Chapter III

Literature Review
3.1. Source of As in the aquifers of Bengal Basin

Presence of elevated level of As in groundwater was first reported in West Bengal in early ‘80s (Saha, 1984). After first reporting of As in groundwater of Bengal Basin many researchers have put forward their effort to characterize the sources and process that lead to the enrichment of As in the groundwater. It is well established that high As groundwater in BDP is derived from nonpoint and geogenic sources (Goodbred and Kuehl, 2000; Mukherjee et al., 2009; Biswas et al., 2012; 2014). Since, the basin is developed by the supply of enormous volume of sediment load, carried by River Ganges and Brahmaputra, which drains the fore slope and back slope of the Himalaya respectively (Milliman and Meade, 1983; Goodbred and Kuehl, 2000; Mukherjee et al., 2009a), it is hypothesized that the source of As in the sediments of Bengal Basin lies in the Himalaya, perhaps the sulphidic minerals, the weathering product of crystalline metamorphic rocks (McArthur et al., 2004; Polizzotto et al., 2006). The Gondwana coal seems in the Rajmahal Basin, located in the upstream of River Ganges, sometimes has also been accounted as the source of As in the aquifer sediment. Acharya et al., (1999); McArthur et al. (2004) has proposed that probably, during weathering of the source rocks As containing sulphide minerals were oxidized to Fe oxyhydroxides, which were later deposited in the basin, while Polizzotto et al. (2006) indicated the oxidation of sulphide minerals after deposition. Beside Fe oxyhydroxides, other metal oxyhydroxides like Mn and Al, clay minerals and phyllosilicate like biotite also play key role in the As transport and cycling (Foster et al., 2000; Kent and Fox, 2004; Charlet et al., 2005; Chakraborty et al., 2007; Charlet et al., 2007; Seddique et al., 2008). However, the high As concentration in the groundwater of Bengal Basin does not coincide with high As concentration in the aquifer sediