121	
KHN-80	24.384	51.9	5.50	6182	
KHN-90	27.432	81.9	5.71	4404	
KHN-100	30.48	444.7	9.51	31748	
KHN-110	33.528	2081.5	9.92	35508	
Montana	Standard reference material	505.1	99.37	20201	www.nist.gov/srm National Institute of Standards and Technology US Department of Commerce NIST

Appendix-E- Sequential Extractions of Sediments

Sequential extraction results for As and Mn of Hariharpara sediment core (High As area, CS-105 HK is described below. The depth wise classifications are shallow depth (HK-30; 3 m); intermediate depth (HK-40-HK-100; 12 m-30 m) and deeper depths (HK-120-HK-140; 37m-43 m). Arsenic concentration in the nonspecifically sorbed phases were absent from intermediate depths while is present in the shallow depths (3-9 m) with a semiquantification of 1-3%. In the deeper depths arsenic concentration in the nonspecifically sorbed phases are only seen at 37 m depth and Arsenic concentration is more or less equally distributed at all depths and it is ~30%. At shallow depths the As concentration in amorphous and poorly crystalline hydrous oxides of Fe and Al phases are the same and it is 10-12 %. But decreases in concentration from shallow to intermediate depths and the ranges are ~15% (12 m) and ~2% (30 m). At deeper depths the As concentration increases in concentration from 20% (37 m) to 55% (43 m). Arsenic concentrations about ~30 % in well crystalline hydrous oxides of Fe and Al as seen at all depths. There is a gradual decrease in concentration of As in residual phases (Fig. A).

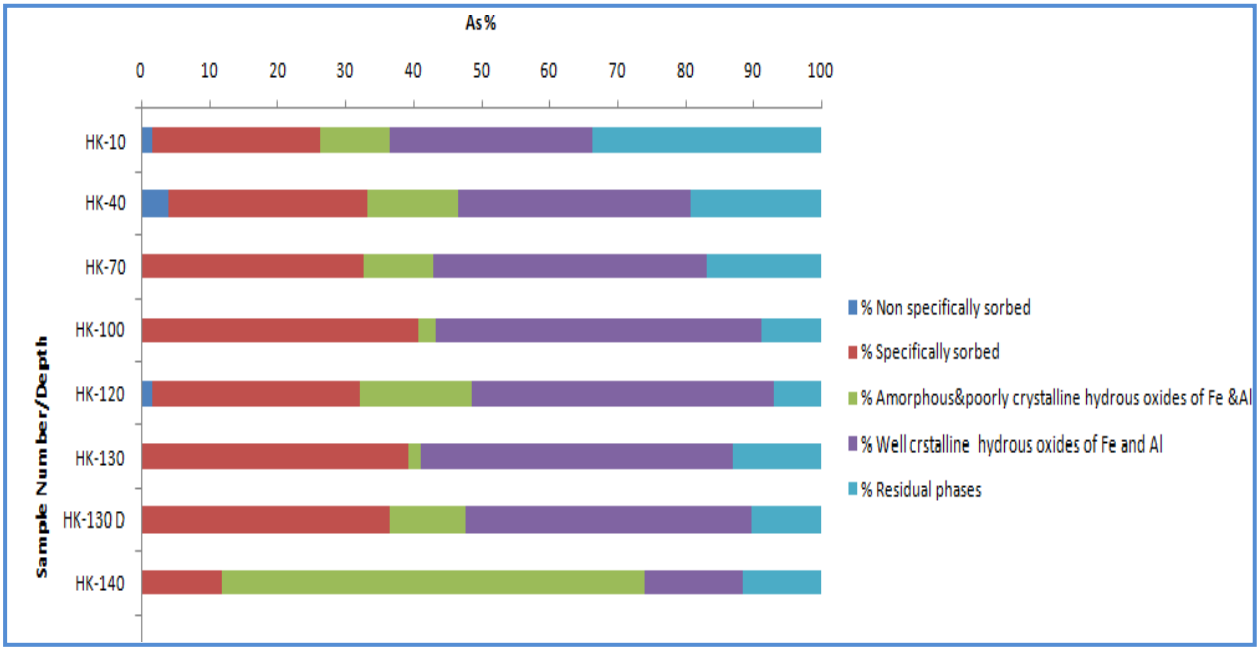


Figure A: Distribution of As within various sediment fractions in Drill Core CS-105 HK. Total depth of the core is 43m. (HK-10 = 10 ft (~3 m) depth; HK-140 = 110 ft (~43 m) depth).

Mn concentration was present in almost all phases of Hariharpara aquifer sediments. Highest concentration was presnt in the residual phases and is equally distributed (60%) in almost all depths except ~32% at 3 m depth (shallow). The lowest Mn concentration is presnt in non specifically sorbed phases and is also equally distributed, 5-6% at all depths except ~23% at 3 m. Mn concentration in specifically sorbed, amorphous and poorly crystalline hydrous oxides of Fe and Al phases and well crystalline hydrous oxides of Fe and Al are equally distributed at all depths and the concentrations are ~10%,~7% and ~17%; except at 3 m depth

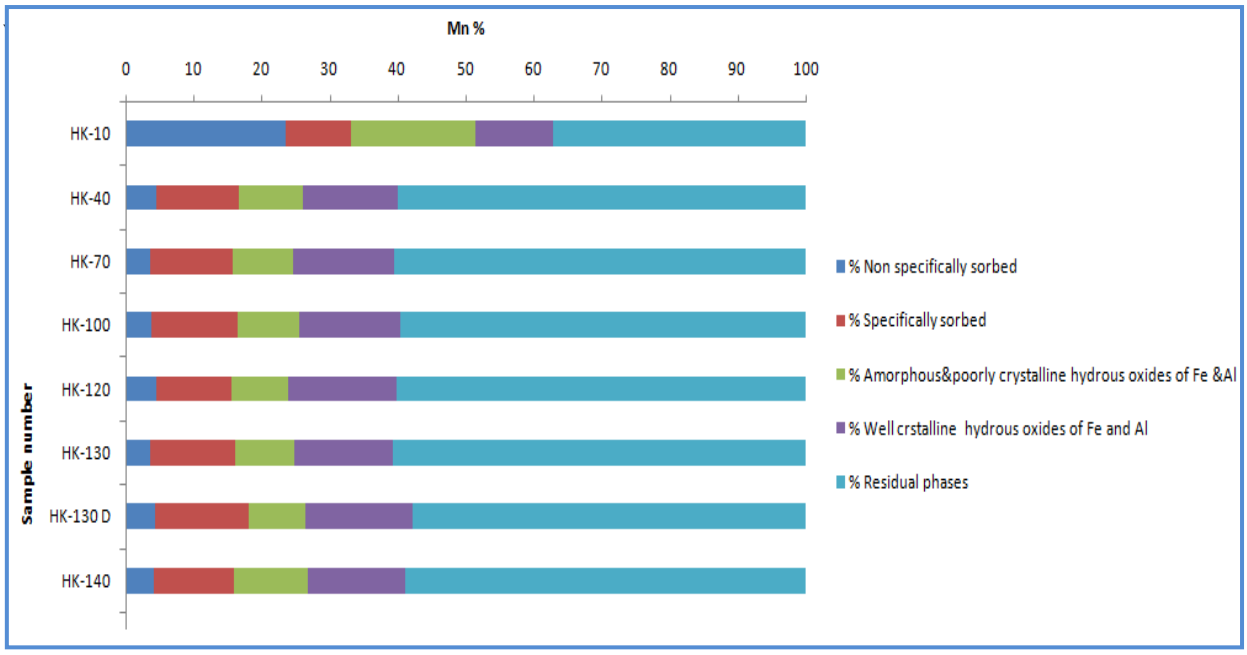


Figure B: Distribution of Mn in various sediment fractions in Drill Core CS-105 HK. Total depth of the core 43m. (e.g. HK-10 = 10 ft (~3 m) depth; HK-140 = 110 ft (~43 m) depth)

Fe (t) is also distributed equally at all depths in Hariharpara in most of the sediment fractions. Maximum concentration of Fe (t) was observed in residual phases and it is 50-60 %. The % of Fe in the residual fractions were almost same at all depths. Concentration of Fe (t) in the well crystalline hydrous oxides of Fe and Al was around 20 % and was equally distributed in all depths. Least amount of Fe (t) was present in amorphous and poorly crystalline hydrous oxides of Fe and Al and was also equally distributed (~5 %) at all depths in this phase. In specifically sorbed fraction, the concentration of Fe (t) is around 15 % are also equally distributed at all depths in this fraction. There is no trace of Fe(t) present in nonspecifically sorbed phase (Fig. C).

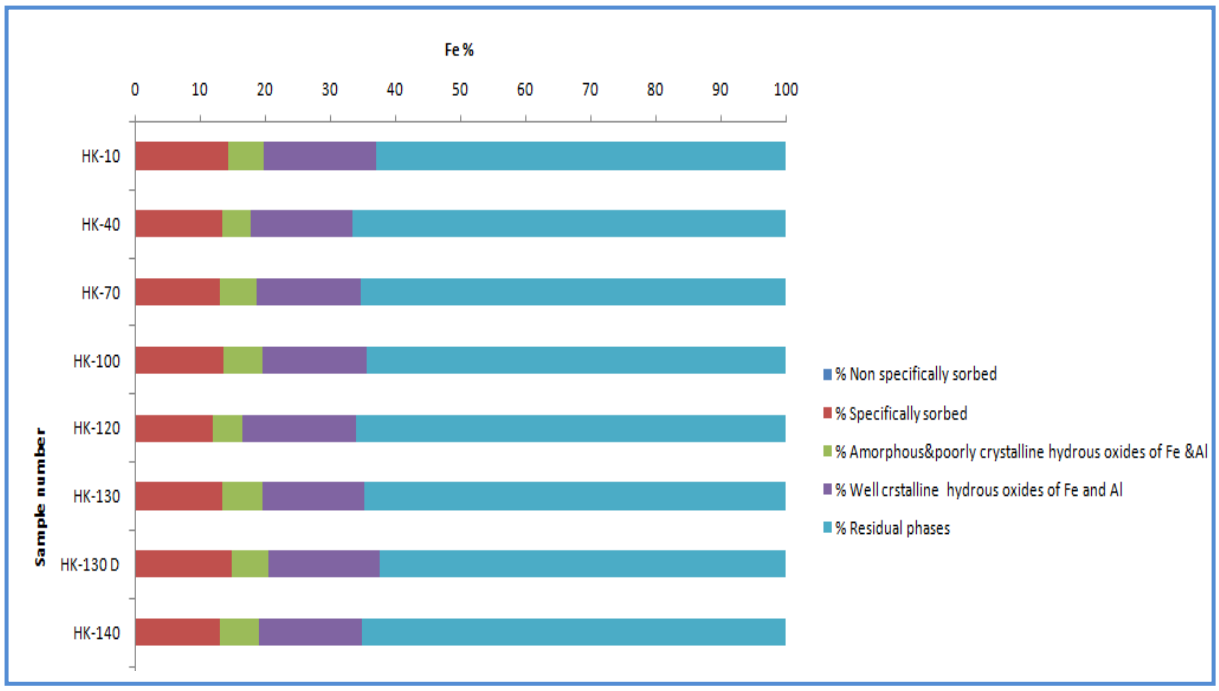


Figure C: Distribution of Fe(t) in various sediment fractions in Drill Core CS-105 HK. Total depth of the core 43m. (e.g. HK-10 = 10 ft (~3 m) depth; HK-140 = 110 ft (~43 m) depth)

Sequential extraction results of Kandi core also shows similar kind of results. As is absent in nonspecifically sorbed phases. But in the specifically sorbed phases the concentration of As was gradually decreasing from the shallow depths (KHN-10 (3m); 35 %) to intermediate depths (KHN-100 (30 m); 20 %). While in this phase at the deeper depths, 34 m (KHN-110) As concentration again increases and was ~ 23 % . In amorphous and poorly crystalline hydrous oxides of Fe and Al, the As concentration was different at different depths. At the shallow depths (KHN-10) , As concentration is ~20%. Intermediate depths the concentration of As increases from top levels(KHN-40; 2%) to bottom level (KHN-100; 12%). Again at deeper levels the concentration of As in this phase decrease (KHN-110; 2%). In the well crystalline hydrous oxides of Fe and Al phase, concentration of As was almost equally distributed from shallow (KHN-10; ~37 %) to deep depths (30 %). As concentration in residual phase were also different at different depths. At shallow depths (KHN-10) the concentration of As was very low and is ~3%. At intermediate depths the concentration of As in this phase decreases from the top levels (KHN-40; 25 %) to certain parts of bottom levels (KHN-70, 15 %), then again increases at the

deeper parts of the intermediate depth (KHN-100, KHN-100 (D); 40 %, 18 %). At the deeper depths (KHN-110, 34 m) the concentration of As in the residual phase was 32 % (Fig. D)

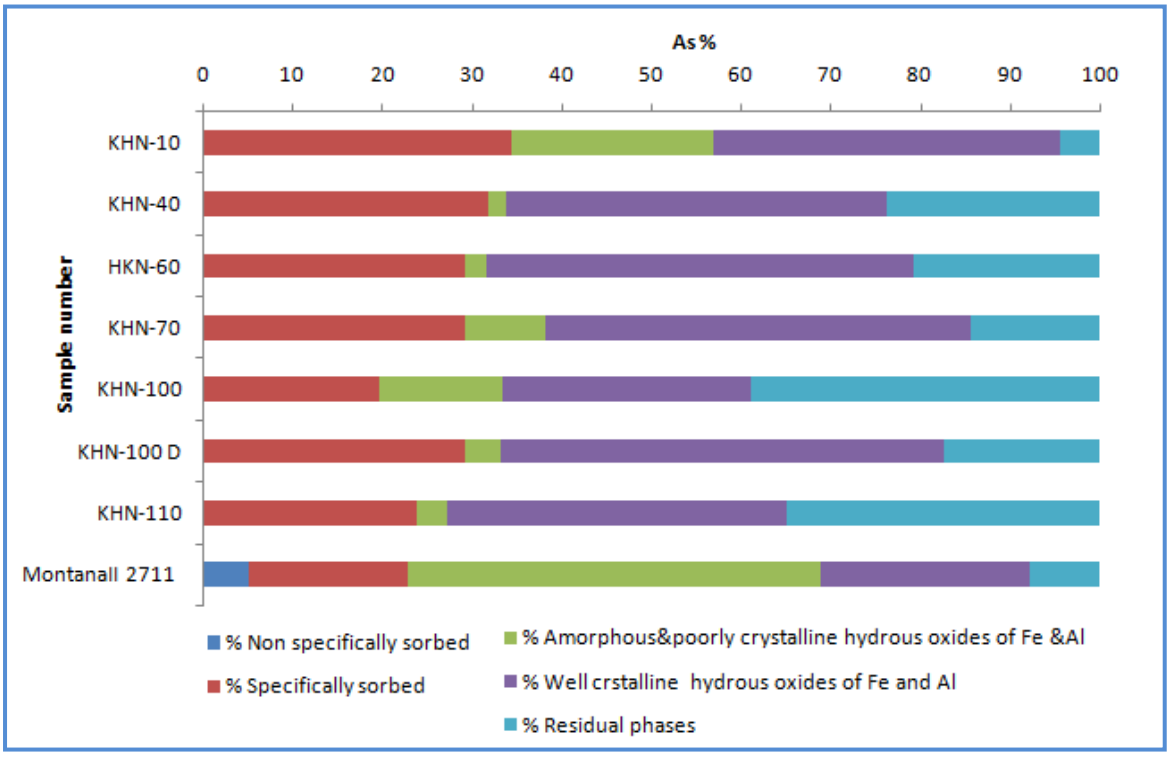


Figure D: Distribution of As in various sediment fractions in Drill Core CS-106 KHN. Total depth of the core 34m. (e.g. KHN-10 = 10 ft (~3 m) depth; KHN-110 = 110 ft (~34 m) depth). *D-duplicate sample (KHN-100 D)

Mn concentration of different sediment fractions in Kandi area was almost similar to the other areas and was distributed unequally among all sediment fractions. Mn concentration in nonspecifically sorbed phases was very less and unequally distributed at different depths. At shallow depths (KHN-10) the concentration was ~3%. In the top portion of the intermediate depth (KHN-40) Mn concentration was 12 % and it decreases to 3 % and <1 % at KHN-60 (18.3 m) and KHN-70 (21.3 m). Mn concentration increased to ~5% and 3% at the bottom portions of intermediate depth (KHN-100 and KHN-100 D). The concentration of Mn again decreased to ~2% at deeper depth (KHN-110, 34 m). Mn concentration in specifically sorbed phase is unequally distributed at all depths. At shallow depth (KHN-10,3 m) the concentration of Mn in this phase (specifically sorbed phase) is ~7 %. There was an overall decrease in Mn concentration with depth in specifically sorbed phase at intermediate depth to deeper depth (KHN-40 to KHN-110). The maximum Mn concentration of 10 % was observed at top portion

of intermediate depth (KHN-40, 12.2 m). The lest Mn concentration was found at deeper depth (KHN-110, 34 m). Most of the Mn was present at the amorphous and poorly crystalline hydrous oxides of Fe and Al phase and the maximum concentration observed was ~70% and was present at the deeper depth (KHN-110, 34 m). The minimum Mn concentration 15 % and was present at 12.2 m (KHN-40) depth (intermediate depth). In the well crystalline hydrous oxides of Fe and Al phase, Mn concentration at the shallow depth was 5%. At the intermediate depth it is almost equally distributed and ranges ~10-15%. Mn concentration changes to 5 % at deeper depths (KHN-110, 34 m). Mn concentration in the residual phase at shallow depth (KHN-10) was ~37 %. There is an increase of Mn concentration at the top level of intermediate depth (KHN-40,12.2 m) and is ~42 %. Then there was a decrease of Mn concentration at the mid portion of the intermediate depth (KHN-60, 18 m) and was 20%, then there was an increase of Mn concentration till deeper portion of intermediate depth (KHN-100 and KHN-100 D, 30 m) and the concentrations are 35 % and 30 % (Fig. E)

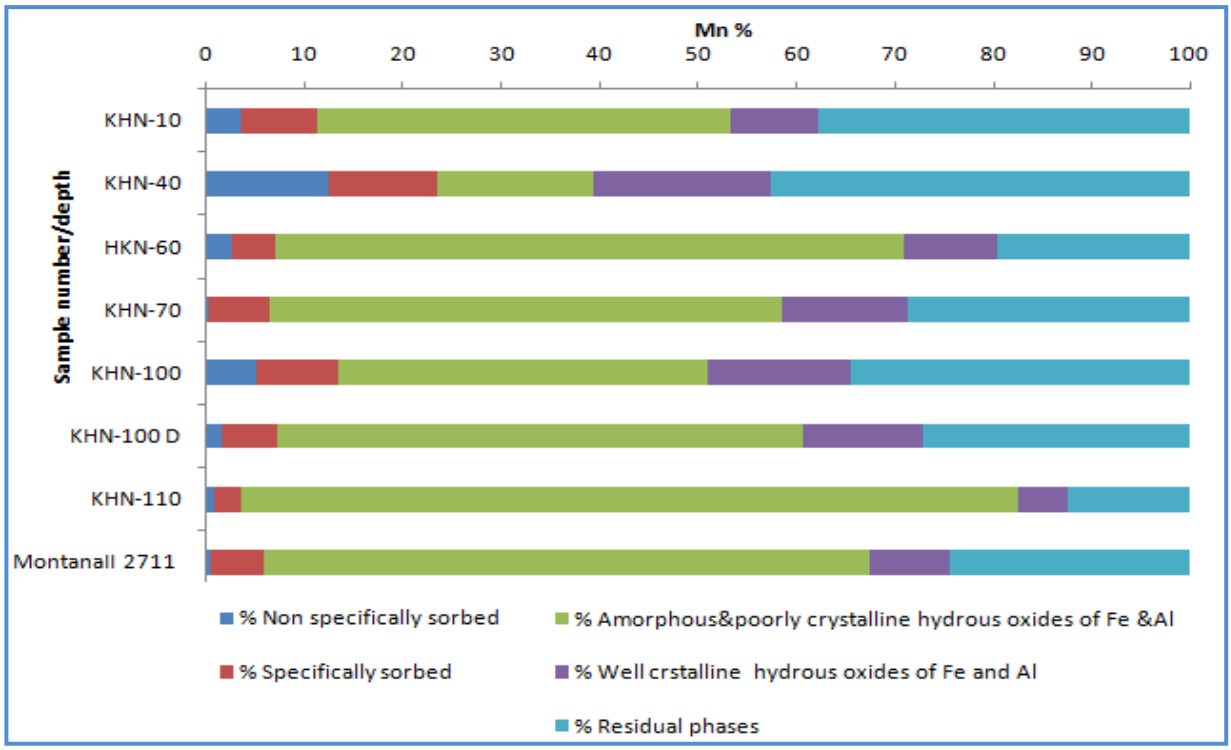


Figure E: Distribution of Mn in various sediment fractions in Drill Core CS-106 KHN. Total depth of the core 34m. (e.g. KHN-10 = 10 ft (~3 m) depth; KHN-110 = 110 ft (~34 m) depth). *D-duplicate sample (KHN-100 D)

The overall distribution of Fe (t) in various sediment fractions of Kandi aquifer sediments look similar to the Hariharpara Fe (t) distribution. The concentration of Fe (t) in non-specifically sorbed phases was totally absent here. Fe (t) concentration in specifically sorbed phases changes with depth. It was high at shallow depths (KHN-10, 3 m) and was ~15 %. In the top portion of the intermediate depth (KHN-40, 12.2 m) the Fe (t) concentration in specifically sorbed phase was 13 % and it decreased to 10% at 18.3 m and remained same throughout till the deeper depths (KHN-110, 34 m). Fe (t) concentration in the amorphous and poorly sorbed phases at shallow depth was ~4% and which decreases to <1% at top portion of intermediate depth (KHN-40,12.2 m). Then it there was an overall increase of Fe (t) concentration from KHN-60 (18.3 m) to deeper depths, KHN-110 (34 m) and was ~27 %. In well crystalline hydrous oxides of Fe and Al phase the Fe(t) concentration is almost equally distributed throughout the depths and it was ~20 %. The maximum amount of Fe (t) concentration is observed at residual phases and there was an overall decrease in trend from shallow depths, KHN-10 (3 m) was 65% and at deep depth , KHN-110 (34 m) it is 45% (Fig. F).

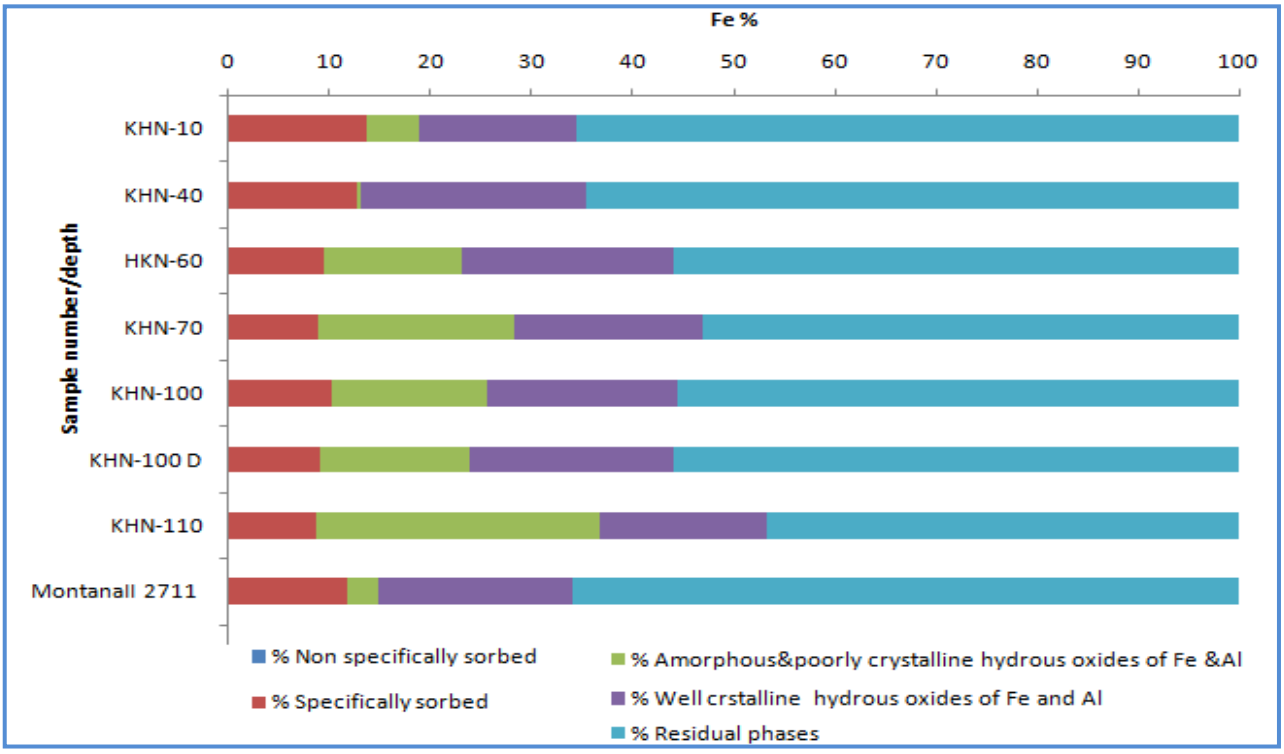


Figure F: Distribution of Fe (t) in various sediment fractions in Drill Core CS-106 KHN. Total depth of the core 34m. (e.g. KHN-10 = 10 ft (~3 m) depth; KHN-110 = 110 ft (~34 m) depth). *D-duplicate sample (KHN-100 D)

Appendix-F- Sequential Extraction Results

Sample ID	Step-1			Step-2			Step-3			Step-4			Step-5		
	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg
BM-10	0.00	11.71	0.54	0.50	18.72	47.71	1.32	35.98	1735.13	0.88	21.82	3521.56	1.30	68.07	6159.70
BM-30	0.00	4.44	0.00	0.45	6.11	0.20	0.18	43.14	1863.01	0.31	12.08	1006.85	0.62	0.32	26.27
BM-40	0.00	4.85	0.19	0.94	5.37	0.24	0.63	183.69	4180.72	0.45	23.50	2360.73	1.55	1.94	225.76
BM-50	0.00	4.07	0.50	1.96	3.69	55.09	1.05	23.92	1759.86	0.17	8.70	2722.62	3.38	52.37	7659.84
BM-70	0.00	7.46	0.00	0.52	9.35	0.22	0.43	323.81	9701.01	0.12	36.38	1940.55	1.29	161.30	6878.65
BM-90	0.00	14.08	0.00	0.86	14.96	0.02	1.54	508.29	4467.01	0.89	41.73	1490.37	2.60	585.90	9185.98
BM-100	0.00	7.73	0.00	0.36	10.02	0.87	0.52	11.35	557.51	0.76	15.02	1971.01	0.98	45.69	4128.78
BM-110	0.00	14.00	0.27	0.29	16.82	8.15	0.46	20.25	581.27	0.50	11.67	1355.63	1.54	60.14	3417.07
BM-110(D)	0.00	14.03	0.00	0.55	17.45	6.47	0.23	18.33	529.12	0.37	12.98	1482.18	1.02	58.17	3199.94

BM= Beldanga, D= Duplicate

Sample ID	Step-1			Step-2			Step-3			Step-4			Step-5		
	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg
HK-10	0.07	45.53	18.65	1.05	18.23	3359.50	0.43	35.32	1315.82	1.28	22.06	4065.26	1.43	71.70	14877.79
HK-40	0.12	5.22	0.12	0.94	13.78	1640.40	0.42	10.63	531.93	1.09	16.08	1914.24	0.61	68.29	8128.61
HK-70	0.00	3.96	0.92	0.92	13.24	1190.60	0.29	9.87	517.66	1.13	16.22	1458.42	0.48	66.27	5957.12
HK-100	0.00	3.24	0.05	0.87	10.66	1041.86	0.05	7.78	463.96	1.03	12.52	1223.48	0.19	50.69	4952.40
HK-120	0.05	4.14	0.00	0.90	10.00	919.95	0.48	7.56	346.16	1.31	14.51	1334.96	0.21	54.74	5036.87
HK-130	0.00	3.76	0.01	0.78	13.23	1140.22	0.03	9.06	529.96	0.91	15.45	1331.68	0.26	63.91	5508.98
HK-130 D	0.00	4.35	0.13	0.91	13.95	1238.52	0.28	8.45	464.80	1.05	16.00	1421.16	0.26	58.45	5190.09
HK-140	0.00	4.75	0.00	0.82	13.74	1016.15	4.23	12.57	467.18	0.99	16.69	1234.33	0.79	68.50	5066.49

HK= Hariharpara, D=Duplicate

Sample ID	Step-1			Step-2			Step-3			Step-4			Step-5		
	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg
NB-10	0.00	20.24	0.48	0.89	19.84	17.67	0.62	78.99	396.22	1.14	28.46	5535.82	1.01	15.07	2626.15
NB-40	0.00	23.28	0.00	0.02	11.60	12.68	0.34	3.84	240.82	0.06	5.80	1536.19	0.68	14.87	1618.71
NB-50	0.00	34.10	0.00	0.67	15.02	26.34	0.10	5.32	208.95	0.30	6.69	1605.08	1.02	25.78	2722.74
NB-90	0.00	46.34	0.00	0.10	20.51	21.42	0.37	8.56	317.03	0.00	6.37	1397.60	1.11	16.00	1717.31
NB-130	0.00	29.67	1.22	0.38	11.09	34.35	0.09	4.22	171.08	0.12	4.06	912.97	0.83	11.72	1404.92
NB-140	0.00	28.92	0.07	0.29	11.91	22.24	0.10	3.47	199.27	0.07	4.49	1033.86	1.13	15.08	1694.22
Montana-II 2711	2.92	1.75	0.21	11.70	4.25	0.08	21.69	191.24	693.38	8.69	20.05	3278.05	2.93	47.20	4347.60

NB-=Nabagram, Montana-II 2711= Soil Reference Material, www.nist.gov/srm, National Institute of Standards and Technology US Department of Commerce, NIS

Sample ID	Step-1			Step-2			Step-3			Step-4			Step-5		
	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg	As mg/kg	Mn mg/kg	Fe mg/kg
KHN-10	0.00	2.61	0.00	0.69	5.90	1659.54	0.45	31.42	627.19	0.78	6.67	1875.70	0.09	28.24	7938.68
KHN-40	0.00	17.50	2.73	2.84	15.28	3982.44	0.17	22.28	118.91	3.81	25.37	6901.13	2.12	59.64	20095.46
HKN-60	0.00	14.98	0.77	0.69	25.66	3103.48	0.06	365.51	4498.63	1.13	54.96	6898.53	0.49	112.08	18437.80
KHN-70	0.00	0.86	0.94	1.07	34.15	3094.20	0.32	285.01	6753.42	1.74	69.95	6551.32	0.53	156.57	18478.08
KHN-100	0.00	8.70	0.76	0.58	13.81	2583.53	0.40	63.44	3936.47	0.82	24.76	4767.99	1.15	58.17	14168.27
KHN-100 D	0.00	4.78	0.66	0.91	17.44	2656.65	0.12	162.44	4350.60	1.55	37.23	5955.21	0.54	82.43	16480.69
KHN-110	0.00	7.53	0.90	0.85	24.91	2305.69	0.12	710.37	7381.84	1.34	44.86	4333.38	1.24	112.40	12327.47
Montana-II 2711	2.67	1.73	0.41	9.31	19.24	2696.44	24.36	219.32	707.03	12.33	29.21	4454.65	4.07	86.92	15193.46

KHN=Kandi, D=Duplicate, Montana-II 2711= Soil Reference Material, www.nist.gov/srm, National Institute of Standards and Technology US Department of Commerce, NIST

Appendix-G- Organic Matter Extractions from Sediment

Organic matter extraction was performed to find out the approximate amount of organic matter and organic bound As, Mn and Fe. During this test, total amount of organic matter present in the sediments were also calculated using combustion method. A total of 14 aquifer samples (Beldanga=4 and 1 duplicate; Hariharpara=4, Nabagram=3 and one duplicate , Kandi=3) 2 duplicates and one standard reference material (Montana II 2711, www.nist.gov/srm ; national institute of standards and technology US department of commerce NIST) were used for the experiment. The experiment started with the preparation of 0.7 *M* NaOCl (adjusted to pH 8.5 with HCl) by adding 790.067 mL of NaOCl in deionized water and adjusted to pH 8.5 by adding 5mL of trace grade HCl. By adding NaOCl to the soil cause digestion of organic matter present in the sediments and during this process the organic bound As and Mn will also comes to the solution and both can be measured. (Hettiarachchi et al., 2003).

Concentration of As, Fe (t) and Mn in Hariharpara core (CS-105 HK; high As area) obtained by the OM extracts changed with depth. Maximum Fe(t) and Mn concentration were found at 30 m (depth) and they are 23.6 mg/kg and 0.091 mg/kg respectively. While As concentration reduced to 0 at 30 m depth (depth). There was slight increase in As concentration from shallow (3 m) depth (0.076 mg/kg) to intermediate (21.3 m) depth (0.077 mg/kg). After 30 m depth, As concentration increased within the sediments. It reached 0.063 mg/kg at 40 m depth. Fe (t) concentration decreases to 17.08 mg/kg and Mn concentration changes to 0 at deeper depth levels (40 m). (Fig. A)

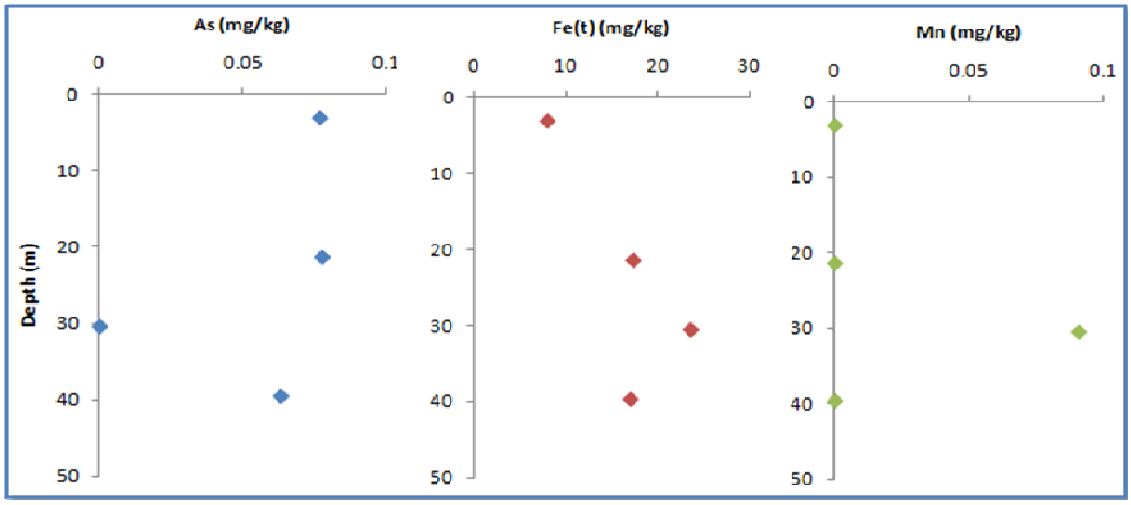


Figure A: Depth variation in concentrations (mg/kg) of As, Fe (t) and Mn in Hariharpara aquifer core sediments (CS-105 HK; high As area). Depths are in meters and concentrations are in mg/kg.

Results of organic matter extraction of Nabagram core (CS-104 NB; low As area) reveled that there were no As and Mn concentration (0). Whereas Fe (t) showed a change in concentration with depth. The maximum Fe (t) concentration was observed at intermediate depth (27.4 m) in sample NB-90. Then it decreased to 12.5 mg/kg at deeper depths (40 m). A duplicate sample (NB-90 D)was also kept for analysis to check the accuracy and concentration of Fe (t) as almost similar to the original sample and it was 12.959 mg/kg (slightly less) where as the concentration of As and Mn were 0 (same as the original sample NB-90) Fig. B.

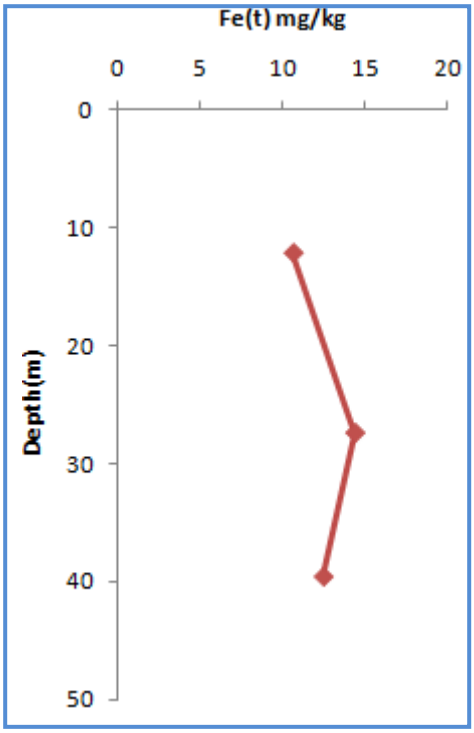


Figure B: Depth variation of concentration of Fe(t) mg/kg in Nabagram aquifer core sediments (CS-104 NB; low As area). The concentration of As and Mn are below detection limit. Depths are in meters and concentrations are in mg/kg.

Sample name	As (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	DOC (mg/ Kg)	Total N %	TOC %
Blank	0.08	5.81	0.00	No data	No data	No data
BM-10	0.00	13.46	1.33	67.35	0.09	0.47
BM-50	0.18	604.67	15.24	171.40	0.28	4.34
BM-90	0.01	12.06	0.00	60.33	0.07	0.35
BM-110	0.06	8.98	0.00	57.07	0.05	0.52
BM-110(D)	0.05	8.71	0.00	56.24	No data	No data
HK-10	0.08	8.00	0.00	58.14	0.05	0.78
HK-70	0.08	17.38	0.00	56.27	0.06	0.19
HK-100	0.00	23.62	0.09	55.58	0.04	0.20
HK-130	0.06	17.08	0.00	61.15	0.03	0.21
NB-40	0.00	10.63	0.00	74.64	0.04	0.18
NB-90	0.00	14.40	0.00	62.78	0.05	0.26
NB-90(D)	0.00	12.96	0.00	62.31	No data	No data
NB-130	0.00	12.47	0.00	71.41	0.05	0.18
KHN-30	0.00	9.84	0.00	118.90	0.06	0.47
KHN-60	0.07	33.22	9.12	120.90	0.08	0.93
KHN-100	0.19	13.99	3.99	122.40	0.10	0.81
Montana std	8.36	31.80	129.82	245.20	0.17	1.60

Table C: Concentration of As, Fe (t), Mn, DOC, TN (total nitrogen) and TOC (total organic carbon) in selected sediments. Concentration of As, Fe (t), Mn and DOC are obtained from OM extraction. TN and TOC are obtained by combustion method (LECO TruSpec CN analyzer), BM-Beldanga; HK-Hariharpara, NB-Nabagram, KHN-Kandi

Appendix-H- Tubewell Water Quality Parameters As Measured in Field, Jan. 2012

Sample No.	Well depth (m)	Salinity(ppt)	Resistivity (Ω cm)	TDS(mg/L)	Conductivity(µS/cm)	pH	Water Temperature(°C)
TW-100	37.19	0.01	271000	1.84g/l	3.48	7.69	26.4
TW-101	33.53	0.15	41500	98	155.5	7.69	25.2
TW-102	39.62	7.21	79.4	2.3g/l	2.6	7.62	27.1
TW-103	39.62	7.18	8.1	6.34	12.27	7.6	26.9
TW-104	33.53	5.95	93.6	5.55	10.6	7.68	27
TW-105	33.53	6.57	85.3	5.79	11.66	7.84	26.8
TW-106	33.53	0.45	1110	457	926	7.71	24.6
TW-108	27.43	0.43	1140	448	925	7.16	26.8
TW-109	25.91	5.91	95.9	5.16g/l	10.35	7.16	27
TW-110	33.53	0.46	1.9	470	906	7.3	26.8
TW-111	36.58	4.03	138	3.68g/l	7.21	6.9	26.7
TW-112	36.58	0.45	1100	462	941	7	26
TW-113	45.72	5.86	96.8	5.21g/l	10.7	6.71	26.7
TW-114	36.58	0.44	1120	453	930	6.59	26.7
TW-115	35.97	0.44	1130	448	908	7.18	27.1
TW-117	30.48	0.45	1090	469	950	7.53	26.5
TW-118	18.29	12.02	49.6	10.08g/l	20.2	7.85	24.1
TW-119	18.29	8.05	70.9	6.99g/l	14.03	7.71	26.4
TW-120	18.29	0.46	1080	469	923	6.76	25.7
TW-121	12.19	0.46	1060	465	939	6.6	24.9
TW-122	15.24	0.44	1050	455	895	7.43	26.3
TW-123	18.29	0.46	1070	480	911	7.63	26.1
TW-124	15.24	7.32	78.4	6.4 g/l	12.81	7.74	25.5
TW-125	15.24	0.46	1.05	470	926	7.26	26
TW-126	15.24	0.44	1100	452	906	7.52	27.4
TW-127	24.38	7.39	76.7	6.43g/l	12.68	7.47	27.5
TW-128	18.29	0.48	1060	489	928	No data	25
TW-129	18.29	0.45	1.05	466	941	No data	26
TW-130	22.86	0.47	1070	457	930	8.14	26.2
TW-131	21.34	0.45	1070	461	926	8.27	26.3
TW-132	21.34	0.47	980	482	988	8.13	26
TW-133	21.34	0.45	10.7	460	921	No data	27.6
TW-134	21.34	0.46	1030	470	931	7.9	26.8
TW-135	36.58	0.46	1060	466	963.3	7.91	24.7
TW-136	36.58	0.45	1090	465	912	8.08	25.3
TW-137	18.29	8.84	67.7	7.06g/l	14.27	No data	26.4
TW-138	12.19	0.47	1050	487	990	No data	25.4
TW-139	36.58	6.59	85.6	5.81g/l	11.67	No data	24.6

Appendix-I- Fe (t), Mn^{2+}, As and NH_4^+Concentration as Measured in Field, Jan. 2012

Sample No.	Fe (t) (SPM) mg/L	Mn^{2+}(kit) mg/L	Mn^{2+} (SPM) mg/L	As mg/L low Range Kit	As EZ mg/L High Range Kit	NH_4^+ (SPM) mg/L
TW-100	0.14	0.2	0.4	10- 30	10	0.02
TW-101	>6.28	0	BDL	70-300	175-500	0.01
TW-102	1.25	0	BDL	500	250-500	0.01
TW-103	0.56	0.9	0.7	10-30	25-50	0.02
TW-104	2.7	0	BDL	300-500	>500	0.02
TW-105	0.09	1.2	1.5	No data	10	0.01
TW-106	>6.33	0	BDL	300-500	250-500	BDL
TW-108	1.06	0.6	0.4	10	0-10	0.01
TW-109	0.8	0.7	0.2	10	0	0.02
TW-110	0.13	2	9 &14.5	10-30	0	0.02
TW-111	0.15	3	2.4	10-30	0	0.01
TW-112	0.96	2.8	1.7 & 1.8	10	0	0.02
TW-113	1.4	2	0.95	0-10	0	0.01
TW-114	1.21	2.4	8.2	10-30	0-10	0.01
TW-115	1.21	2.3	5.1	10-30	0	No data
TW-117	0.75	0.4	3.1	10	0	0.04
TW-118	0.05	0-0.2	1	0-10	0	BDL
TW-119	OMR	0.6	0.5	300-500	250-500	BDL
TW-120	OMR	0.4	0.5	300-500	250-500	BDL
TW-121	OMR	1.4	1.3	70-300	250-500	No data
TW-122	OMR	1.4	1.2	> 500	70	BDL
TW-123	OMR	0.4	0.3	300-500	250-500	BDL
TW-124	OMR	0.4	BDL	70-300	250-500	No Data
TW-125	OMR	1.4	1.1	70-300	50-100	0.01
TW-126	OMR	0.4	BDL	70-300	100-250	BDL
TW-127	0.43	0.8	1.6	70-300	100-250	No data
TW-130	0.21	0.4	1	0-10	10	0.01
TW-131	1.03	0.4	1.2	10-30	25-50	0.05
TW-132	0.89	BDL	0.5	10-30	0-10	0.06
TW-133	0.43	BDL	1.5	10-30	0-10	BDL
TW-134	0.96	BDL	0.9	10-30	0-10	BDL
TW-135	0.53	BDL	0.8	0-10	0-10	BDL
TW-136	0.44	BDL	1	10-30	0-10	0.01

SPM= Spectrophotometer; Kit= Test kit; OMR= Over Measuring Range of Spectrophotometer, BDL= Below Detection Limit

Appendix-J- Concentration of Anions & Dissolved Oxygen for Tubewells as Measured in Field, January 2012

Sample No.	Well depth (m)	NO_3^- (Kit) mg/L	NO_3^- (SPM) mg/L	SO_4^{2-} (Kit) mg./L	SO_4^{2-} (SPM) mg/L	PO_4^{3-} (Kit) mg/L	PO_4^{3-} (SPM) mg/L	Cl^- Kit mg/L	DO Kit mg/L	Alkalinity as (HCO_3^-)mg/L
TW-100	37.1856	BDL	0.1	BDL	BDL	0.9	0.37	29	1	270
TW-101	33.528	BDL	BDL	BDL	BDL	3.5	0.89	20	5	540
TW-102	39.624	BDL	0.1	BDL	BDL	0.9	0.6	20	4	486
TW-103	39.624	BDL	0.1	BDL	2	0	0.54	18	3	648
TW-104	33.528	BDL	BDL	BDL	BDL	0-5	0.49	24	5	324
TW-105	33.528	BDL	BDL	BDL	BDL	0.2	0.18	60	4	378
TW-106	33.528	BDL	BDL	BDL	BDL	1	1.91	20	3	324
TW-108	27.432	BDL	0.3	BDL	11	BDL	1.04	49	3	378
TW-109	25.908	4	1.8	BDL	17	0.27	0.48	52	3	378
TW-110	33.528	No data	0.5	50-55	29	0.35	0.68	50	5	486
TW-111	36.576	BDL	0.2	BDL	11	0.4	0.31	40	1.5	270
TW-112	36.576	BDL	0.1	65	55	0.3	0.31	80	3	378
TW-113	45.72	BDL	0	<50	22	0.3	0.47	40	4	378
TW-114	36.576	0-4	0.9	55	33	0.33	0.79	62	4	324
TW-115	35.9664	0-4	2.1	<50	26	0.2	0.38	60	5	324
TW-117	30.48	0-4	0.2	52	36	0.27	0.59	63	4	378
TW-118	18.288	No data	2.7	95	>90	BDL	0.56	53	5	324
TW-119	18.288	BDL	BDL	<50	2	11	OMR	40	4	432
TW-120	18.288	0-4	BDL	BDL	11	3.9	2.39	56	5	432
TW-121	12.192	BDL	BDL	55	33	1	1.91	42	3	432
TW-122	15.24	No data	BDL	BDL	BDL	2	1.53	28	4	324
TW-123	18.288	BDL	BDL	BDL	BDL	7.5	OMR	10	4	432

TW-124	15.24	No data	BDL	BDL	9	2.9	2.49	12	3	486
TW-125	15.24	No data	BDL	BDL	5	1.5	2.15	32	4	432
TW-126	15.24	No data	BDL	<50	15	2.2	1.43	45	5	378
TW-127	24.384	No data	0.2	BDL	3	1.2	1.1	28	5	432
TW-130	22.86	No data	0.1	BDL	BDL	1.5	1.34	100	4	486
TW-131	21.336	No data	BDL	BDL	BDL	1.1	1.33	110	No data	432
TW-132	21.336	No data	BDL	BDL	BDL	0.2	0.97	138	No data	378
TW-133	21.336	No data	0.1	BDL	BDL	1	0.55	140	No data	430
TW-134	21.336	No data	0.5	BDL	BDL	0.4	0.4	148	No data	545
TW-135	36.576	No data	0.4	BDL	BDL	0.4	0.42	142	4	630
TW-136	36.576	No data	0.1	BDL	BDL	0.06	0.8	144	No data	435

OMR= Over Measuring Range of Spectrophotometer; SPM= Spectrophotometer ; Kit= Test Kit; BDL=Below Detection Limit, TW- Tubewells

Appendix-K- Concentration of As in Tubewells, Murshidabad, 2009 Through 2013

Si no.	Well name	Latitude	Longitude	Depth in m	As ppb	Year of collection
Beldanga						
1	TW-1 (BM)	N23°56.371	E88°16.167	36.6	4394	2009
2	TW-2 (BM)	N23°56.359	E88°16.174	33.56	4622	2009
3	TW-3 (BM)	N23°56.396	E88°16.130	33.56	310	2009
4	TW-5 (BM)	N23°56.331	E88°16.131	33.56	1299	2009
5	TW-6 (BM)	N23°56.351	E88°16.187	35.7	14	2009
6	TW-8 (BM)	N23°56.399	E88°16.187	35.97	1	2009
7	TW-38(BM)	N23°56.276	E88°16.178	33.6	81	2010
8	TW-39(BM)	N23°56.392	E88°16.129	33.6	310	2010
9	TW-40(BM)	N23°56.329	E88°16.131	33.6	1299	2010
10	TW-71(BM)	N23°56.390	E88°16.203	36.6	3	2010
11	TW-100 BM	N 23 56.379	E 88 16.166	37.2	15	2012
12	TW-101 BM	N 23 56.369	E 88 16.116	33.52	275.9	2012
13	TW-102 BM	N23 56.319	E 88 16.213	39.62	265.2	2012
14	TW-103 BM	N 23 56.254	E 88 16.170	39.62	30	2012
15	TW-104 BM	N 23 56.223	E 88 16.104	33.5	1263.7	2012
16	TW-105 BM	N 23 56.393	E 88 16.206	33.5	10	2012
17	TW-106 BM	N 23 56.347	E 88 16.128	33.5	346	2012
18	TW-151	N23 56 10.5	E 88 16 39.1	42.7	40	2013
19	TW-152	N23 56 10.5	E 88 16 39.1	42.8	60	2013
20	TW-154	N23 56 8.5	E88 16 32.9	35.1	75	2013
21	TW-155	N 23 56 6.7	E88 16 34.6	36.6	5	2013
22	TW-156	N23 56 11.5	E 88 16 32.4	36.6	30	2013
23	TW-157	N 23 56 14	E 88 16 22.5	36.6	50	2013
Hariharpara						
1	TW-11 (HK)	N24 03.61	E88 21.509	21.4	504	2009
2	TW-12 (HK)	N24 03.69	E88 21.479	9.1	475	2009
3	TW-13 (HB)	N24 03.17	E88 21.206	33.6	250	2009
4	TW-14 (HB)	N24 03.15	E88 21.225	21.3	280	2009
5	TW-15 (HB)	N24 03.18	E88 21.215	33.53	375	2009
6	TW-17 (HB)	N24 03.182	E88 21.199	30.5	417	2009
7	TW-18 (HK)	N24 03.559	E88 21.531	18.3	582	2009
8	TW-19 (HK)	N24 03.69	E88 21.528	15.2	630	2009
9	TW-43(HK)	N24 03.570	E88 21.532	15.2	695	2010
10	TW-46(HK)	N2403.557	E88 21.533	18.3	582	2010

11	TW-48(HK)	N24 03.673	E88 21.470	9.1	476	2010
12	TW-49(HK)	N 24 03.696	E8821.477	15.2	102	2010
13	TW-50(HK)	N2403.701	E8821.373	36.6	19	2010
14	TW-118	N 24 03.692	E 88 21.606	18.3	5	2012
15	TW-119	N 24 03.684	E 88 21.614	18.3	237.6	2012
16	TW-120	N 24 03.686	E 88 21.628	18.3	400	2012
17	TW-121	N 24 03.712	E 88 21.565	12.2	285	2012
18	TW-122	N 24 03.651	E 88 21.395	15.22	400	2012
19	TW-123	N 24 03.550	E 88 21.535	18.3	376.3	2012
20	TW-124	N 24 03.654	E 88 21.363	15.3	185	2012
21	TW-125	N 24 03.654	E 88 21.363	15.2	186	2012
22	TW-127	N 24 03.999	E 88 21.682	24.4	185	2012
23	TW-158	N24 04' 48.3"	E88 21 52.4	21.3	10	2013
24	TW-159	N24 04' 39.2"	E88 21 49.3"	21.3	60	2013
25	TW-160	N24 04 32.4".	E88 21 49.3"	18.3	30	2013
26	TW-161	N24 04 36.6".	E88 21 47.1"	18.3	10	2013
27	TW-162	N24 04 28.8".	E88 21 49.6"	18.3	40	2013
28	TW-163	N24 04 12.8".	E88 21 48.2"	22.9	50	2013
Nabagram						
1	TW-32 (NB)	N2411.863	E88 13.540	24.4	1	2009
2	TW-33 (NB)	N2411.881	E88 13.534	21.3	8	2009
3	TW-34 (NB)	N2411.845	E88 13.439	21.3	0	2009
4	TW-35 (NB)	N2412.075	E88 13.385	21.3	1	2009
5	TW-60(NB)	N2411.877	E88 13.528	30.5	1	2010
6	TW-61(NB)	N2411.866	E88 13.538	30.5	2	2010
7	TW-62(NBK)	N2412.124	E88 13.464	24.4	3	2010
8	TW-108	N 24 11.846	E 88 13.435	27.4	10	2012
9	TW-109	N 24 11.876	E 88 13.453	25.9	10	2012
10	TW-110	N 24 11.847	E 88 13.376	33.5	0.4	2012
11	TW-111	N 24 11.960	E 88 13.354	36.6	15	2012
12	TW-112	N 24 12.084	E 88 13.29	36.6	15.5	2012
13	TW-113	N 24 12.141	E 88 13.289	45.7	5	2012
14	TW-114	N 24 12.139	E 88 13.243	36.6	0.4	2012
15	TW-115	N 24 12.104	E 88 13. 195	35.9	15	2012
16	TW-117	N 24 12.064	E 88 13.125	30.5	10	2012
17	TW-141 NB	N 24 11 58.7	E88 14 12.6	30.5	5	2013
18	TW-143	N 24 11 56.3	E 88 14 21.3	24.9	5	2013
Kandi						

1	TW-64(KHN)	N2358.524	E88 06.824	33.5	11	2010
2	TW-65(KHN)	N2358.585	E88 06.815	33.5	10	2010
3	TW-130	N 23 58.602	E 88 06.682	22.8	10	2012
4	TW-131	N 23 58.612	E 88 06.725	21.3	50	2012
5	TW-132	N 2358.586	E 88 06.738	21.3	15	2012
6	TW-133	N 2358.592	E 88 07.229	21.3	10	2012
7	TW-134	N 2358.587	E 88 06.813	21.3	10	2012
8	TW-135	N 2358.609	E 88 06.763	36.5	10.2	2012
9	TW-136	N 2358.320	E 88 07.192	36.5	10	2012
10	TW-144	N 2358 32.9	E88 6 46.8	54.8	5	2013
11	TW-145	N23 58 31.6	E 88 6 48.9	30.5	5	2013
12	TW-147	N 2359 54.8	E 88 6 17.4	42.7	5	2013

BM=Beldanga, HK= Hariharpara, NB=Nabagram, KHN=Kandi; Analysis was performed in ICP MS and As Test Kit

Appendix-L- Concentration of Cations in Surface and Groundwaters of Murshidabad, Jan. 2012

Sample Name	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Fe (mg/L)	Mn (mg/L)	Fe^{2+} (mg/L) (SPM)
Tubewells							
TW-100	123.05	37.82	33.92	0.55	11.13	0.85	No analysis
TW-101	122.08	31.75	30.67	3.3	11.13	0.18	0.06
TW-102	91.40	39.11	32.64	0.22	1.25	0.15	No analysis
TW-103	bdl	37.71	bdl	bdl	0.56	0.7	No analysis
TW-104	113.81	22.64	26.86	2.62	1.995	1.29	0.01
TW-105	107.95	33.54	36.49	bdl	0.09	1.11	No analysis
TW-106	121.29	29.199	30.11	2.58	13.57	0.35	0.02
TW-107	119.93	38.19	36.24	0.51	bdl	0.11	No analysis
TW-139	85.68	33.86	30.36	0.057	bdl	0.44	No analysis
TW-108	82.62	18.91	35.099	bdl	1.06	0.51	No analysis
TW-109	87.45	20.04	51.36	bdl	0.8	0.53	No analysis
TW-110	112.84	18	55.49	1.12	0.12	2.33	No analysis
TW-111	52.96	21.04	17.98	bdl	0.15	4.23	No analysis
TW-112	94.11	33.74	43.59	bdl	0.96	2.63	0.06
TW-113	77.99	26.08	27.96	bdl	1.4	0.72	No analysis
TW-113D	139.94	16.77	33.42	1.05	0.007	2.2	No analysis
TW-115	105.52	25.75	26.65	bdl	1.21	2.05	No analysis
TW-116	85.12	28.82	40.36	bdl	bdl	0.91	No analysis
TW-117	92.79	29.44	50.83	bdl	0.75	0.89	No analysis
TW-118	129.25	51.71	25.98	79.79	0.05	bdl	No analysis
TW-119	155.43	28.63	23.39	3.63	5.19	0.60	0.09
TW-120	119.46	41.52	26.66	2.37	3.97	0.24	0.11
TW-121	132.17	44.14	36.38	24.78	4.065	1.199	No analysis
TW-122	121.10	24.08	14.36	2.27	4.91	1.23	No analysis
TW-123	122.94	37.24	22.64	2.71	3.25	0.26	No analysis
TW-124	117.06	39.87	22.68	2.80	4.62	0.18	0.04
TW-125	137.64	40.27	27.53	1.20	1.52	1.33	No analysis
TW-126	113.54	40.12	33.25	3.49	bdl	0.22	No analysis
TW-127	127.55	38.67	20.71	2.95	0.43	0.82	No analysis
TW-128	114.97	35.35	16.35	1.81	bdl	bdl	No analysis
TW-129	124.13	41.06	31.16	2.93	7.20	0.35	0.11
TW-137	106.21	42.22	28.97	2.92	1.45	0.09	No analysis
TW-138	174.94	47.17	32.89	1.76	6.75	0.95	No analysis
Sajaldhara	94.24	40.12	25.57	2.92	bdl	bdl	No analysis
TW-130	27.43	7.19	266.05	bdl	0.21	1	0.04
TW-131	23.51	7.04	286.18	bdl	1.03	1.2	No analysis
TW-132	29.35	9.45	307.99	bdl	0.89	0.5	0.04
TW-133	20.99	7.36	282.01	bdl	0.43	1.5	No analysis
TW-134	282.02	9.11	328.71	bdl	0.96	0.9	No analysis
TW-135	38.01	2.29	10.05	1.97	0.07	0.04	0.06
TW-136	34.34	9.84	301.15	bdl	0.44	1	No analysis
Pond Water							
PW-102	110.45	31.17	71.80	54.58	70.85	0.47	0.03
PW-103	80.30	26.26	124.99	55.48	0.72	0.11	No analysis
PW-104	35.44	28.59	76.72	44.02	bdl	bdl	No analysis

PW-105	25.40	12.29	27.02	27.02	bdl	bdl	No analysis
PW-106	15.52	2.36	5.64	6.47	0.15	0.08	No analysis
PW-107	32.10	19.96	33.06	50.29	bdl	0.14	No analysis
PW-108	40.76	16.67	23.07	4.13	bdl	bdl	No analysis
PW-109	55.94	13.28	20.79	22.11	0.02	0.53	0.15
PW-110	60.49	19.66	32.91	12.97	bdl	bdl	No analysis
PW-111	16.14	13.67	52.50	35.36	bdl	0.22	No analysis
PW-112	29.03	19.44	80.30	40.86	bdl	0.63	No analysis
Irrigation water							
IW-101	116.34	40.64	40.45	0.266	0.66	bdl	0.04
IW-102	105.21	25.85	36.50	1.64	0.599	0.21	0.03
IW-103	97.91	37.57	27.75	2.17	0	bdl	No analysis
IW-104	121.76	29.11	28.83	3.13	7.16	0.44	0.03
IW-105	97.81	36.38	21.45	1.92	bdl	bdl	No analysis
Sajaldhara	94.24	40.12	5.57	2.92	bdl	bdl	No analysis
Elahigunj deep tube well	102.47	35.88	38.30	0.84	bdl	bdl	No analysis
IW-106	36.34	15.94	300.72	1.12	bdl	bdl	No analysis
IW-107	28.12	9.16	279.54	1.98	bdl	bdl	0.01
IW-108	62.30	17.62	150.79	bdl	bdl	bdl	No analysis

TW=Tubewell (Shallow and Deep); PW= Ponds; IW= Irrigation wells; D= duplicate samples; bdl=Below Detection Limit; SPM-Spectrophotometer; D- Duplicate sample

Appendix-M- Anion concentration Measured using ion chromatography (IC), January 2012 Samples

Sample no	Cl^- (mg/L)	Br^- (mg/L)	NO_3^{2-} (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	F^- (mg/L)	NO_2^- (mg/L)
Tubewells							
TW-100 BM	9.73	0.01	0.58	bdl	1.48	0.59	bdl
TW-101 BM	5.73	0.01	0.67	1.22	1.45	0.41	bdl
TW-102 BM	12.03	0.94	0	0	1.21	0.49	bdl
TW-103 BM	6.51	0.01	0.68	bdl	1.5	0.64	bdl
TW-104 BM	3.99	0.01	0.53	0	1.23	0.47	bdl
TW-105 BM	9.18	0.01	0.60	bdl	1.42	0.69	bdl
'TW-106 BM	9.1	< 0.06	0.07	< 0.04	0.39	0.17	< 0.02
TW-107 BM	10.48	0.01	bdl	bdl	1.46	0.46	bdl
TW-139 BM	12.9	< 0.06	< 0.02	< 0.04	< 0.06	0.27	< 0.02
TW-108 NB	38.10	0.85	1.18	bdl	15.59	0.83	bdl
TW-109 NB	54.75	0.01	10.14	bdl	18.80	1.21	bdl
TW-110 NB	46.11	0.86	0.65	bdl	30.32	0.54	bdl
TW-111 NB	29.10	0.01	bdl	bdl	14.64	0.60	bdl
TW-112-NBK	103.28	1.01	1.31	bdl	55.93	0.66	bdl
TW-113 NBK	31.99	0.01	1.97	bdl	24.26	0.65	bdl
TW-114 NBK	67.24	1.25	5.15	bdl	35.32	0.77	bdl
TW-115 NBK	60.94	1.45	13.76	2.52	26.57	0.81	1.01
TW-115 NBK (D)	61.27	1.48	13.86	1.28	26.61	1.11	bdl
TW-115 NBK (T)	60.26	0.01	13.37	bdl	26.51	0.70	bdl
TW-116 NB	68.94	0.89	0.65	bdl	27.79	0.70	bdl
TW-117 NBK	60.04	1.47	2.47	1.29	33.83	0.62	0.89
TW-118 HK	53.79	0.01	21.22	bdl	71.01	0.36	bdl
TW119HK	29.15	0.95	0.51	bdl	1.24	0.31	bdl
TW-119 HK	27.7	< 0.09	< 0.03	< 0.06	< 0.09	< 0.03	< 0.03
TW-120 HK	78.44	0.84	0.93	1.158	1.98	0.44	1.18
TW-121 HK	37.18	0.84	1.87	bdl	35.86	0.49	1.52
TW-122 HK	16.67	0.01	0.89	bdl	5.99	0.47	1.10
TW-123HK	2.42	0.01	0.99	2.21	1.52	0.18	0.31
TW-123HK (D)	2.35	0.01	0.92	1.39	1.48	0.17	bdl
TW-123HK (T)	2.36	0.01	0.92	1.30	1.44	0.17	bdl
TW-124 HK	2.40	0.01	1.31	bdl	1.46	0.32	3.12
TW-125 HK	21.90	0.01	0.64	bdl	15.25	0.46	2.00
TW-126 HK	44.44	0.01	1.09	bdl	20.74	0.32	0.31
TW-126 HK (D)	44.24	0.01	1.06	bdl	20.90	0.29	0.30
TW-126 HK (T)	44.52	0.01	1.04	bdl	20.69	0.37	0.37
TW-127 HK	17.58	0.01	0.60	1.52	7.47	0.49	bdl
TW-128 HK	19.42	0.01	2.64	1.71	14.15	0.48	bdl
TW-128 HK	20.10	0.01	2.75	1.71	14.43	0.48	bdl
TW-129 HB	67.42	1.01	4.48	bdl	1.46	0.50	2.88
SAJALDHARA-HK	10.47	0.01	3.85	bdl	1.46	0.35	bdl
TW-130 KHN	134.51	1.08	bdl	1.91	1.45	bdl	bdl
TW-131-KHN	157.89	1.24	0.51	2.24	1.23	bdl	bdl
TW-132 KHN	180.23	1.22	0.64	1.18	1.45	bdl	bdl
TW-133 KHN	122	0.49	< 0.04	< 0.08	< 0.1	1.76	< 0.04
TW-134 KHN	200.97	1.29	0.69	2.05	1.56	bdl	0.30
TW-135 KHN	183.37	1.26	bdl	1.28	1.43	bdl	bdl

TW-136 KHN	183.65	1.22	0.64	1.64	1.46	bdl	bdl
TW-137 HK	24.08	0.01	bdl	bdl	4.07	0.26	bdl
TW-138 HK	83.83	0.01	0.64	bdl	6.69	0.33	bdl
Irrigation wells							
IW-101 BM	3.24	0.01	7.68	1.28	9.99	0.57	bdl
IW-101 (D)	2.97	0.01	7.71	1.24	9.85	0.52	bdl
IW-101 (T)	2.93	0.01	7.75	1.21	9.83	0.51	bdl
IW-102 BM	8.55	0.01	0.79	bdl	1.51	0.71	bdl
IW-102 BM (D)	8.55	0.01	0.77	bdl	1.49	0.71	bdl
IW-103 HK	1.80	0.01	0.87	bdl	1.52	0.31	3.19
IW-104 HB	1.32	0.01	0.59	bdl	1.59	0.44	0.48
IW-105 HB	1.56	0.01	0.70	1.31	2.94	0.26	bdl
IW-106 KHN	251.21	1.35	0.79	1.38	1.53	bdl	bdl
IW-107 KHN	162.71	1.13	0.92	1.52	1.43	bdl	bdl
IW-108 KHN	162.71	1.02	0.01	1.17	1.44	0.52	0.44
Jaydhar-Jaygunj	14.25	0.01	0.66	1.57	7.44	0.72	bdl
Ponds							
PW-102 BM	77.6	< 0.1	0.24	3.73	5.58	< 0.04	8.14
PW-103 BM	305.71	0.96	0.83	5.03	24.18	bdl	3.90
PW-104 BM	143.28	<0.1	1.09	1.77	16.39	0.51	0.83
PW-107 NB	72.63	<0.1	12.59	2.20	11.06	0.57	0.33
PW-108 HK	24.87	<0.1	2.86	1.40	6.98	0.25	<0.3
PW-108 HK (D)	24.92	<0.1	2.89	1.40	6.39	0.25	<0.3
PW-109 HK	28.32	<0.1	7.91	2.45	7.81	0.29	0.41
PW-110 HK	40.22	1.59	<0.3	1.41	9.47	0.35	3.12
PW-110 HK (D)	39.81	<0.1	1.60	1.46	9.49	0.33	3.10
PW-110 HK (T)	39.76	<0.1	1.55	1.46	9.43	0.33	3.10
PW-111 KHN	75.34	0.99	7.85	1.90	6.59	0.62	0.41
PW-112 KHN	105.83	0.88	5.92	1.54	6.46	0.70	<0.3

TW= Tubewell (Shallow and Deep); IW= Irrigation wells; PW-Ponds; bdl-Below Detection Limit; D= Duplicate; T= Triplicate, BM= Beldanga; HK= Hariharpara; NB= Nabagram; KHN= Kandi

Appendix-N- Cl/Br ratio for Tubewells, January 2011

Sample No.	Cl^- (mg/L)	Br^- (mg/L)	As (mg/L)	Cl/Br Molar ratio
TW-100	9.7263	0.01	15	2192.114279
TW-101	5.7305	0.01	276	1291.540552
TW-102	12.0287	0.9376	500	28.91456246
TW-103	6.5112	0.01	30	1467.494781
TW-104	3.9942	0.01	1263	900.2131182
TW-105	9.1845	0.01	10	2070.003351
TW-106	9.1	0.06	346	341.8264557
TW-107	10.4842	0.01	No data	2362.929842
TW-108	38.1029	0.8481	10	101.2573361
TW-109	54.7532	0.01	10	12340.28063
TW-110	46.1146	0.8647	0.4	120.1955854
TW-111	29.0976	0.01	15	6558.019435
TW-112	103.2833	1.0144	10	229.4755371
TW-113	31.9896	0.01	5	7209.818629
TW-114	67.2418	1.2454	0.4	121.6875085
TW-115	60.9402	1.4505	15	94.68946703
TW-116	68.937	0.892	No data	174.1819128
TW-117	60.0437	1.4735	10	91.84020326
TW-118	53.7854	0.01	5	12122.15779
TW-119	27.7	0.09	238	693.6698038
TW-120	78.4412	0.8407	300	210.2900438
TW-121	37.183	0.8436	300	99.33982384
TW-122	16.6657	0.01	400	3756.11681
TW-123	2.4234	0.01	300	546.1860875
TW-124	2.3996	0.01	300	540.8220416
TW-125	21.9037	0.01	185	4936.657673
TW-126	44.4436	0.01	15	10016.70215
TW-127	17.5847	0.01	185	3963.241105
TW-128	19.4193	0.01	No Data	4376.723401
TW-129	67.4243	1.0076	No Data	150.8147496
TW-130	134.5098	1.0805	10	280.5722311
TW-131	157.8942	1.2377	25	287.5188457
TW-132	180.2338	1.2191	15	333.2057123
TW-133	122	0.49	15	561.1504049
TW-134	200.9703	1.2881	15	351.6396431
TW-135	183.3696	1.2601	10.2	327.9728215
TW-136	183.6511	1.2164	No Data	340.2770448
TW-137	24.0839	0.01	No Data	5428.031325
TW-138	83.8294	0.01	No Data	18893.47693
TW-139	12.9	0.06	No Data	484.5671734

Appendix-O- Oxygen and Hydrogen Isotopic Data for Murshidabad waters, Jan.2012

Sample. ID	δD‰	$\delta^{18}O$‰	Location	Year of collection
TW 100	-29.0	-4.09	Beldanga	January 2012
TW-101	-25	-3.5	Beldanga	January 2012
TW-102	-26	-3.8	Beldanga	January 2012
TW-103	-22	-3.1	Beldanga	January 2012
TW-104	-25	-3.8	Beldanga	January 2012
TW 105	-31.1	-4.52	Beldanga	January 2012
TW-106	-24	-3.5	Beldanga	January 2012
TW-107	-26	-3.7	Beldanga	January 2012
TW-108	-23	-3.4	Nabagram	January 2012
TW-109	-24	-3.4	Nabagram	January 2012
TW-110	-26	-3.6	Nabagram	January 2012
TW-111	-21	-2.7	Nabagram	January 2012
TW 112	-32.6	-4.04	Nabagram	January 2012
TW-113	-25	-3.3	Nabagram	January 2012
TW-114	-25	-3.2	Nabagram	January 2012
TW 115	-29.6	-3.75	Nabagram	January 2012
TW 116	-25.4	-2.93	Nabagram	January 2012
TW-118	-29	-4.7	Hariharpara	January 2012
TW 119	-29.4	-4.26	Hariharpara	January 2012

TW 123	-28.0	-4.17	Hariharpara	January 2012
TW-125	-26	-4.2	Hariharpara	January 2012
TW-126	-27	-4.2	Hariharpara	January 2012
TW-128	-27	-4.2	Hariharpara	January 2012
TW-129	-25	-3.9	Hariharpara	January 2012
TW-138	-31	-4.8	Hariharpara	January 2012
TW 130	-29.7	-4.32	Kandi	January 2012
TW-131	-26	-3.9	Kandi	January 2012
TW-135	-26	-3.9	Kandi	January 2012
TW 136	-31.9	-4.45	Kandi	January 2012
PW 102	-28.2	-3.43	Beldanga	January 2012
PW 103	-29.0	-2.40	Beldanga	January 2012
PW 104	-30.1	-2.67	Beldanga	January 2012
PW 105	-31.0	-1.81	Nabagram	January 2012
PW 106	-42.0	-4.24	Nabagram	January 2012
PW 107	-32.7	-2.42	Nabagram	January 2012
PW 108	-30.1	-2.74	Hariharpara	January 2012
PW-109	-30	-2.7	Hariharpara	January 2012
PW-110	-27	-2.7	Hariharpara	January 2012
PW 111	-34.8	-3.55	Kandi	January 2012
PW 112	-41.0	-4.62	Kandi	January 2012
IW 101	-29.8	-4.12	Beldanga	January 2012

IW 102	-32.4	-4.56	Beldanga- Ador Ali	January 2012
IW 103	-24.9	-3.53	Hariharpara-Khoslpur	January 2012
IW 104	-27.9	-4.04	Hariharpara	January 2012
IW-105	-24	-3.4	Hariharpara	January 2012
SAJALDHARA	-28.2	-4.22	Hariharpara	January 2012
IW 106	-31.6	-4.23	Kandi	January 2012
IW 107	-29.2	-4.17	Kandi	January 2012
IW-108	-27	-4.1	Kandi	January 2012
rw-3	-53.30	-8.09	Bhagirathi	2010
rw-1	-55.78	-7.94	Bhagirathi	2010
rw-4	-55.51	-8.04	Bhagirathi	2010
RW-5	-51.83	-8.1	Bhagirathi	2010
RW-2	-52.53	-8.22	Bhagirathi	2010
Rain-wet season	-49	-7.3	Calcutta, 2007	2007
Rain-wet season	-64	-9.3	Behrampur, 2007	2007
Rain-wet season	-46	-6.7	2007	2007
Rain-dry season	-32	-5.1	2007	2007
Rain-dry season	-31	-5.1	Beldanga, 2007	2007
Rain-dry season	-36	-4.7	Hariharpara, 2007	2007
Rain-dry season	-31	-4.7	2007	2007

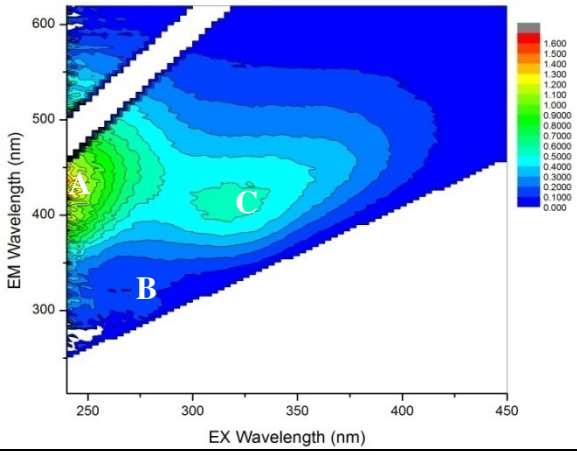
TW=Tubewell (Shallow and Deep); PW= Ponds; IW= Irrigation wells, RW= River water

Appendix-P- C/N Ratio Calculation Table, January 2012 Water Samples , C and N Concentrations were Measured Using TOC-L SHIMADZU®, Total Organic Carbon Analyzer

Sample No.	Depth m	DOC mol/L	DON mol/L	C/N molar ratio
TW-100	37.1856	0.000122	9.54E-06	12.84
TW-101	33.528	0.000161	0.000167	0.97
TW-102	39.624	0.000143	1.04E-05	13.78
TW-103	39.624	0.000129	9.69E-06	13.29
TW-104	33.528	0.0002	0.000155	1.29
TW-105	33.528	0.000109	3.97E-06	27.34
TW-106	33.528	0.000158	0.000118	1.35
TW-109	25.908	9.79E-05	5.74E-05	1.71
TW-112	36.576	6.02E-05	6.38E-06	9.43
TW-113	45.72	6.47E-05	2.48E-05	2.61
TW-114	36.576	7.12E-05	1.84E-05	3.86
TW-117	30.48	9.83E-05	1.17E-05	8.44
TW-118	18.288	0.000275	0.00021	1.31
TW-119	18.288	0.000111	7.15E-05	1.56
TW-120	18.288	0.000164	0.000117	1.41
TW-122	12.192	0.000124	2.99E-05	4.15
TW-123	18.288	0.000104	0.000072	1.44
TW-124	15.24	0.000123	8.35E-05	1.48
TW-125	15.24	0.00026	5.06E-05	5.13
TW-126	18.288	0.000111	0.000114	0.97
TW-131	21.336	5.26E-05	0.000005	10.52
TW-132	21.336	0.000104	2.73E-06	38.06
TW-133	21.336	7.33E-05	2.83E-06	25.91

TW- Tubewell

Appendix-Q- Excitation Emission Matrix 9EEM) for Water Samples, January 2012, HORIBA Aqualog® Benchtop Fluorometer



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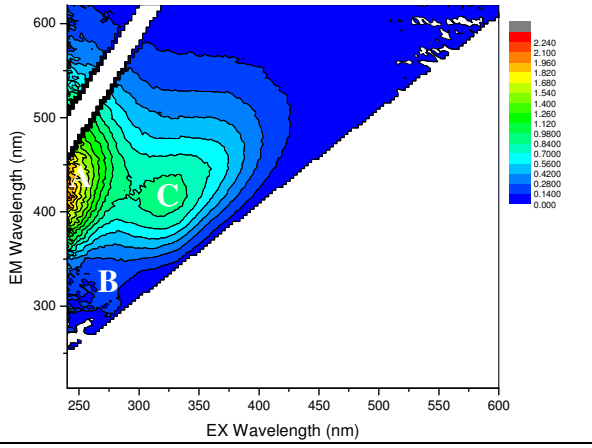

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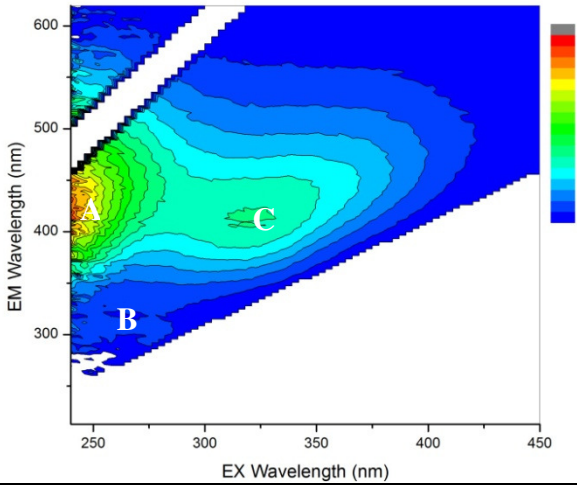

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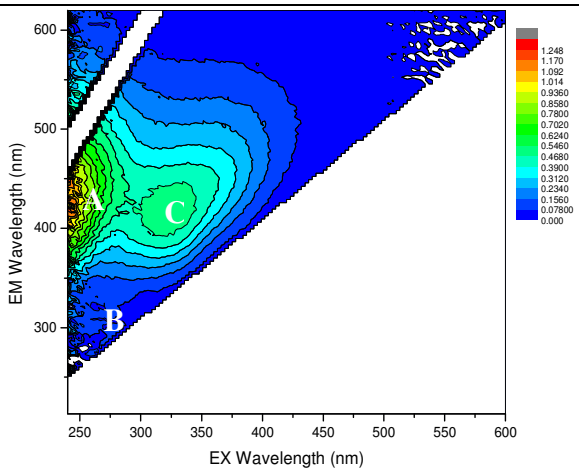

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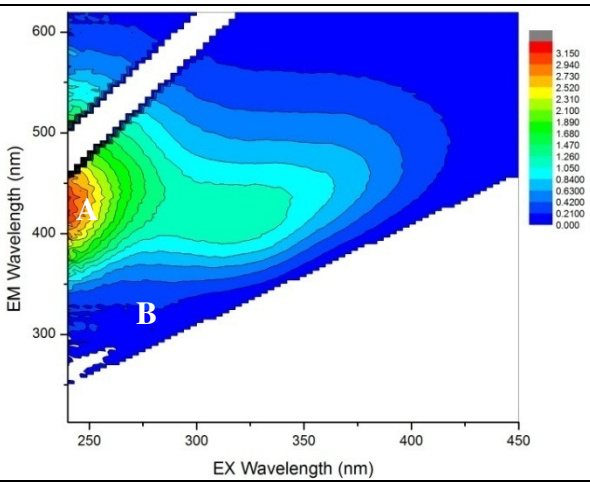

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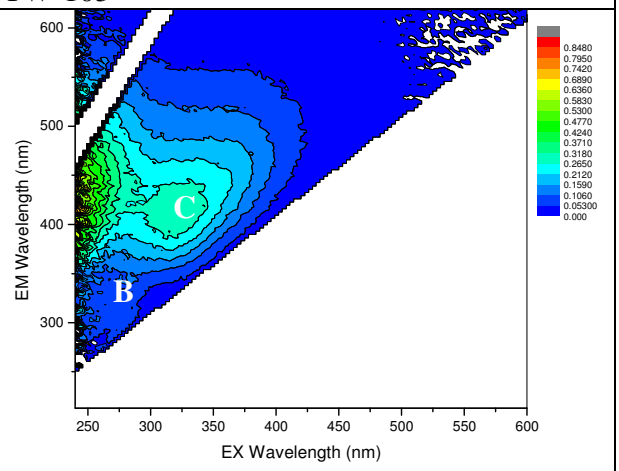

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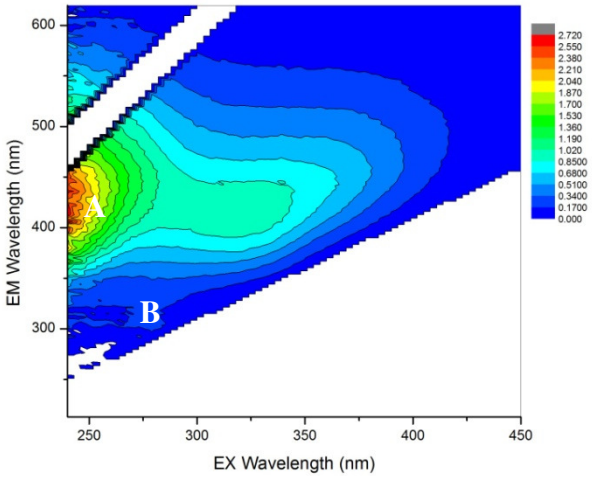

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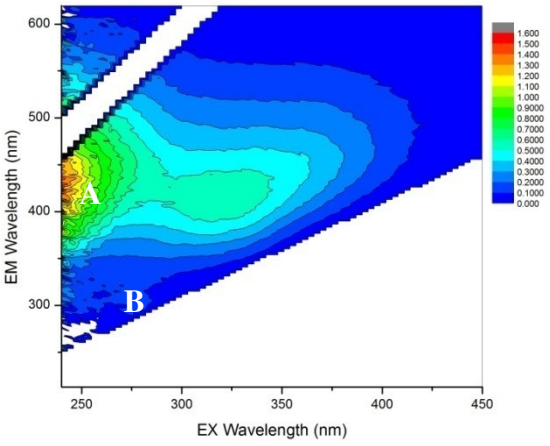

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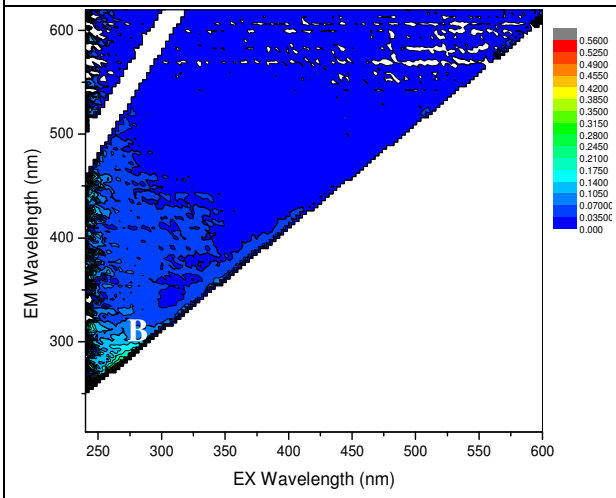

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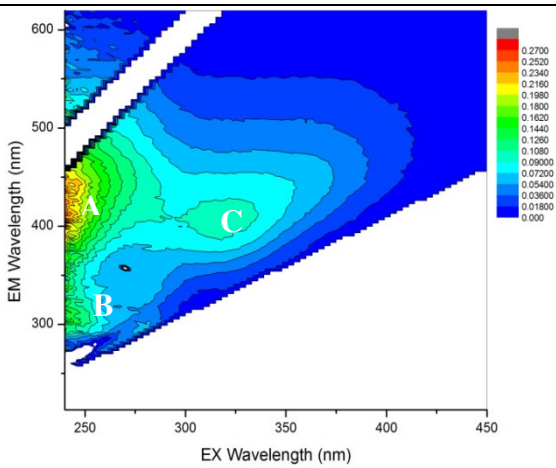

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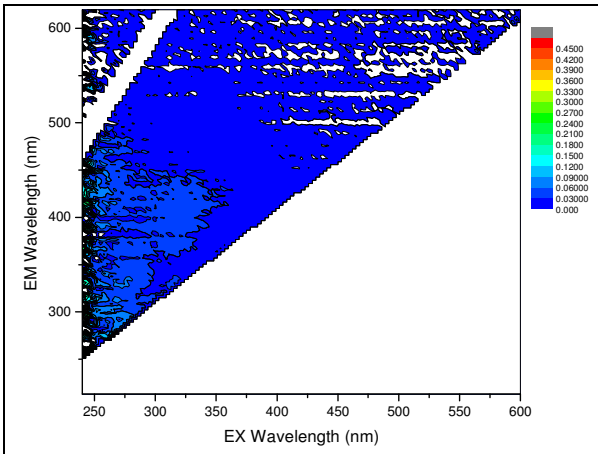
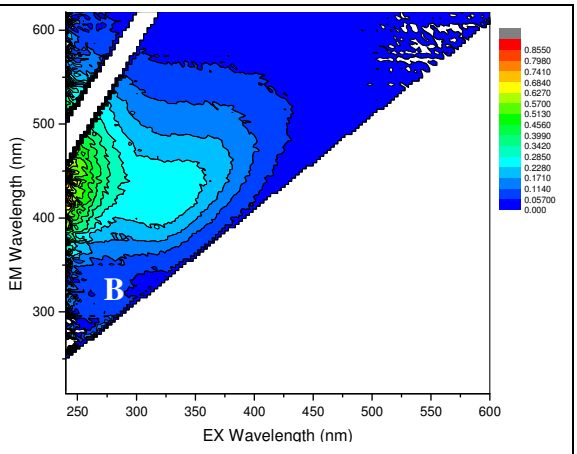
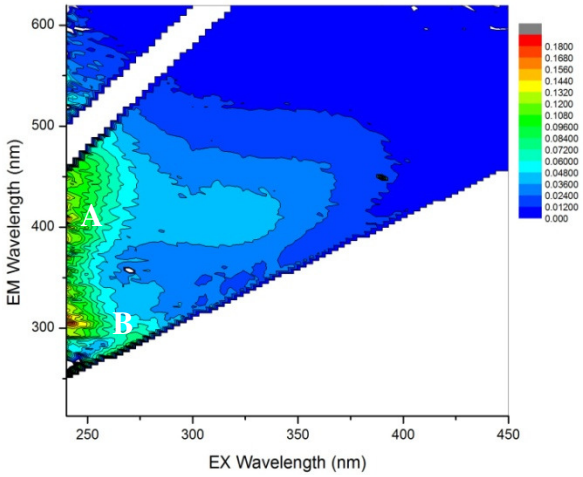

EM Wavelength (nm)
EX Wavelength (nm)
600
500
400
300
250
300
350
400
450
500
550
600
0.4500
0.4200
0.3900
0.3600
0.3300
0.3000
0.2700
0.2400
0.2100
0.1800
0.1500
0.1200
0.09000
0.06000
0.03000
0.000

TW-110


EM Wavelength (nm)
EX Wavelength (nm)
B
600
500
400
300
250
300
350
400
450
500
550
600
0.8550
0.7980
0.7410
0.6840
0.6270
0.5700
0.5130
0.4560
0.3990
0.3420
0.2850
0.2280
0.1710
0.1140
0.05700
0.000

TW-111



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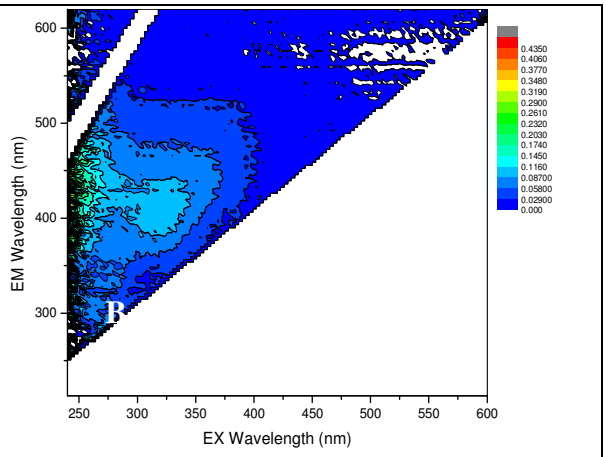
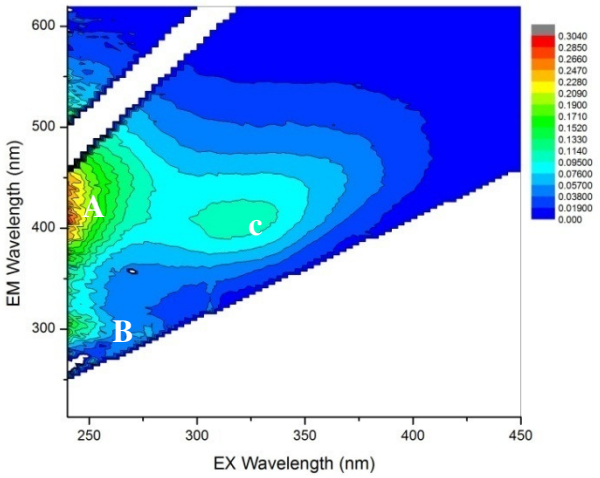
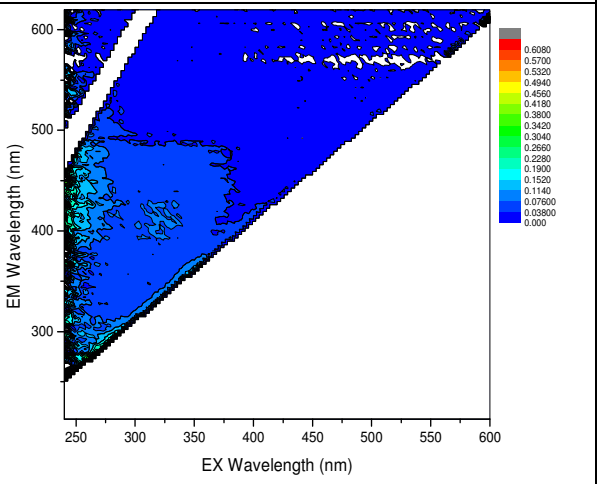


TW-113



TW-114



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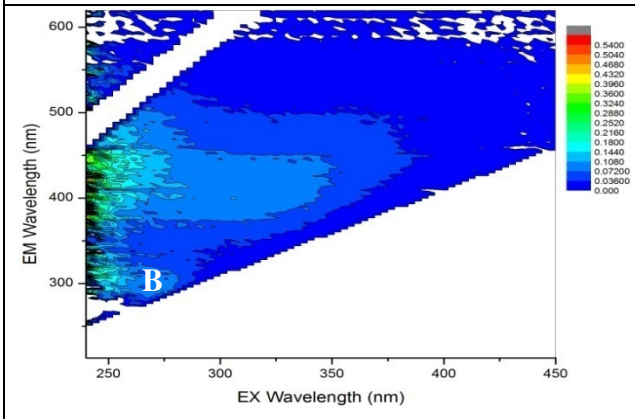

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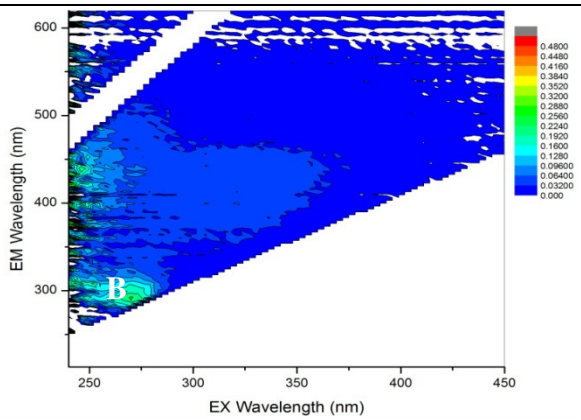

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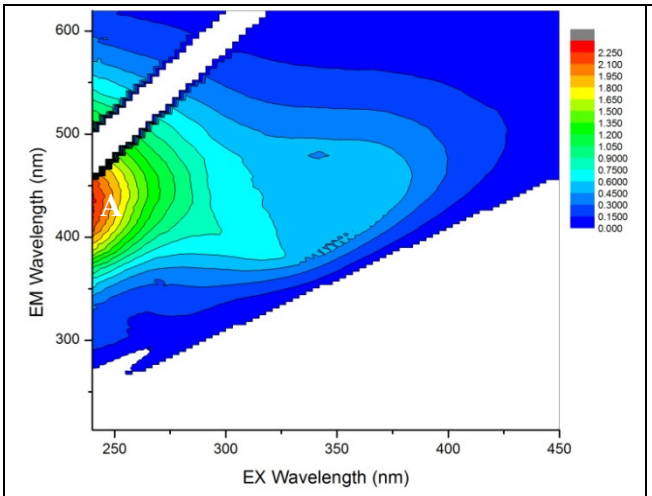

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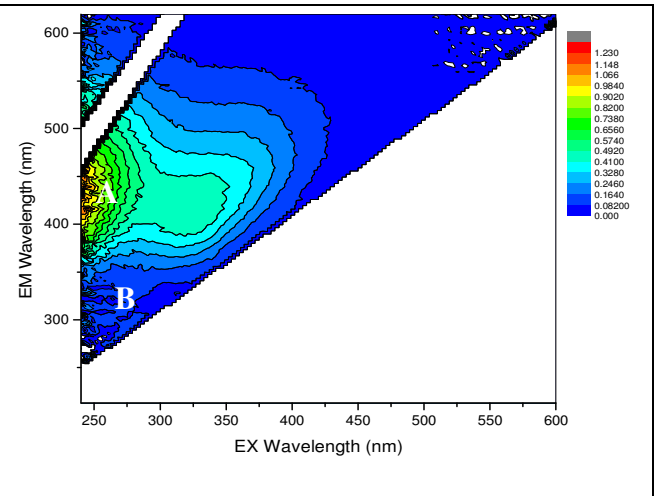

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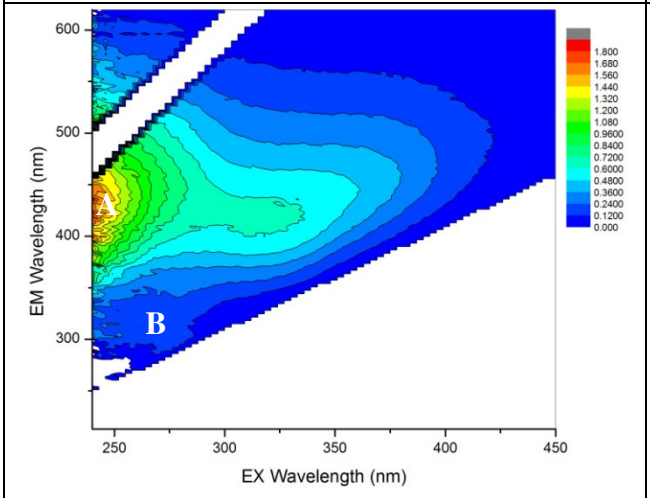

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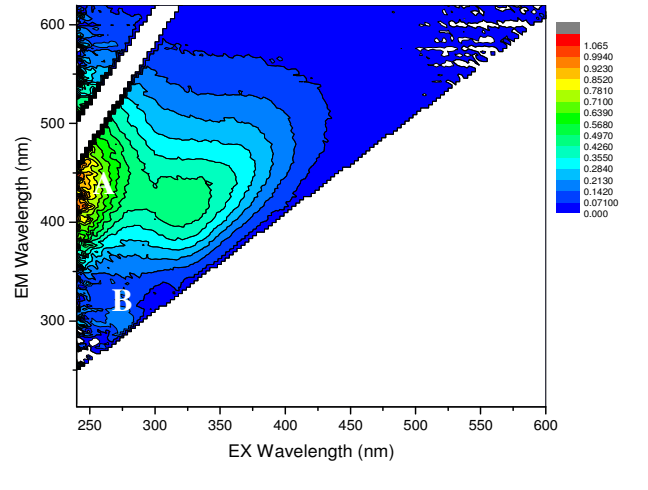

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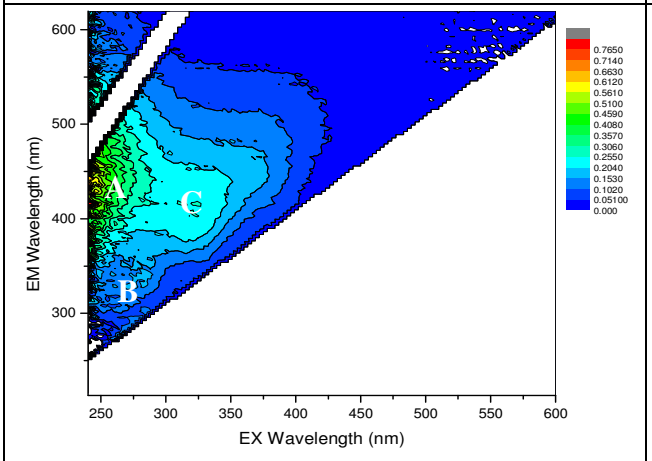

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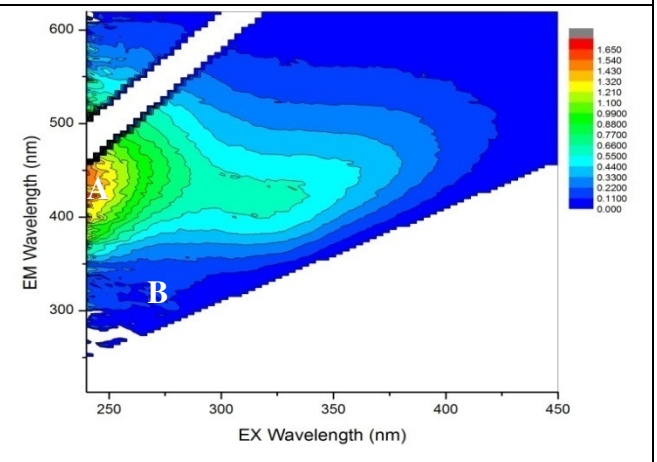

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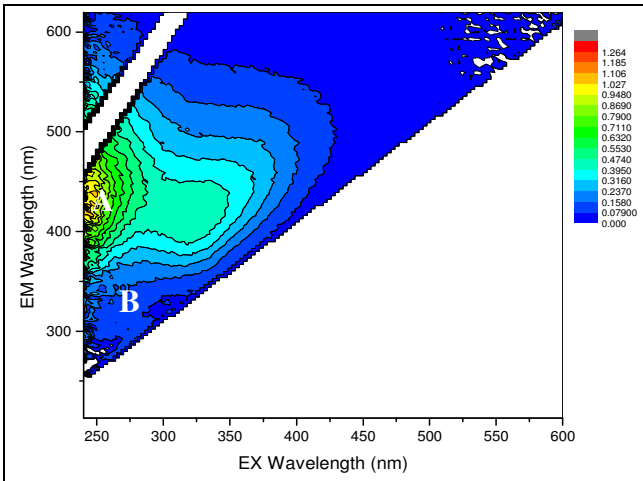

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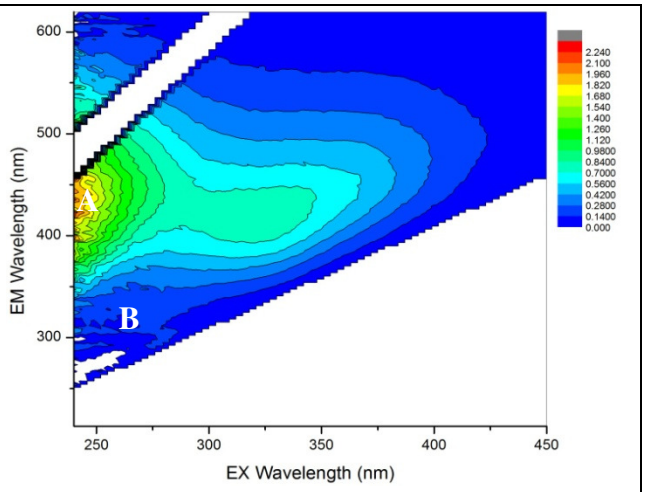

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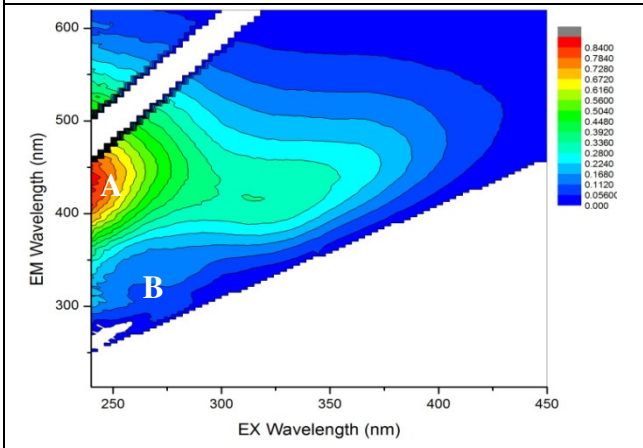

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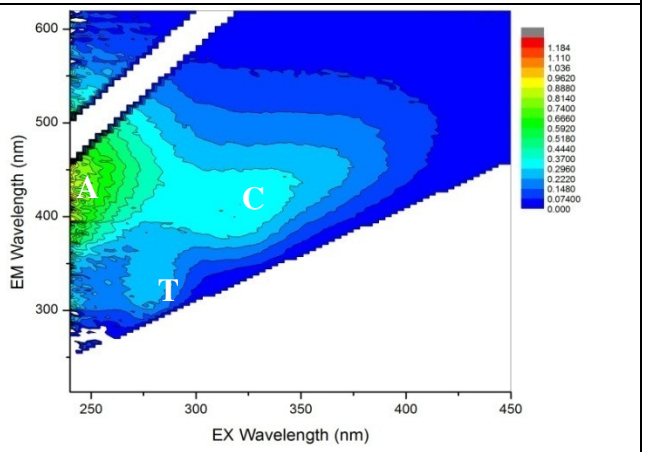

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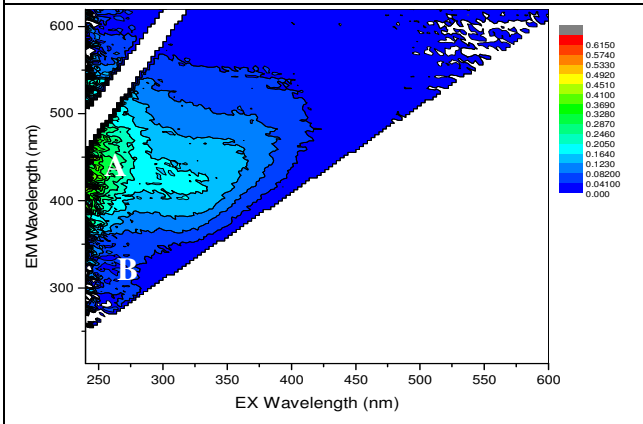

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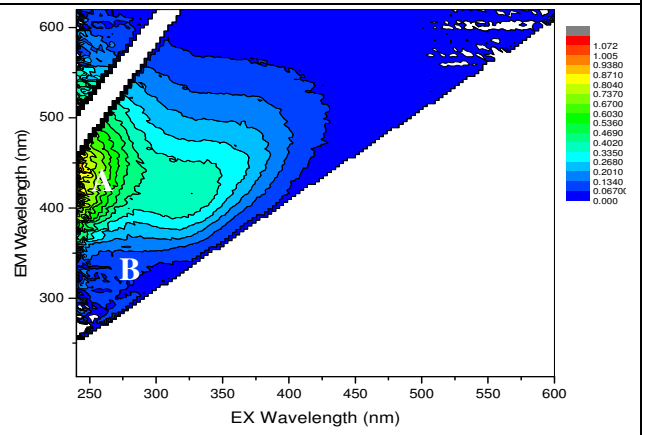

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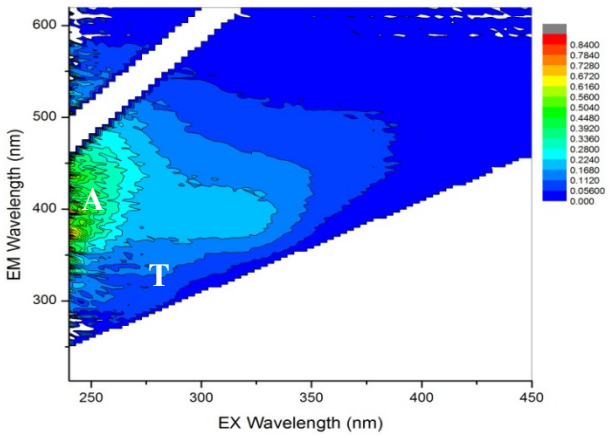

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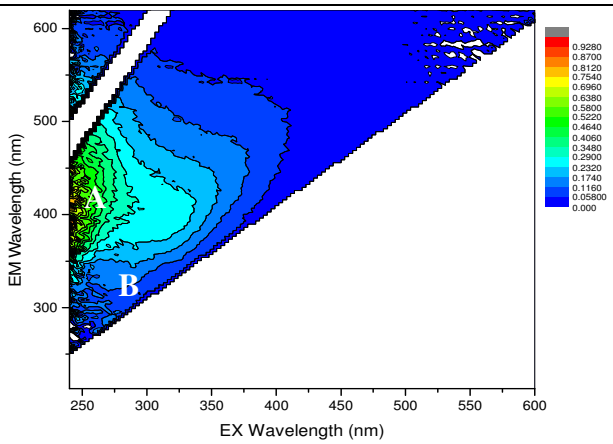

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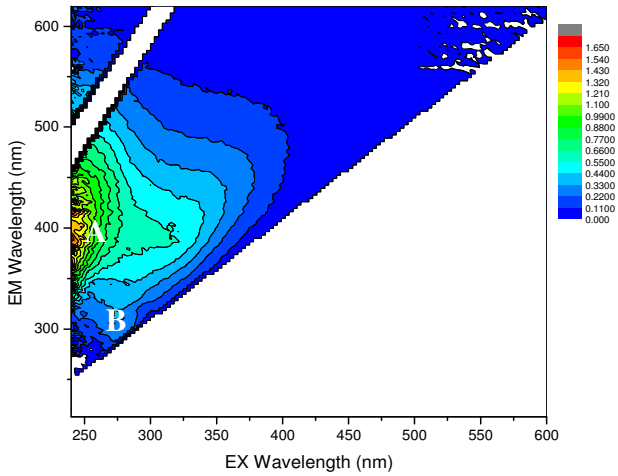

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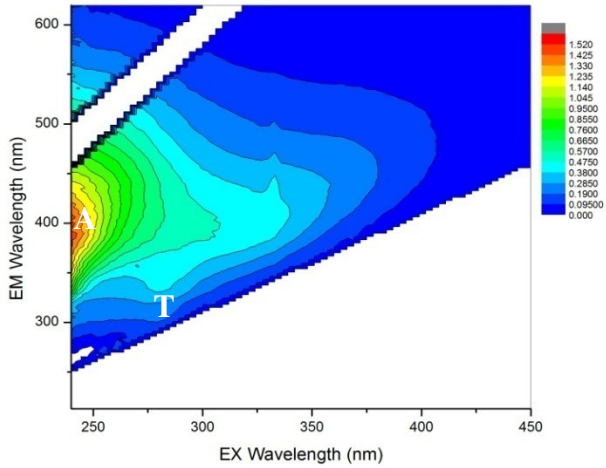

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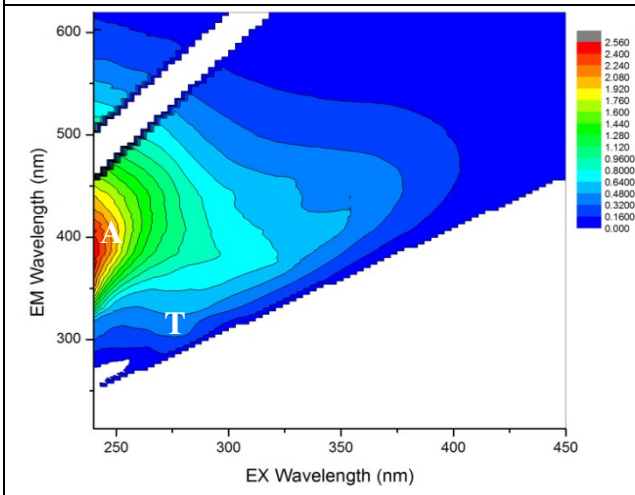

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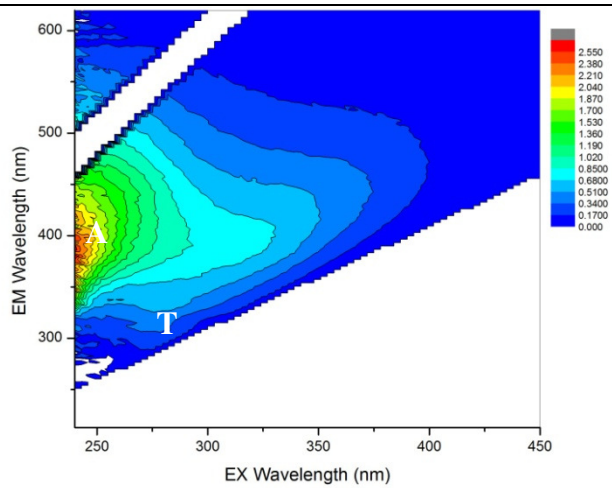

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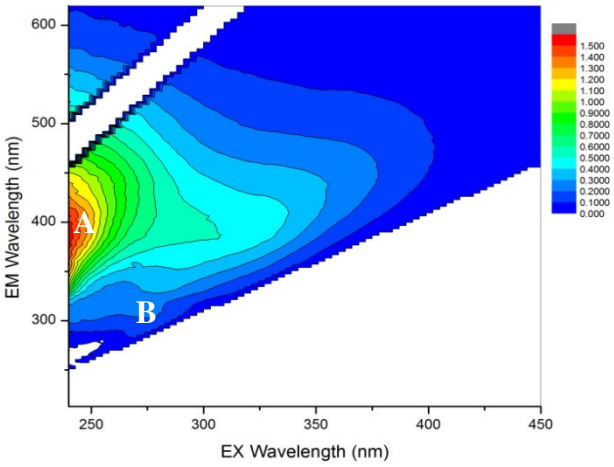

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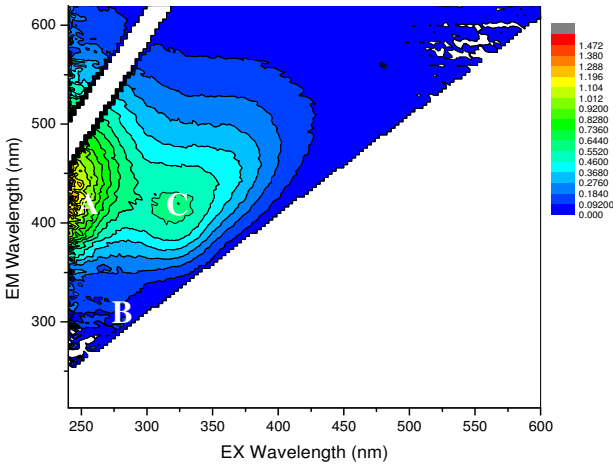

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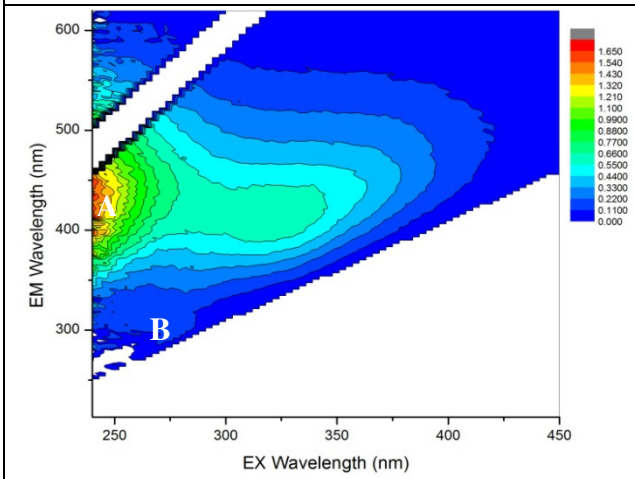

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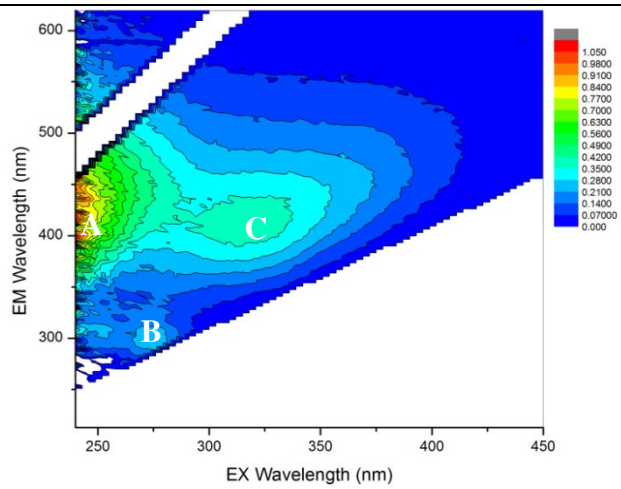

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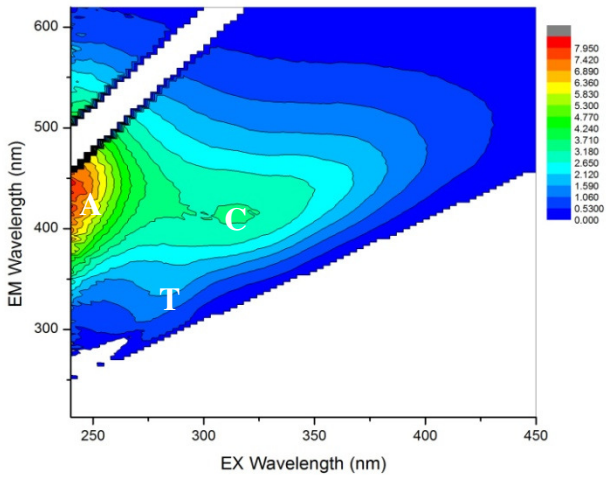	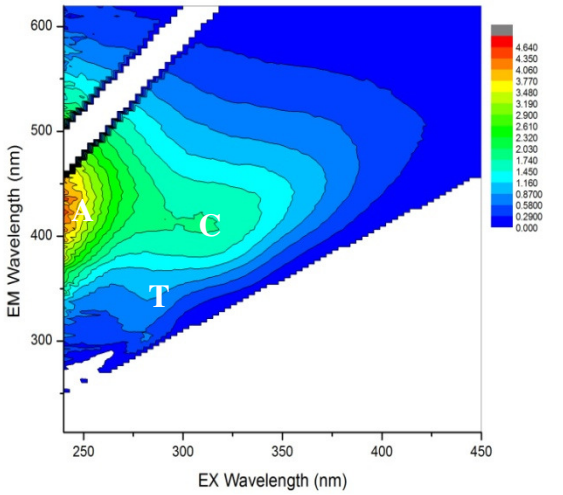
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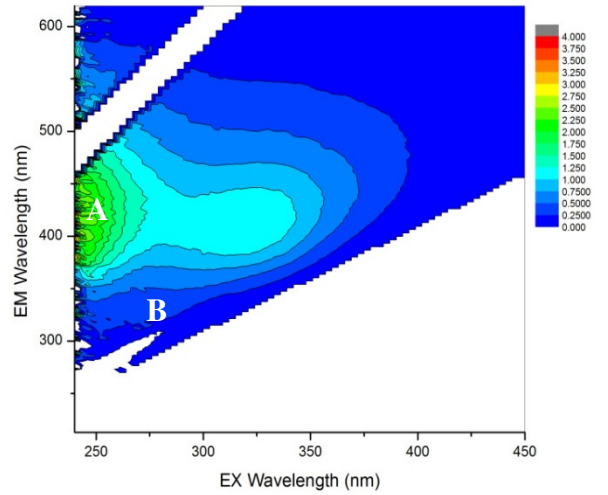	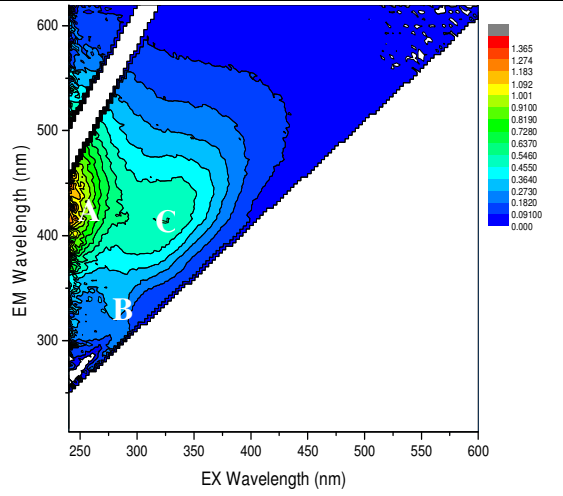
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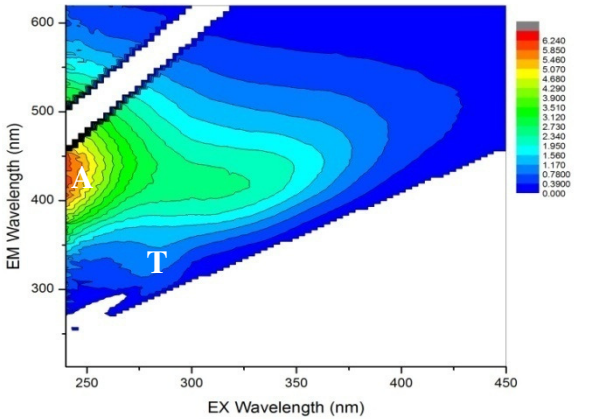	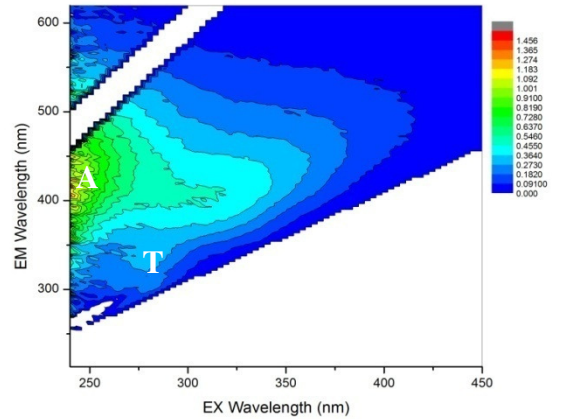
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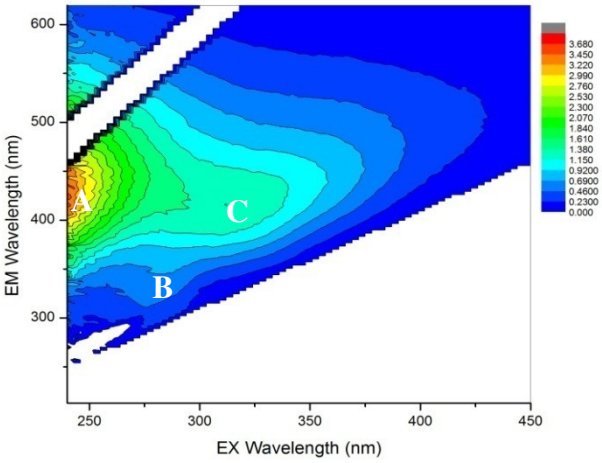	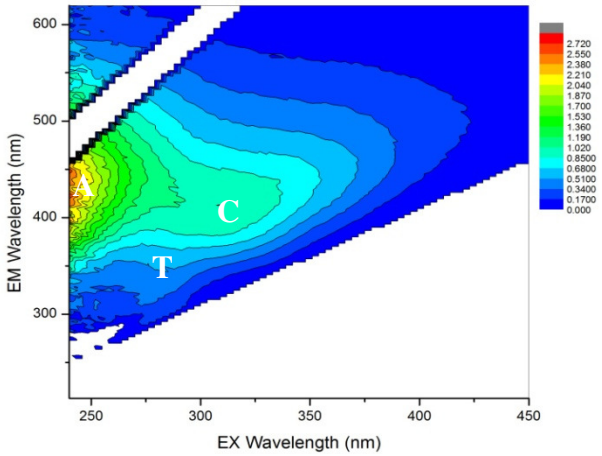
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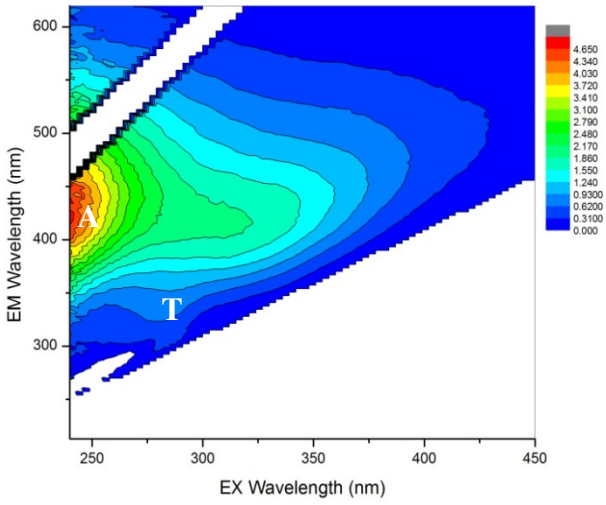	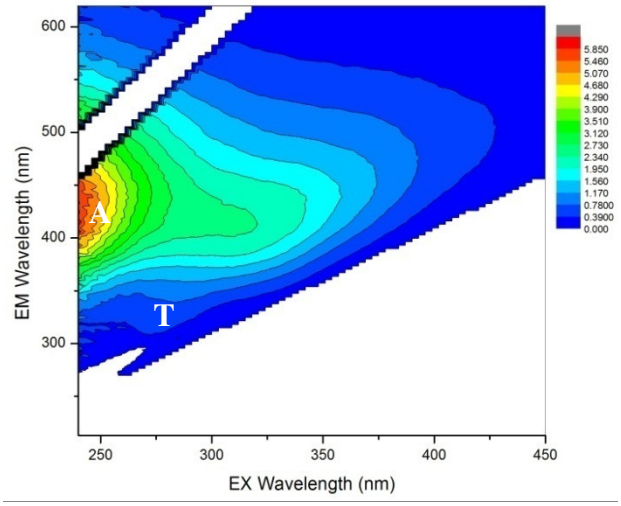
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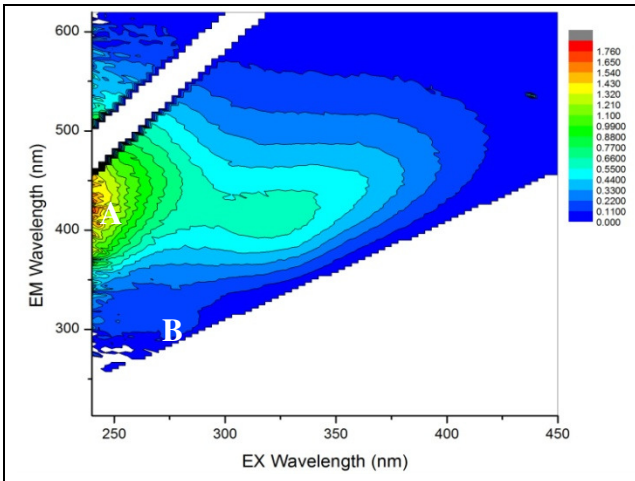	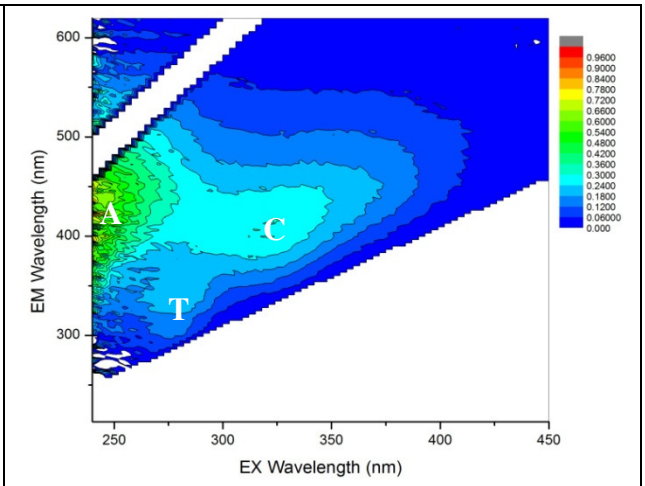
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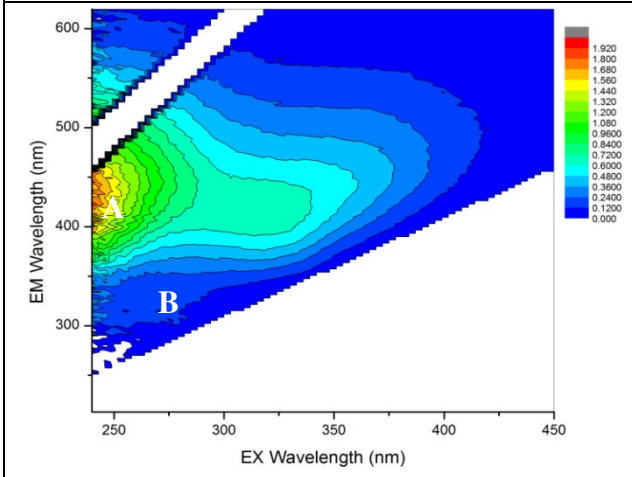	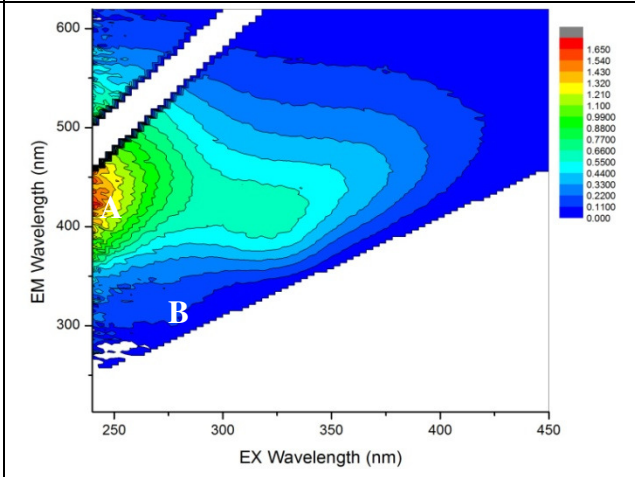
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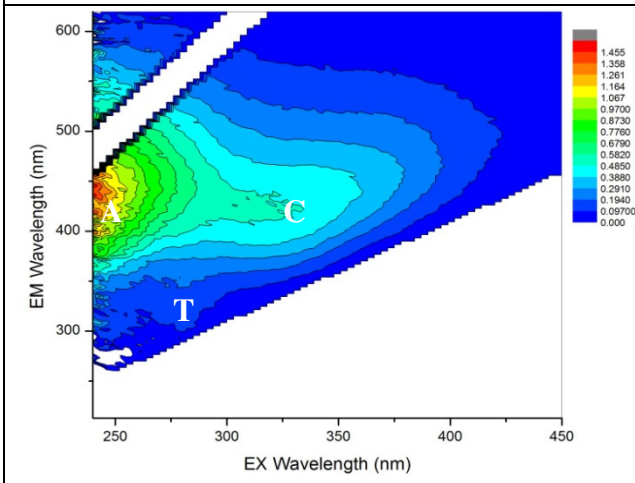	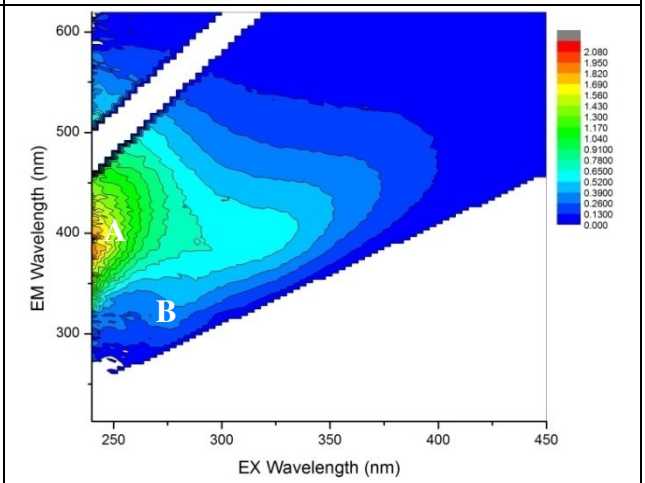
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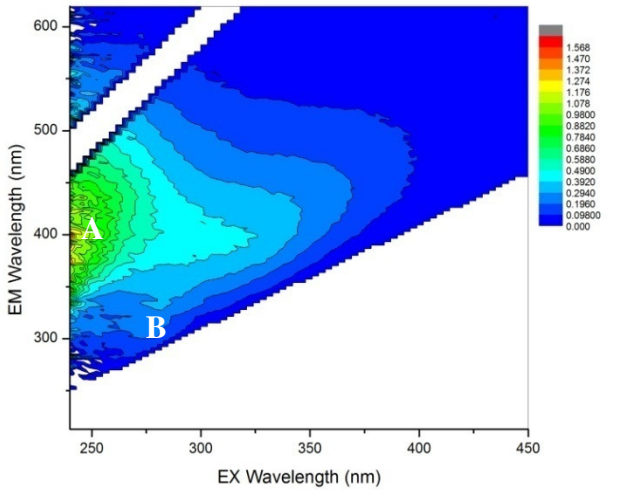	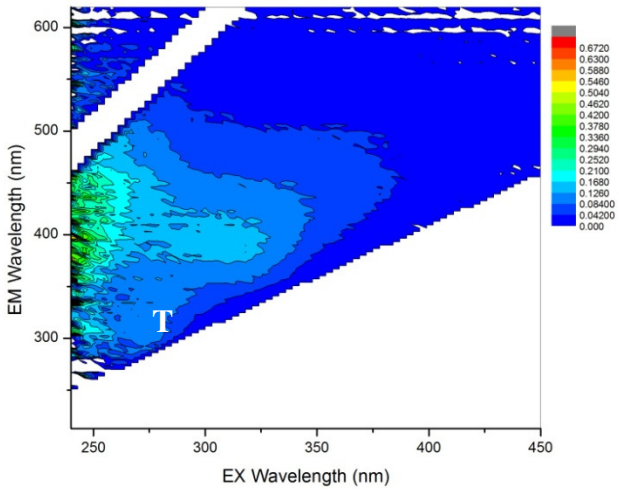
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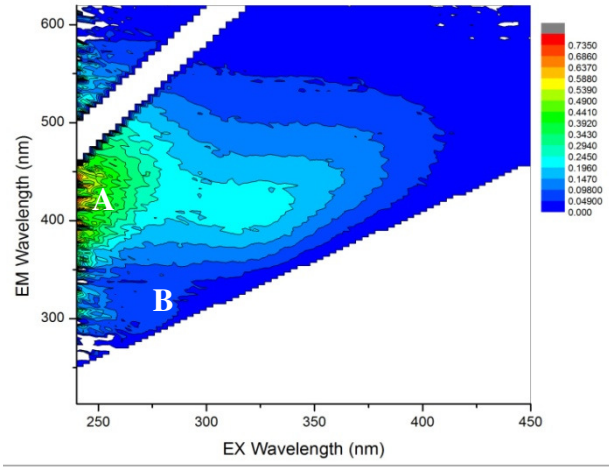	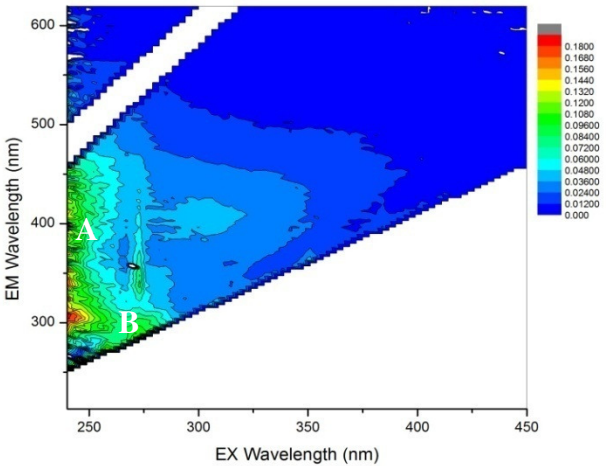
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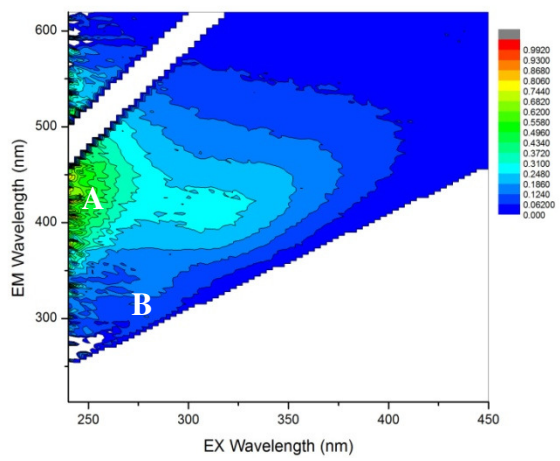
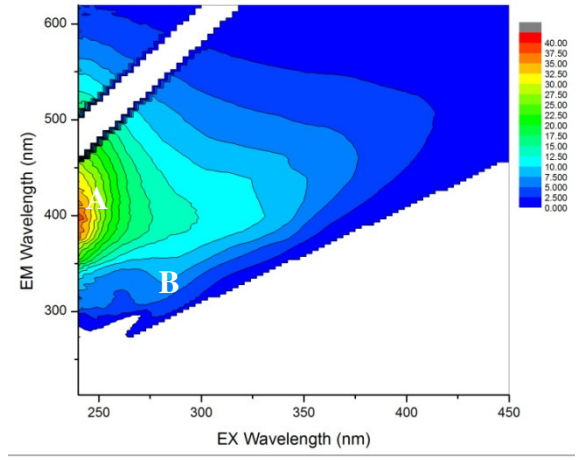
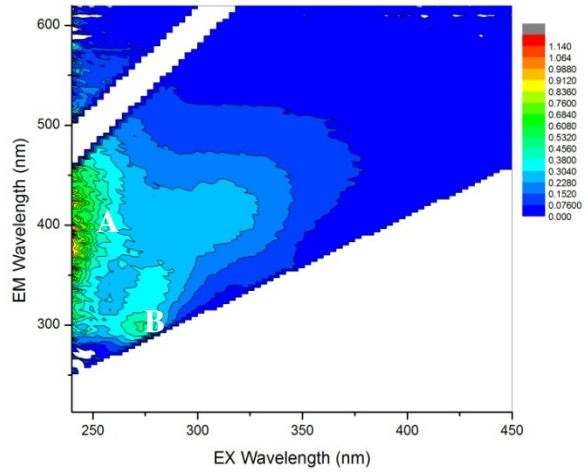
	
RW-100 BHAGIRATHI	RAIN WATER MURSHIDABAD JAN 2012
	
Rain water (Kolkata) Jan 2012	

TW= Tubewells, PW=Ponds, IW=Irrigation wells, RW=River water, Rain=Rain water;

BM=Beldanga, HK=Hariharpara, NB=Nabagram, KHN=Kandi

Appendix-R- Statistical Tables for Fluorescence Data Analysis of Water Samples (January 2012); Calculations by SPSS

Table1: Correlation Matrix Among Fluorescence Parameters for the Total Tubewells (High As & Low As Together)

Table-1	Fluorescence Index (FI)	Freshness Index (Fr I)	Tyrosine- like, Protein like (B) nm	Tryptophane-like, Protein like or Phenol Like (T)nm	A, Humic like nm	C, Humic like nm	DOC mg/l	DON mg/l	SUVA (L mg-1 m-1)
Fluorescence Index (FI)		P=0 R^2=0	P=0 R^2=0.069(+)	P=0 R^2=0.063(+)	P=0 R^2=0.041(+)	P=0 R^2=0.044(+)	P=0.972 R^2=0.003(-)	P=0.00007 R^2=0.052(-)	P=0.0000000001 R^2=0
Freshness Index (Fr I)			P=0 R^2=0.369+	P=0 R^2=0.375+	P=0.523 R^2=0	P=0.0000001 R^2=0.038-	P=0.000034 R^2=0.103-	P=0.905 R^2=0.018-	P=0 R^2=0.023+
Tyrosine- like, Protein like (B) nm				P=0.00008 R^2=0.853+	P=0.0000000034 R^2=0.253+	P=0.00000087 R^2=0.111+	P=0 R^2=0.022-	P=0.0085 R^2=0.036-	P=0 R^2=0.030+
Tryptophane-like, Protein like or Phenol Like (T)nm					P=0.0000000043 R^2=0.36+	P=0.000024 R^2=0.195+	P=0.0000000001 R^2=0	P=0.02 R^2=0.014-	P=0 R^2=0.007+
A, Humic like nm						P=0.000000012 R^2=0.8+	P=0.0000024 R^2=0.4+	P=0.672 R^2=0.12+	P=0 R^2=0.013-
C, Humic like nm							P=0.0000000001 R^2=0.3+	P=0.096 R^2=0.05	P=0 R^2=0
DOC mg/l								P=0.00042 R^2=0.5+	P=0.0000004 R^2=0.27-
DON mg/l									P=0.00000006 R^2=0.08-
SUVA (L mg-1 m-1)									

Table1: Correlation Matrix Among Fluorescence Parameters for the Total Tubewells (High As & Low As Together)

Table-1 cont.	Tyrosine- like, Protein like (B) nm/DOC	Tryptophane-like, Protein like or Phenol Like (T)nm/DOC	A, Humic like nm/DOC	C, Humic like nm/DOC	As ppb	Mn ppb
Fluorescence Index (FI)	P=0 R^2= 0.02(+)	P=0 R^2=0.026(+)	P=0 R^2=0.06(+)	P=0 R^2=0.016(+)	P=0.002 R^2=0.02(+)	p=0.000000076 R^2=0.26(-)
Freshness Index (Fr I)	P=0 R^2=0.577+	P=0 R^2=0.53+	P=0.00025 R^2=0.128+	P=0 R^2=0.018+	P=0.002 R^2=0.176-	P=0.000000075 R^2=0.001-
Tyrosine- like, Protein like (B) nm	P=0.00067 R^2=0.733+	P=0.531 R^2=0.738+	P=0.0000000002 R^2=0.602+	P=0.000048 R^2=0.253+	P=0.002 R^2=0.00004+	P=0.000000073 R^2=0.009-
Tryptophane-like, Protein like or Phenol Like (T)nm	P=0.00001 R^2=0.6+	P=0.0002 R^2=0.8+	P=0.0000000001 R^2=0.7+	P=0.01 R^2=0.314+	P=0.002 R^2=0.001-	P=0.000000074 R^2=0.007-
A, Humic like nm	P=0.000000006 R^2=0.017+	P=0.000000009 R^2=0.083+	P=0.00021 R^2=0.5+	P=0.00000007 R^2=0.232+	P=0.002 R^2=0.3+	P=0.000000075 R^2=0.04-
C, Humic like nm	P=0.00000075 R^2=0.001+	P=0.0000079 R^2=0.036+	P=0.00089 R^2=0.34+	P=0.00023 R^2=0.495+	P=0.002 R^2=0.322+	P=0.000000074 R^2=0.007-
DOC mg/l	P=0.0000000001 R^2=0.3-	P=0.0000000002 R^2=0.14-	P=0.0000009 R^2=0.01*	P=0.0000000008 R^2=0.011-	P=0.002 R^2=0.2+	P=0.000000076 R^2=0.000005+
DON mg/l	P=0.006 R^2=0.17-	P=0.01 R^2=0.118-	P=0.42 R^2=0.03-	P=0.04 R^2=0.03-	P=0.002 R^2=0.03+	P=0.000000075 R^2=0.023-
SUVA (L mg-1 m-1)	P=0 R^2=0.2+	P=0 R^2=0.1+	P=0 R^2=0.08+	P=0 R^2=0.14+	P=0.002 R^2=0.01-	P=0.00000008 R^2=0.03+
Tyrosine/DOC					P=0.002 R^2=0.08-	P=0.00000006 R^2=0.001-

Tryptophane/DOC					P=0.002 R^2=0.06-	P=0.00000006 R^2=0
Ahumic/DOC					P=0.002 R^2=0.01+	P=0.00000006 R^2=0.03-
Chumic/DOC					P=0.002 R^2=0.02+	P=0.00000006 R^2=0

Table 2: Correlation Matrix Among As, Mn, DOC and DON for Total Tubewells (High As & low As Together)

Table-2	DON µg/l	As µg/l	Mn µg/l
DOC µg/l	P=0.011 R^2=0.001	P=0.000000 R^2=0.214+	P= 0.300368 R^2=0.08-
DON µg/l		P=0.002008 R^2=0.018-	P=0.246537 R^2=0.026-

Table 3 :Correlation Matrix Among Fluorescence Parameters for Pond Water

Table-3	Fluorescence Index (FI)	Freshness Index (Fr I)	Tyrosine- like, Protein like (B) nm	Tryptophane-like, Protein like or Phenol Like (T)nm	A, Humic like nm	C, Humic like nm	DOC mg/l	DON mg/l	SUVA (L mg-1 m-1)
Fluorescence Index (FI)		P=0 R^2=0.031	P=0.000001 R^2=0.154	P=0.00024 R^2=0.116	P=0.031 R^2=0.037	P=0.222 R^2=0.088	P=0.0001 R^2= 0.002	P=0.344 R^2=0.030	P=0.0000039 R^2=0.078
Freshness Index (Fr I)			P=0.013 R^2=0.176-	P=0.923 R^2= 0.341	P=0.003 R^2=0.656-	P=0.071 R^2=0.556-	P=0.000064 R^2=0.547-	P=0.333 R^2=0.038	P=0.00000011 R^2=0
Tyrosine- like, Protein like (B) nm				P= 0.000401 R^2= 0.954+	P= 0.000360 R^2=0.654+	P= 0.000846 R^2=0.754+	P= 0.000027 R^2=0.594+	P= 0.329777 R^2=0.134-	P= 0.000001 R^2=0.076-
Tryptophane-like, Protein like or Phenol Like (T)nm					P= 0.000367 R^2=0.828+	P= 0.001468 R^2=0.901+	P= 0.000025 R^2=0.720+	P= 0.333947 R^2=0.115-	P= 0.000005 R^2=0.026-
A, Humic like nm						P= 0.000236 R^2=0.970+	P= 0.000022 R^2=0.742+	P= 0.363211 R^2=0.099-	P= 0.958250 R^2=5E-05-
C, Humic like nm							P= 0.00002 R^2=0.778+	P= 0.341166 R^2=0.061-	P= 0.000340 R^2=0
DOC mg/l								P= 0.452088 R^2=0.002+	P=0.000486 R^2=0.004-
DON mg/l									P= 0.360705 R^2=0.287+
SUVA (L mg-1 m-1)									

Table 3 cont.: Correlation Matrix Among Fluorescence Parameters for Pond Water

Table-3 cont.	Tyrosine- like, Protein like (B) nm/DOC	Tryptophane-like, Protein like or Phenol Like (T)nm/DOC	A, Humic like nm/DOC	C, Humic like nm/DOC
Fluorescence Index (FI)	P=0 R^2=0.455+	P=0 R^2=0.484+	P=0 R^2=0.084+	P=0 R^2=0.224+
Freshness Index (Fr I)	P=0.0000000001 R^2=0.163+	P=0.0000000004 R^2=0.015+	P=0.0000032 R^2=0.393-	P=0.000000015 R^2=0.386-
Tyrosine- like, Protein like (B) nm	P=0.001365 R^2= 0.179+	P=0.002041 R^2=0.280+	P=0.080221 R^2= 0.197+	P=0.003947 R^2=0.386+
Tryptophane-like, Protein like or Phenol Like (T)nm	P= 0.000674 R^2=0.088+	P= 0.000838 R^2=0.217+	P= 0.005381 R^2=0.309+	P= 0.001102 R^2=0.512+
A, Humic like nm	P= 0.000351 R^2=0	P= 0.000369 R^2=0.080+	P= 0.000496 R^2=0.581+	P= 0.000374 R^2=0.721+
C, Humic like nm	P= 0.000655 R^2=0.006+	P= 0.000736 R^2=0.100+	P= 0.001675 R^2=0.472+	P= 0.000794 R^2=0.672+
DOC mg/l	P= 0.000031 R^2=0.050-	P= 0.000032 R^2=0.002-	P= 0.000036 R^2=0.115+	P=0.000032 R^2=0.224+
DON mg/l	P= 0.323908 R^2=0.360-	P= 0.324360 R^2=0.465-	P= 0.327409 R^2=0.368-	P= 0.325074 R^2= 0.269-
SUVA (L mg-1 m-1)	P= 0.000000 R^2=0.033-	P= 0.000000 R^2=0.001-	P= 0.000000 R^2=0.010+	P= 0.000000 R^2=0.021+

Table 4: Correlation Matrix Among Fluorescence Parameters for Pond Water for Irrigation Wells

Table-4	Fluorescence Index (FI)	Freshness Index (Fr I)	Tyrosine- like, Protein like (B) nm	Tryptophane-like, Protein like or Phenol Like (T)nm	A, Humic like nm	C, Humic like nm	DOC mg/l	DON mg/l	SUVA (L mg-1 m-1)
Fluorescence Index (FI)		P=0.000003 R^2=0.182	P=0.0000000004 R^2=0.071	P=0.000000001 R^2=0.030	P=0.0002 R^2=0.009	P=0.0000001 R^2=0.005	P=0.04 R^2= 0.027	P=0.003 R^2=0.148	P=0.002 R^2=0.151
Freshness Index (Fr I)			P=0.0000009 R^2=0.383	P=0.000004 R^2=0.203	P=0.62 R^2=0.123	P=0.002 R^2=0.317	P=0.09 R^2= 0.182	P=0.44 R^2=0.147	P=0.0001 R^2=0.227
Tyrosine- like, Protein like (B) nm				P=0.012 R^2=0.869	P=0.002 R^2=0.155	P=0.012 R^2=0.022	P=0.0005 R^2= 0.489+	P=0.09 R^2=0	P=0.00001 R^2=0.377+
Tryptophane-like, Protein like or Phenol Like (T)nm					P=0.002 R^2=0.336	P=0.02 R^2=0.134	P=0.0005 R^2= 0.664+	P=0.12 R^2=0.012	P=0.00002 R^2=0.595+
A, Humic like nm						P=0.0006 R^2=0.914+	P=0.003 R^2= 0.204+	P=0.49 R^2=0.337+	P=0.0003 R^2=0.194
C, Humic like nm							P=0.0003 R^2= 0.060	P=0.2 R^2=0.496+	P=0.00003 R^2=0.059
DOC mg/l								P=0.036 R^2=3E-05	P=0.006 R^2=0.719+
DON mg/l									P= 0.0003 R^2=0.013
SUVA (L mg-1 m-1)									

Table 4 cont.: Correlation Matrix Among Fluorescence Parameters for Irrigation Wells

Table-4 cont.	Tyrosine- like, Protein like (B) nm/DOC	Tryptophane-like, Protein like or Phenol Like (T)nm/DOC	A, Humic like nm/DOC	C, Humic like nm/DOC
Fluorescence Index (FI)	P=0.0000000004 R^2=0	P=0.0000000005 R^2=0.005	P=0.000002 R^2=0.051	P=0.0000000008 R^2=0.164
Freshness Index (Fr I)	P=0.00000043 R^2=0.034	P=0.0000009 R^2=0.008	P=0.07 R^2=0.287-	P=0.0002 R^2=0.516-
Tyrosine- like, Protein like (B) nm	P=0.43 R^2=0.001	P=0.17 R^2=0.023	P=0.0003 R^2=0.079	P=0.007 R^2=0.178
Tryptophane-like, Protein like or Phenol Like (T)nm	P=0.07 R^2=0.070	P=0.19 R^2=0.002	P=0.00043 R^2=0.122	P=0.045 R^2=0.186
A, Humic like nm	P=0.002 R^2=0.254	P=0.003 R^2=0.058	P=0.21 R^2=0.038	P=0.003 R^2=0.036
C, Humic like nm	P=0.02 R^2=0.259	P=0.03 R^2=0.052	P=0.004 R^2=0.110	P=0.21 R^2=0.144
DOC mg/l	P=0.001 R^2=0.373-	P=0.001 R^2=0.324-	P=0.016 R^2=0.412-	P=0.001 R^2=0.41-
DON mg/l	P= 0.09 R^2=0.016	P= 0.11 R^2=0.004	P= 0.98 R^2=0.115	P= 0.18 R^2=0.198
SUVA (L mg-1 m-1)	P= 0.000008 R^2=0.402-	P= 0.000009 R^2=0.226-	P= 0.00002 R^2=0.548-	P= 0.000008 R^2=0.602-

Table-5: Correlation Matrix Among Fluorescence Parameters for High As Tubewells

Table-5	Fluorescence Index (FI)	Freshness Index (Fr I)	Tyrosine- like, Protein like (B) nm	Tryptophane-like, Protein like or Phenol Like (T)nm	A, Humic like nm	C, Humic like nm	DOC µg/l	DON µg/l	SUVA (L mg-1 m-1)
Fluorescence Index (FI)		P= 0 R^2= 0.304	P= 0 R^2=0.004	P= 0 R^2=0.016	P= 0.000009 R^2=0	P= 0 R^2=0.066	P= 0.0000001 R^2=0.144	P= 0.003206 R^2=0.404	P= 0 R^2=0.195
Freshness Index (Fr I)			P= 0 R^2=0.036	P= 0 R^2=0.145	P= 0.039106 R^2=0.007	P= 0 R^2=0.016	P= 0 R^2=0.216	P= 0.003184 R^2=0.298	P= 0 R^2=0.113
Tyrosine- like, Protein like (B) nm				P= 0 R^2=0.477	P= 0 R^2=0.201	P= 0 R^2=0.169	P= 0 R^2=0	P= 0.003 R^2=0.018	P= 0 R^2=0
Tryptophane-like, Protein like or Phenol Like (T)nm					P= 0 R^2=0.533	P= 0 R^2=0.478	P= 0 R^2=0.368	P= 0.003172 R^2=0.141	P= 0 R^2=0.061
A, Humic like nm						P= 0 R^2=0.894	P= 0 R^2=0.393	P= 0.003186 R^2=0.311	P= 0 R^2=0.013
C, Humic like nm							P= 0 R^2=0.283	P= 0.003178 R^2=0.095	P= 0 R^2=0.03
DOC mg/l								P= 0.008 R^2=0.498	P= 0 R^2=0.107
DON mg/l									P= 0.003230 R^2=0.002
SUVA (L mg-1 m-1)									

Table-5 cont.: Correlation Matrix among Fluorescence Parameters for High As Tubewells

Table-5 cont.	Tyrosine- like, Protein like (B) nm/DOC	Tryptophane-like, Protein like or Phenol Like (T)nm/DOC	A, Humic like nm/DOC	C, Humic like nm/DOC	As µg/l	Mn µg/l
Fluorescence Index (FI)	P= 0 R^2=0.007	P= 0 R^2=0.015	P= 0 R^2=0.127	P= 0 R^2=0.304	P= 0.001588 R^2=0.027	P=0.000012 R^2=0.082
Freshness Index (Fr I)	P= 0 R^2=0	P= 0 R^2=0.012	P= 0.001110 R^2=0.088	P= 0 R^2=0.213	P= 0.001545 R^2=0.043	P= 0 R^2=0.12
Tyrosine- like, Protein like (B) nm	P= 0 R^2=0.689+	P= 0.005 R^2=0.586+	P= 0 R^2=0.21+	P= 0 R^2=0.153	P= 0.002 R^2=0.2	P= 0 R^2=0.005
Tryptophane-like, Protein like or Phenol Like (T)nm	P= 0 R^2=0.086	P= 0 R^2=0.318+	P= 0 R^2=0.151	P= 0.000534 R^2=0.085	P= 0.001517 R^2=0.021	P= 0 R^2=0.009
A, Humic like nm	P= 0 R^2=0	P= 0 R^2=0.022	P= 0 R^2=0.55	P= 0 R^2=0.408+	P= 0.002 R^2=0.369+	P= 0 R^2=0.035
C, Humic like nm	P= 0 R^2=0	P= 0 R^2=0.028	P= 0.077083 R^2=0.575	P= 0 R^2=0.555	P= 0.002 R^2=0.398	P= 0 R^2=0.053
DOC mg/l	P= 0 R^2=0.230	P= 0 R^2=0.082	P= 0 R^2=0	P=0 R^2=0.014	P= 0 R^2=0.024	P= 0 R^2=0.014
DON mg/l	P= 0.003171 R^2=0.07	P= 0.003171 R^2=0.051	P= 0.003180 R^2=0.023	P= 0.003175 R^2=0.004	P= 0.021589 R^2=0	P= 0.329925 R^2= 9E-05
SUVA (L mg-1 m-1)	P= 0 R^2=0.003	P= 0 R^2=0.001	P= 0 R^2=0.187	P= 0 R^2=0.244+	P= 0.002 R^2=0.077	P= 0 R^2=0.131

Tyrosine- like, Protein like (B) nm/DOC					P=0.002 R^2=0.035+	P=0.000012 R^2=0
Tryptophane-like, Protein like or Phenol Like (T)nm/DOC					P= 0.0015 R^2=0.06+	P=0.000012 R^2=0.006-
A, Humic like nm/DOC					P=0.002 R^2=0.288+	P=0.000012 R^2=0.28-
C, Humic like nm/DOC					P=0.002 R^2=0.247+	P=0.000012 R^2=0.306-

Table 6: Correlation Matrix Among Fluorescence Parameters for Low As Tubewells

Table-6	Fluorescence Index (FI)	Freshness Index (Fr I)	Tyrosine- like, Protein like (B) nm	Tryptophane-like, Protein like or Phenol Like (T)nm	A, Humic like nm	C, Humic like nm	DOC µg/l	DON µg/l	SUVA (L mg-1 m-1)
Fluorescence Index (FI)		P= 0 R^2= 0.002	P= 0 R^2=0.08	P= 0 R^2=0.06	P= 0 R^2=0.096	P= 0 R^2=0.113	P= 0 R^2=0.113	P= 0.044 R^2=0	P= 0.001 R^2=0.103
Freshness Index (Fr I)			P= 0 R^2=0.42	P= 0 R^2=0.386	P= 0.001097 R^2=0.276	P= 0 R^2=0.144	P= 0 R^2=0.063	P= 0.043775 R^2=0.12	P= 0 R^2=0.062
Tyrosine- like, Protein like (B) nm				P= 0.082814 R^2=0.946	P= 0.002535 R^2=0.903	P= 0.089959 R^2=0.621	P= 0 R^2=0.311	P= 0.043517 R^2=0.123	P= 0 R^2=0.019
Tryptophane-like, Protein like or Phenol Like (T)nm					P= 0.000931 R^2=0.968	P= 0.392423 R^2=0.704	P= 0 R^2=0.271	P= 0.043535 R^2=0.104	P= 0 R^2=0.024
A, Humic like nm						P= 0.004 R^2=0.688	P= 0 R^2=0.292	P= 0.044 R^2=0.117	P= 0 R^2=0.038
C, Humic like nm							P= 0 R^2=0.139	P= 0.044 R^2=0.104	P= 0 R^2=0.098
DOC mg/l								P= 0.196 R^2=0.011	P= 0 R^2=0.137
DON mg/l									P= 0.044511 R^2=0.035
SUVA (L mg-1 m-1)									

Table-6 cont: Correlation Matrix Among Fluorescence Parameters for Low As Tubewells

Table-6 cont.	Tyrosine- like, Protein like (B) nm/DOC	Tryptophane-like, Protein like or Phenol Like (T)nm/DOC	A, Humic like nm/DOC	C, Humic like nm/DOC	As µg/l	Mn µg/l
Fluorescence Index (FI)	P= 0 R^2=0.097	P= 0 R^2=0.073	P= 0 R^2=0.122	P= 0 R^2=0.11	P= 0 R^2=0.336	P= 0 R^2=0.022
Freshness Index (Fr I)	P= 0 R^2=0.414	P= 0 R^2=0.374	P= 0 R^2=0.253	P= 0 R^2=0.1	P= 0 R^2=0.021	P= 0 R^2=0.109
Tyrosine- like, Protein like (B) nm	P= 0.666732 R^2=0.88	P= 0.051071 R^2=0.86	P= 0.000837 R^2=0.799	P= 0.115772 R^2=0.431	P= 0 R^2=0.139	P=0 R^2=0.188
Tryptophane-like, Protein like or Phenol Like (T)nm	P= 0.217069 R^2=0.84	P= 0.217069 R^2=0.94	P= 0 R^2=0.89	P= 0.442836 R^2=0.518	P= 0 R^2=0.13	P= 0 R^2=0.196
A, Humic like nm	P= 0.004397 R^2=0.79	P= 0.002103 R^2=0.914	P= 0.940737 R^2=0.933	P= 0.009240 R^2=0.501	P= 0 R^2=0.164	P= 0 R^2=0.184
C, Humic like nm	P= 0.125614 R^2=0.652	P= 0.315579 R^2=0.787	P= 0.000699 R^2=0.748	P= 0.715968 R^2=0.942	P= 0 R^2=0.161	P= 0 R^2=0.092
DOC mg/l	P= 0 R^2=0.075	P= 0 R^2=0.13	P= 0 R^2=0.139	P= 0 R^2=0.035	P= 0 R^2=0.009	P= 0.097933 R^2=0.08
DON mg/l	P= 0.043517 R^2=0.136	P= 0.043534 R^2=0.113	P= 0.043649 R^2=0.122	P= 0.043547 R^2=0.087	P= 0.047308 R^2=0.002	P= 0.005389 R^2=0.236
SUVA (L mg-1 m-1)	P= 0 R^2=0.108	P= 0 R^2=0.065	P= 0 R^2=0.092	P= 0 R^2=0.145	P= 0 R^2=0.37	P= 0 R^2=0.012

Tyrosine/DOC					P=0.00004 R^2=0.14+	P=0.001 R^2=0.199-
Tryptophane/DOC					P=0.00004 R^2=0.132+	P=0.0012 R^2=0.106-
AHumic/DOC					P=0.00004 R^2=0.193+	P=0.0012 R^2=0.048-
CHumic/DOC					P=0.00004 R^2=0.13+	P=0.0012 R^2=0.004-

Table 7: Correlation Matrix Among Fluorescence Parameters and Cations for High As Tubewells

Table-7	Ca µg/l	Mg µg/l	Na µg/l	K µg/l	Fe µg/l
Fluorescence Index (FI)	P= 0 R^2=0.032	P= 0 R^2=0.002	P= 0 R^2=0.011	P= 0.084442 R^2=0.014	P= 0.000947 R^2=0.050
Freshness Index (Fr I)	P= 0 R^2=0.054	P= 0 R^2=0.038	P= 0 R^2=0.015	P= 0.084 R^2=0.103	P= 0.001 R^2=0.004
Tyrosine- like, Protein like (B) nm	P= 0 R^2=0.009	P= 0 R^2=0.041	P= 0 R^2=0.074	P= 0.084 R^2=1E-05	P= 0.001 R^2=0.059
Tryptophane-like, Protein like or Phenol Like (T)nm	P= 0 R^2=0.061	P= 0 R^2=0.005	P= 0 R^2=0.016	P= 0.084 R^2=0.02	P= 0.001 R^2=0.086
A, Humic like nm	P= 0 R^2=0.01	P= 0 R^2=0.016	P= 0 R^2=0.022	P= 0.084 R^2= 0.067	P= 0.001 R^2=0.134+
C, Humic like nm	P= 0 R^2=0.006	P= 0 R^2=0.04	P= 0 R^2=0.031	P= 0.084 R^2=0	P= 0.001 R^2=0.187+
DOC mg/l	P= 0 R^2=0.081	P= 0 R^2=0.127	P= 0 R^2=0.021	P= 0.197546 R^2=0.285	P= 0.123361 R^2=0.008
DON mg/l	P= 0 R^2=0.033	P= 0 R^2=0.108	P= 0 R^2=3E-05	P= 0.118883 R^2=0.742	P= 0.016309 R^2=0.033
SUVA (L mg-1 m-1)	P= 0 R^2=8E-06	P= 0 R^2=0.281-	P= 0 R^2=0.011	P= 0.084 R^2=0.016	P= 0.001 R^2=0.256+

Tyrosine- like, Protein like (B) nm/DOC	P=0.0000000001 R^2=0.045+	P=0.00000000001 R^2=0.046-	P=0.000000002 R^2=0.042+	P=0.109 R^2=0.083-	P=0.004 R^2=0.075+
Tryptophane-like, Protein like or Phenol Like (T)nm/DOC	P=0.0000000001 R^2=0.027+	P=0.00000000001 R^2=0.099+	P=0.0000000002 R^2=0.00001	P=0.109 R^2=0.15-	P=0.0047 R^2=0.099+
A, Humic like nm /DOC	P=0.0000000001 R^2=0.00002-	P=0.000000000001 R^2=0.13-	P=0.000000002 R^2=0.01+	P=0.109 R^2=0.03-	P=0.004 R^2=0.258+
C, Humic like nm/DOC	P=0.0000000001 R^2=0.005-	P=0.0000000001 R^2=0.182-	P=0.0000000002 R^2=0.009+	P=0.109 R^2=0.143-	P=0.004 R^2=0.285+

Table 8: Correlation Matrix Among Fluorescence Parameters and Cations for Low As Tubewells

Table-8	Ca µg/l	Mg µg/l	Na µg/l	K µg/l	Fe µg/l
Fluorescence Index (FI)	P= 0 R^2=0.274	P= 0 R^2=0.118	P= 0.001 R^2=0.085	P= 0.101 R^2=0.1	P= 0.23 R^2=0.461
Freshness Index (Fr I)	P= 0 R^2=0.246	P= 0 R^2=0.391	P= 0.001 R^2=0.429	P= 0.1 R^2=0.029	P= 0.195 R^2=0.077
Tyrosine- like, Protein like (B) nm	P= 0 R^2=0.478	P= 0 R^2=0.451	P= 0.001 R^2=0.306	P= 0.098491 R^2=0.047	P= 0.166103 R^2=0.005
Tryptophane-like, Protein like or Phenol Like (T)nm	P= 0 R^2=0.497	P= 0 R^2=0.545	P= 0.001 R^2=0.336	P= 0.098524 R^2=0.075	P= 0.167229 R^2=0.013
A, Humic like nm	P= 0 R^2=0.537	P= 0 R^2=0.549	P= 0.001 R^2=0.298	P= 0.098857 R^2=0.078	P= 0.177383 R^2=0.009
C, Humic like nm	P= 0 R^2=0.504	P= 0 R^2=0.453	P= 0.001 R^2=0.316	P= 0.098574 R^2=0.013	P= 0.168485 R^2=5E-05
DOC mg/l	P= 0 R^2=0.009	P= 0 R^2=0.088	P= 0.001 R^2=0.023	P= 0.075516 R^2= 0.012	P= 0.034959 R^2=0.010
DON mg/l	P= 0	P= 0	P= 0.001	P= 0.321782	P= 0.047102

	R^2=0.220	R^2=0.084	R^2=0.12	R^2=0.004	R^2=0.025
SUVA (L mg-1 m-1)	P= 0 R^2=0.1	P= 0 R^2=0.066	P= 0.001 R^2=0.051	P= 0.103 R^2=0.053	P= 0.303 R^2=0.063
Tyrosine/DOC	P=0.001 R^2=0.393-	P=0.001 R^2=0.512-	P=0.002 R^2=0.171+	P=0.19 R^2=0.056+	P=0.31 R^2=0.199+
Tryptophane/DOC	P=0.001 R^2=0.435-	P=0.0001 R^2=0.643-	P=0.002 R^2=0.222+	P=0.188 R^2=0.089+	P=0.311 R^2=0.232+
AHumic/DOC	P=0.001 R^2=0.47-	p=0.0001 R^2=0.616-	P=0.002 R^2=0.18+	P=0.189 R^2=0.106+	P=0.336 R^2=0.266+
CHumic/DOC	P=0.001 R^2=0.324-	P=0.0001 R^2=0.323-	P=0.002 R^2=0.167+	P=0.189 R^2=0.004+	P=0.32 R^2=0.034+

Table-9: Correlation Matrix Among Fluorescence Parameters and Cations for Pond Water

Table-9	Ca µg/l	Mg µg/l	Na µg/l	K µg/l	Fe µg/l
Fluorescence Index (FI)	P= 0.001382 R^2=0.265+	P= 0.000022 R^2= 0.071	P= 0.000425 R^2= 0.007	P= 0.000362 R^2=0.002	P= 0.346542 R^2=0.424+
Freshness Index (Fr I)	P= 0.001382 R^2= 0.002	P= 0.000022 R^2=0.001	P= 0.000425 R^2=0.108	P= 0.000362 R^2=0.483-	P= 0.346496 R^2=0.019
Tyrosine- like, Protein like (B) nm	P= 0.001382 R^2=0.545+	P= 0.000022 R^2=0.625+	P= 0.000425 R^2=0.265+	P= 0.000362 R^2= 0.468+	P= 0.346472 R^2=0.769+
Tryptophane-like, Protein like or Phenol Like (T)nm	P= 0.001382 R^2=0.379+	P= 0.000022 R^2= 0.511+	P= 0.000425 R^2=0.313+	P= 0.000362 R^2=0.622+	P= 0.346488 R^2= 0.664+
A, Humic like nm	P= 0.001382 R^2=0.111+	P= 0.000022 R^2=0.305+	P= 0.000425 R^2=0.452+	P= 0.000362 R^2=0.754+	P= 0.346597 R^2=0.352+
C, Humic like nm	P= 0.001382 R^2= 0.201+	P= 0.000022 R^2=0.341+	P= 0.000425 R^2=0.387+	P= 0.000362 R^2=0.746+	P= 0.346597 R^2=0.501+
DOC mg/l	P= 0.004096 R^2=0.108+	P= 0.000584 R^2=0.232+	P= 0.001157 R^2=0.208+	P= 0.000781 R^2=0.885+	P= 0.903266 R^2=0.318+
DON mg/l	P= 0.795133 R^2=0.069	P= 0.658975 R^2=0.165	P= 0.765340 R^2=0.091	P= 0.961648 R^2=0.006	P= 0.461538 R^2=0.016-

SUVA (L mg-1 m-1)	P= 0.001382 R^2=0.156-	P= 0.000022 R^2=0.176-	P= 0.000425 R^2=0.004	P= 0.000362 R^2=0.012-	P= 0.346615 R^2=0.006
Tyrosine/DOC	P= 0.002 R^2=0.264+	P= 0.00004 R^2=0.121+	P= 0.0008 R^2=0.016-	P= 0.001 R^2=0.054-	P= 0.35 R^2=0.27+
Tryptophane/DOC	P= 0.002 R^2=0.186+	P= 0.00005 R^2=0.116+	P= 0.0008 R^2=0.005+	P= 0.001 R^2=0.001+	P= 0.35 R^2=0.37+
A Humic/DOC	P= 0.002 R^2=0.011+	P= 0.00004 R^2=0.018+	P= 0.0008 R^2=0.464+	P= 0.001 R^2=0.394+	P= 0.35 R^2=0.066+
C humic/DOC	P= 0.002 R^2=0.031+	P= 0.00005 R^2=0.089+	P= 0.0008 R^2=0.416+	P= 0.001 R^2=0.473+	P= 0.35 R^2=0.286+

Table-10: Correlation Matrix Among Fluorescence Parameters and Cations for Irrigation Wells

Table-10	Ca µg/l	Mg µg/l	Na µg/l	K µg/l	Fe µg/l
Fluorescence Index (FI)	P= 0 R^2= 0.258	P= 0 R^2=0.305	P= 0.033 R^2=0.263	P= 0.004 R^2=0.056	P=0.270 R^2=0.103
Freshness Index (Fr I)	P= 0 R^2=0.698	P= 0 R^2=0.78	P= 0.033 R^2=0.741	P= 0.004 R^2= 0.251	P= 0.270 R^2=0.107
Tyrosine- like, Protein like (B) nm	P= 0 R^2=0.535	P= 0 R^2=0.367	P= 0.033 R^2=0.738	P= 0.004 R^2= 0.007	P= 0.270 R^2=0.06
Tryptophane-like, Protein like or Phenol Like (T)nm	P= 0 R^2=0.287	P= 0 R^2=0.186	P= 0.033 R^2=0.493	P= 0.004 R^2= 0.005	P= 0.270 R^2=0.006
A, Humic like nm	P= 0 R^2=0.041	P= 0 R^2=0.193	P= 0.033 R^2=0.009	P= 0.004 R^2= 0.231	P= 0.270 R^2=0.06
C, Humic like nm	P= 0 R^2=0.241	P= 0 R^2=0.477	P= 0.033 R^2=0.158	P= 0.004 R^2= 0.211	P= 0.270 R^2=0.096
DOC mg/l	P= 0.001 R^2=0.203	P= 0.001 R^2=0.092	P= 0.034 R^2=0.342	P= 0.484 R^2= 0.004	P= 0.386 R^2=0.007
DON mg/l	P= 0 R^2=0.234	P= 0 R^2=0.603	P= 0.034 R^2=0.19	P= 0.124 R^2= 0.076	P= 0.705 R^2=0.027

SUVA (L mg-1 m-1)	P= 0 R^2=0.194	P= 0 R^2=0.196	P= 0.033 R^2=0.291	P= 0.004 R^2= 0.035	P= 0.271 R^2=0.019
Tyrosine/DOC	P=0.0004 R^2=0.617-	P=0.0006 R^2=0.514-	P=0.064 R^2=0.752+	P=0.008 R^2=0.068-	P=0.274 R^2=0.177-
Tryptophane/DOC	P=0.0004 R^2=0.364-	P=0.0006 R^2=0.336-	P=0.06 R^2=0.489+	P=0.008 R^2=0.009-	P=0.274 R^2=0.115-
Ahumic/DOC	P=0.0004 R^2=0.006+	P=0.0006 R^2=0.135+	P=0.06 R^2=0.001-	P=0.008 R^2=0.055+	P=0.274 R^2=0.013-
Chumic/DOC	P=0.0004 R^2=0.147+	P=0.0006 R^2=0.407+	P=0.06 R^2=0.126-	P=0.008 R^2=0.022+	P=0.274 R^2=0.004-

Table 11: Correlation Matrix Among Fluorescence Parameters and Anions High As Tubewells

Table-11	Cl µg/l	Br µg/l	NO3 µg/l	PO4 µg/l	SO4 µg/l	F µg/l	NO2 µg/l
Fluorescence Index (FI)	P= 0 R^2=1E-05	P= 0.004 R^2=0.004	P= 0.065 R^2=0.011	P= 0.015 R^2= 0.012	P= 0.017 R^2= 0.006	P= 0 R^2=0.036	P= 0.011 R^2=0.003
Freshness Index (Fr I)	P= 0 R^2=0.017	P= 0.004 R^2=1E-07	P= 0.065 R^2=0.116	P= 0.015 R^2= 0.013	P= 0.017 R^2=0.098	P= 0 R^2=0.052	P= 0.011 R^2=0
Tyrosine- like, Protein like (B) nm	P= 0 R^2=0.003	P= 0.004 R^2=0.001	P= 0.065 R^2=0.016	P= 0.015 R^2= 0.012	P= 0.017 R^2=0.012	P= 0 R^2=0.023	P= 0.011 R^2=0.082
Tryptophane-like, Protein like or Phenol Like (T)nm	P= 0 R^2=0.003	P= 0.004 R^2=0.014	P= 0.065 R^2=0.004	P= 0.015 R^2= 0.002	P= 0.017 R^2=0.004	P= 0 R^2=0.017	P= 0.011 R^2=0.029
A, Humic like nm	P= 0 R^2=0.003	P= 0.004 R^2=0.003	P= 0.065 R^2=0.041	P= 0.015 R^2= 0.007	P= 0.017 R^2=0.011	P= 0 R^2=0.044	P= 0.011 R^2=0.029
C, Humic like nm	P= 0 R^2=0.018	P= 0.004 R^2=0.002	P= 0.065 R^2=0.002	P= 0.015 R^2= 0.011	P= 0.017 R^2=0.009	P= 0 R^2=0.028	P= 0.011 R^2=0.016
DOC mg/l	P= 0 R^2=0.112	P= 0 R^2=0.006	P= 0.992 R^2=0.239	P= 0 R^2= 0.08	P= 0.049 R^2=0.255	P= 0 R^2=0	P= 0 R^2=0
DON mg/l	P= 0 R^2=0.091	P= 0.006 R^2=0.003	P= 0.278 R^2=0.084+	P= 0.041 R^2= 0	P= 0.025 R^2=0.54+	P= 0.032 R^2=0.04	P= 0.17 R^2=0.007

SUVA (L mg-1 m-1)	P= 0 R^2=0.089	P= 0.004 R^2=0.014	P= 0.065 R^2=0.022	P= 0.016 R^2= 0.013	P= 0.017 R^2=0.097	P= 0 R^2=0.016	P= 0.011 R^2=0.017
Tyrosine/DOC	P=0.0008 R^2=0.012-	P=0.012 R^2=0.024+	P=0.132 R^2=0.134-	P=0.034 R^2=0.264+	P=0.00000003 R^2=0.011-	P=0.019 R^2=0.09-	P=0.039 R^2=0.016-
Tryptophane/DOC	P=0.00082 R^2=0.022-	P=0.012 R^2=0.033-	P=0.132 R^2=0.015-	P=0.034 R^2=0.35+	P=0.00000003 R^2=0.055-	P=0.019 R^2=0.074	P=0.0393 R^2=015
A humic/DOC	P=0.00082 R^2=0.1-	P=0.012 R^2=0.02-	P=0.132 R^2=0.03-	P=0.0338 R^2=0.083+	P=0.0000003 R^2=0.2-	P=0.0194 R^2=0.117-	P=0.0393 R^2=0.121-
C Humic/DOC	P=0.00082 R^2=0.19-	P=0.012 R^2=0	P=0.132 R^2=0.157-	P=0.0338 R^2=0.065+	P=0.000000031 R^2=0.127-	P=0.0194 R^2=0.08-	P=0.0392 R^2=0.264-

Table 12: Correlation Matrix Among Fluorescence Parameters and Anions Low As Tubewells

Table-12	Cl µg/l	Br µg/l	NO3 µg/l	PO4 µg/l	SO4 µg/l	F µg/l	NO2 µg/l
Fluorescence Index (FI)	P= 0 R^2=0.04+	P= 0 R^2=0.001	P= 0.024 R^2=1E-05	P= 0.001 R^2= 0.136	P= 0.001 R^2=0.293	P= 0 R^2=0.002	P= 0.045 R^2=0.016
Freshness Index (Fr I)	P= 0 R^2=0.704+	P= 0 R^2=0.481+	P= 0.024 R^2=0.155-	P= 0.001 R^2= 0.463+	P= 0.001 R^2=0.503-	P= 0 R^2=0.203-	P= 0.045 R^2=0.11+
Tyrosine- like, Protein like (B) nm	P= 0 R^2=0.657+	P= 0 R^2=0.106	P= 0.024 R^2=0.136	P= 0.001 R^2= 0.143	P= 0.001 R^2=0.461	P= 0 R^2=0.151	P= 0.045 R^2=0.004
Tryptophane-like, Protein like or Phenol Like (T)nm	P= 0 R^2=0.712	P= 0 R^2=0.075	P= 0.024 R^2=0.116	P= 0.001 R^2= 0.149	P= 0.001 R^2=0.483	P= 0 R^2=0.131	P= 0.045 R^2=0.017
A, Humic like nm	P= 0 R^2=0.634+	P= 0 R^2=0.159+	P= 0.024 R^2=0.242-	P= 0.001 R^2= 0.219+	P= 0.001 R^2=0.425-	P= 0 R^2=0.153-	P= 0.043 R^2=0.257+
C, Humic like nm	P= 0 R^2=0.383	P= 0 R^2=9E-05	P= 0.024 R^2=0.125	P= 0.001 R^2= 0.018	P= 0.001 R^2=0.455	P= 0 R^2=0.005	P= 0.043 R^2=0.035
DOC mg/l	P= 0 R^2=0.011	P= 0.335 R^2=0	P= 0.573 R^2=0.015	P= 0.345 R^2= 0.043	P= 0.001 R^2=0.019	P= 0.145 R^2=0.003	P= 0.056 R^2=0.010
DON mg/l	P= 0 R^2=0.106	P= 0.175 R^2=5E-05	P=0 .2 R^2=0.99	P= 0.282 R^2= 0.032	P= 0.001 R^2=0.065	P= 0.954 R^2=0.132	P= 0.096 R^2=0.297

SUVA (L mg-1 m-1)	P= 0 R^2=0.016	P= 0 R^2=0.012	P= 0.024 R^2=0.038	P= 0.001 R^2= 0.066	P= 0.001 R^2=0.12	P= 0 R^2=0.008	P= 0.046 R^2=0.004
Tyrosine/DOC	P=0.00009 R^2=0.552+	P=0.0001 R^2=0.226+	P=0.097 R^2=0.343-	P=0.0052 R^2=0.146+	P=0.033 R^2=0.507-	P=0.021 R^2=0.065-	P=0.023 R^2=0.095-
Tryptophane/DOC	P=0.000089 R^2=0.681+	P=0.0001 R^2=0.193+	P=0.097 R^2=0.253-	P=0.005 R^2=0.205+	P=0.033 R^2=0.519-	P=0.021 R^2=0.059-	P=0.023 R^2=0.15+
AHumic/DOC	P=0.000089 R^2=0.658+	P=0.0001 R^2=0.171+	P=0.097 R^2=0.312-	P=0.005 R^2=0.249+	P=0.033 R^2=0.519-	P=0.021 R^2=0.1-	P=0.024 R^2=0.13+
CHumic/DOC	P=0.0000894 R^2=0.18+	P=0.0001 R^2=0.000003+	P=0.097 R^2=0.198-	P=0.0052 R^2=0.001+	P=0.033 R^2=0.313-	P=0.021 R^2=0.095+	P=0.024 R^2=0.011+

Table 13: Correlation Matrix Among Fluorescence Parameters and Anions for Ponds

Table-13	Cl µg/l	Br µg/l	NO3 µg/l	PO4 µg/l	SO4 µg/l	F µg/l	NO2 µg/l
Fluorescence Index (FI)	P= 0.002 R^2=0.099	P= 0.048 R^2= 7E-06	P= 0.019 R^2=0.097	P= 0 R^2= 0.113	P= 0 R^2=0.455	P=0.001 R^2=0.267	P= 0.137 R^2=0.333
Freshness Index (Fr I)	P= 0.002 R^2=0.092	P= 0.048 R^2=0.002	P= 0.019 R^2=0.428	P= 0 R^2= 0.158	P= 0 R^2=0.018	P=0.001 R^2=0.2	P= 0.137 R^2=0
Tyrosine- like, Protein like (B) nm	P= 0.002 R^2=0.1+	P= 0.047 R^2=0.164-	P= 0.019 R^2=0.026-	P= 0 R^2= 0.843+	P= 0 R^2=0.003-	P= 0.001 R^2=0.209-	P= 0.137 R^2=0.665+
Tryptophane-like, Protein like or Phenol Like (T)nm	P= 0.002 R^2=0.148	P= 0.048 R^2=0.146	P= 0.019 R^2=0	P= 0 R^2= 0.795	P= 0 R^2=0.01	P= 0.001 R^2=0.076	P= 0.137 R^2=0.498+
A, Humic like nm	P= 0.002 R^2=0.282	P= 0.048 R^2=0.03	P= 0.019 R^2=0.058	P= 0 R^2= 0.458	P= 0 R^2=0.018	P= 0.001 R^2=0.016	P= 0.137 R^2=0.203
C, Humic like nm	P= 0.002 R^2=0.2	P= 0.048 R^2=0.044	P= 0.019 R^2=0.025	P= 0 R^2= 0.586+	P= 0 R^2=0.036	P= 0.001 R^2=0	P= 0.137 R^2=0.329+
DOC mg/l	P= 0.003 R^2=0.249	P= 0 R^2=0.075	P= 0.06 R^2=0.05	P= 0 R^2= 0.575+	P= 0.975 R^2=0.01	P= 0 R^2=3E-05	P= 0 R^2=0.245
DON mg/l	P= 0.002 R^2=0	P= 0.002 R^2=0.075	P= 0.069 R^2=0.567+	P= 0.49 R^2= 0.016	P= 0.001 R^2=0	P= 0 R^2=0.382	P= 0.930 R^2=0.232

SUVA (L mg-1 m-1)	P= 0.002 R^2=0	P= 0.048 R^2=0.048	P= 0.019 R^2=0.168	P= 0 R^2= 0.005	P= 0 R^2=0.294-	P= 0.001 R^2=0.070	P= 0.137 R^2=0.087
Tyrosine/DOC	P= 0.001 $R^{2=}$0.088-	P= 0.05 R^2=0.211-	P= 0.02 R^2=0.246-	P= 0.0001 R^2=0.076+	P= 0.002 R^2=0.052-	P= 0.001 R^2=0.574-	P= 0.014 R^2=0.187+
Tryptophane/DOC	P= 0.002 R^2=0.02-	P= 0.047 R^2=0.298-	P= 0.02 R^2=0.07-	P= 0.0001 R^2=0.168+	P= 0.0002 R^2=0.16-	P= 0.001 R^2=0.338-	P= 0.14 R^2=0.163+
Ahumic/DOC	P= 0.001 R^2= 0.229+	P= 0.05 R^2=0.01+	P= 0.02 R^2=0.069+	P= 0.0001 R^2=0.04+	P= 0.0002 R^2=0.162+	P= 0.001 R^2=0.197+	P= 0.14 R^2=0.005+
Chumic/DOC	P= 0.001 R^2= 0.142+	P= 0.05 R^2=0.000002+	P= 0.02 R^2=0.025+	P= 0.0001 R^2=0.206+	P= 0.0002 R^2=0.247-	P=0.001 R^2=0.027+	P= 0.14 R^2=0.125+

Table-14: Correlation Matrix Among Fluorescence Parameters and Anions for Irrigation Wells

Table-14	Cl µg/l	Br µg/l	NO3 µg/l	PO4 µg/l	SO4 µg/l	F µg/l	NO2 µg/l
Fluorescence Index (FI)	P= 0.107 R^2=0.196	P= 0.001 R^2=0.32	P= 0.871 R^2=0.193	P= 0.011 R^2= 0.053	P= 0.345 R^2=0.201	P= 0 R^2=0.339	P= 0.021 R^2=0.006
Freshness Index (Fr I)	P= 0.103 R^2=0.669+	P= 0.034 R^2=0.867+	P= 0.483 R^2=0.065	P= 0.879 R^2= 0.22	P= 0.124 R^2=0.099	P= 0.003 R^2=0.092	P= 0.425 R^2=0.103
Tyrosine- like, Protein like (B) nm	P= 0.1 R^2=0.524+	P= 0.173 R^2=0.245+	P= 0.16 R^2=0.006	P= 0.021 R^2= 0.143+	P= 0.044 R^2=0.001	P= 0.095 R^2=0.251-	P= 0.373 R^2=0.072
Tryptophane-like, Protein like or Phenol Like (T)nm	P= 0.1 R^2=0.13+	P= 0.275 R^2=0.003+	P= 0.179 R^2=0.078+	P= 0.033 R^2= 0.09	P= 0.048 R^2=0.004	P= 0.275 R^2=0.396	P= 0.463 R^2=0.059
A, Humic like nm	P= 0.103 R^2=4E-07	P= 0.188 R^2=0.07	P= 0.444 R^2=0.075	P= 0.984 R^2= 0.011	P= 0.108 R^2=0.053	P= 0.028 R^2=0.192	P= 0.411 R^2=0.125
C, Humic like nm	P= 0.101 R^2=0.093	P= 0.727 R^2=0.293	P= 0.214 R^2=0.158	P= 0.11 R^2= 0.065	P= 0.054 R^2=0.143	P= 0.936 R^2=0.026	P= 0.665 R^2=0.164
DOC mg/l	P= 0.059 R^2=0.253-	P= 0.058 R^2=0.301-	P= 0.058 R^2=0.002	P= 0.058 R^2= 0.048-	P= 0.059 R^2=0.032	P= 0.058 R^2=0.002-	P= 0.058 R^2=0.49+
DON mg/l	P= 0.044 R^2=0.259-	P= 0.024 R^2=0.278-	P= 0.024 R^2=0.684+	P= 0.024 R^2= 0.001+	P= 0.024 R^2=0.664+	P= 0.024 R^2=0.037+	P= 0.024 R^2=0.113+

SUVA (L mg-1 m-1)	P= 0.112 R^2=0.00004+	P= 0.005 R^2=0.001-	P= 0.358 R^2=0.539+	P= 0.006 R^2= 0.482+	P= 0.649 R^2=0.625+	P= 0 R^2=0.005+	P= 0.012 R^2=0.251-
Tyrosine/DOC	P=0.17 R^2=0.738+	P=0.285 R^2=0.514+	P=0.18 R^2=0.012+	P=0.04 R^2=0.386+	P=0.06 R^2=0.001+	P=0.03 R^2=0.155-	P=0.32 R^2=0.232-
Tryptophane/DOC	P=0.17 R^2=0.48+	P=0.39 R^2=0.232+	P=0.19 R^2=0.027+	P=0.05 R^2=0.255+	P=0.06 R^2=0.008+	P=0.04 R^2=0.111-	P=0.36 R^2=0.303-
Ahumic/DOC	P=0.17 R^2=0.002-	P=0.28 R^2=0.086-	P=0.32 R^2=0.258+	P=0.53 R^2=0.154+	P=0.09 R^2=0.263+	P=0.22 R^2=0.243-	P=0.998 R^2=0.019-
Chumic/DOC	P=0.169 R^2=0.135-	P=0.79 R^2=0.313-	P=0.21 R^2=0.399+	P=0.1 R^2=0.06+	P=0.06 R^2=0.435+	P=0.225 R^2=0.041-	P=0.48 R^2=0.013-

Table-15: Mean Median and Standard Deviation Table for Fluorescence Parameters for the Murshidabad Water Samples, January 2012

Table-15	**Fluorescence Index**	**Freshness Index**	**Tyrosine**	**Tryptophane**	**A humic**	**C humic**	**DOC ppb**	**DON ppb**
High As Tube wells	Mean=1.73 Median=1.75 Std. dev=0.062 N=17	Mean=0.77 Median=0.76 Std. dev=0.065 N=17	Mean=0.13 Median=0.11 Std. dev=0.05 N=17	Mean=0.18 Median=0.15 Std. dev=0.06 N=17	Mean=1.01 Median=0.83 Std. dev=0.46 N=17	Mean=0.50 Median=0.45 Std. dev=0.21 N=17	Mean=1808.89 Median=1546 Std. dev=604.38 N=17	Mean=1095..51 Median=941 Std. dev=1302.33 N=17
Low As Tube wells	Mean=1.73 Median=1.74 Std. dev=0.096 N=11	Mean=0.96 Median0.99 Std. dev=0.14 N=11	Mean=0.18 Median0.11 Std. dev=0.12 N=11	Mean=0.26 Median=0.16 Std. dev=0.21 N=11	Mean=0.67 Median=0.50 Std. dev=0.51 N=11	Mean=0.30 Median=0.25 Std. dev=0.24 N=11	Mean=989.43 Median1045 Std. dev=233.69 N=11	Mean=415.31 Median=98.22 Std. dev=802.22 N=11
Ponds	Mean=1.61 Median=1.61 Std. dev=0.05 N=8	Mean=0.79 Median=0.77 Std. dev=0.06 N=8	Mean=0.51 Median=0.42 Std. dev=0.27 N=8	Mean=0.82 Median=0.77 Std. dev=0.41 N=8	Mean=2.97 Median=3.003 Std. dev=1.42 N=8	Mean=1.37 Median=1.3 Std. dev=0.72 N=8	Mean=8741 Median=8742.5 Std. dev=3333 N=8	Mean=1767.61 Median=1893 Std. dev=689.68 N=8
Irrigation wells	Mean=1.69 Median=1.7 Std. dev=0.07 N=7	Mean=0.85 Median=0.79 Std. dev=0.15 N=7	Mean=0.14 Median=0.13 Std. dev=0.05 N=7	Mean=0.20 Median=0.21 Std. dev=0.05 N=7	Mean=0.81 Median=0.93 Std. dev=0.36 N=7	Mean=0.36 Median=0.43 Std. dev=0.17 N=7	Mean=1330.4 Median=1120 Std. dev=464.51 N=7	Mean=706.7 Median=318.2 Std. dev=716.16 N=7

Table-16: Mean Median and Standard Deviation Table for Fluorescence Parameters for the Murshidabad Water Samples, January 2012

Table-16	**SUVA**	**Tyrosine/DOC**	**Tryptophane/DOC**	**A humic/DOC**	**C humic/DOC**	**As ppb**	**Mn ppb**
High As Tube wells	Mean=2.84 Median=2.79 Std. dev=0.51 N=17	Mean=0.08 Median=0.08 Std. dev=0.03 N=17	Mean=0.10 Median=0.10 Std. dev=0.03 N=17	Mean=0.56 Median=0.52 Std. dev=0.18 N=17	Mean=0.28 Median=0.28 Std. dev=0.09 N=17	Mean=274.59 Median=276 Std. dev=296.42 N=17	Mean=756.63 Median=602.31 Std. dev=499.75 N=17
Low As Tube wells	Mean=3.52 Median=3.62 Std. dev=1.03 N=11	Mean=0.18 Median=0.19 Std. dev=0.10 N=11	Mean=0.25 Median=0.25 Std. dev=0.18 N=11	Mean=0.65 Median=0.76 Std. dev=0.44 N=11	Mean=0.30 Median=0.30 Std. dev=0.26 N=11	Mean=12.78 Median15 Std. dev=5.98 N=11	Mean=1031.18 Median=1000 Std. dev=765.28 N=11
Ponds	Mean=2.78 Median=2.83 Std. dev=0.31 N=8	Mean=0.06 Median=0.05 Std. dev=0.02 N=8	Mean=0.09 Median=0.09 Std. dev=0.02 N=8	Mean=0.33 Median=0.31 Std. dev=0.07 N=8	Mean=0.15 Median=0.14 Std. dev=0.03 N=8	Mean=. 36.25 Median= 25.11 Std. dev= 42.25 N=5	Mean= 295.68 Median= 289.43 Std. dev= 234.91 N=4
Irrigation wells	Mean=2.58 Median=2.57 Std. dev=0.51 N=7	Mean=0.12 Median=0.12 Std. dev=0.06 N=7	Mean=0.16 Median=0.14 Std. dev=0.07 N=7	Mean=0.61 Median=0.60 Std. dev=0.22 N=7	Mean=0.27 Median=0.27 Std. dev=0.10 N=7	Mean= 237.96 Median= 237.96 Std. dev= 275.85 N=2	Mean= 325.49 Median= 325.49 Std. dev= 157.68 N=2

Table-17: Mean Median and Standard Deviation Table for Cations and Anions for the Murshidabad Water Samples, January 2012

Table-17	**Ca ppb**	**Mg ppb**	**Na ppb**	**K ppb**	**Fe ppb**	**Cl ppb**	**Br ppb**	**NO_3 ppb**
High As Tube wells	Mean=115041.3 Median=121285.8 Std. dev=32515.92 N=17	Mean=36353.46 Median=37819.06 Std. dev=7338.931 N=17	Mean=26132.35 Median=26851 Std. dev=8971.274 N=17	Mean=7956.06 Median=2618 Std. dev=19350.56 N=17	Mean=3190.22 Median=1995 Std. dev=4005.877 N=17	Mean=21106.22 Median=12028.7 Std. dev=21174.83 N=17	Mean=215.99 Median=90 Std. dev=314.87 N=17	Mean=1923.14 Median=669.3 Std. dev=4995.69 N=17
Low As Tube wells	Mean=51199.57 Median=34339.39 Std. dev=37368.14 N=11	Mean=11730.92 Median=9445.931 Std. dev=6317.40 N=11	Mean=174546.1 Median=266049.8 Std. dev=140035 N=11	Mean=275.15 Median=0 Std. dev=645.97 N=11	Mean=7.32 Median=0 Std. dev=22.08 N=11	Mean=122893.1 Median=134509.8 Std. dev=64669.05 N=11	Mean=905.95 Median=121 6.4 Std. dev=489.67 N=11	Mean=1738.86 Median=640.9 Std. dev=3148.54 N=11
Ponds	Mean=47543.42 Median=38102.53 Std. dev=29169.27 N=8	Mean=20303.6 Median=19548.56 Std. dev=6486.72 N=8	Mean=48894.62 Median=42780.9 Std. dev=24673.3 N=8	Mean=33041.82 Median=38110.75 Std. dev=18150.18 N=8	Mean=8859.09 Median=0 Std. dev=25049.23 N=8	Mean=71011.55 Median=73986.25 Std. dev=40354.86 N=8	Mean=495.93 Median=100 Std. dev=583.76 N=8	Mean=4811.83 Median=4392.95 Std. dev=4503.551 N=8
Irrigation wells	Mean=89919.54 Median=97909.03 Std. dev=33299.59 N=7	Mean=28048.16 Median=29106.51 Std. dev=11475.05 N=7	Mean=83615.26 Median=36496.36 Std. dev=97441.24 N=7	Mean=1588.28 Median=1916.90 Std. dev=1101.11 N=7	Mean=1203.214 Median=0 Std. dev=2643.86 N=7	Mean=37.14 Median=3.22 Std. dev=62.51 N=7	Mean=0.33 Median=0.03 Std. dev=0.51 N=7	Mean=1.65 Median=0.79 Std. dev=2.68 N=7

Table-17 cont: Mean Median and Standard Deviation Table for Anions and Cl/Br Ratio for the Murshidabad Water Samples, January 2012

Table-17 cont.	**PO_4 ppb**	**F ppb**	**NO_2 ppb**	**SO_4 ppb**	**Cl/Br Ratio**
High As Tube wells	Mean=386.24 Median=40 Std. dev=685.15 N=17	Mean=412.49 Median=456.6 Std. dev=171.33 N=17	Mean=574.69 Median=30 Std. dev=910.93 N=17	Mean=10004.14 Median=1500 Std. dev=18373.38 N=17	Mean= 3391.85 Median= 1768.75 Std. dev= 4531.4 N=17
Low As Tube wells	Mean=973.21 Median=1182.5 Std. dev=906.28 N=11	Mean=492.03 Median=40 Std. dev=595.77 N=11	Mean=63.83 Median=40 Std. dev=79.03 N=11	Mean=8456.68 Median=1459.2 Std. dev=11329.62 N=11	Mean= 1736.69 Median= 287.52 Std. dev= 3509.56 N=11
Ponds	Mean=2051.25 Median=1836.5 Std. dev=775.06 N=8	Mean=416.96 Median=431.05 Std. dev=222.63 N=8	Mean=1664.36 Median=413.85 Std. dev=2802.52 N=8	Mean=8794.11 Median=7399 Std. dev=3549.42 N=8	Mean= 6368.22 Median= 1231.92 Std. dev= 10440.74 N=8
Irrigation wells	Mean=0.77 Median=1.17 Std. dev=0.70 N=7	Mean=0.40 Median=0.44 Std. dev=0.22 N=7	Mean=0.60 Median=0.03 Std. dev=1.16 N=7	Mean=2.92 Median=1.52 Std. dev=3.17 N=7	Mean= 1020.57 Median= 413.21 Std. dev= 1074.83 N=7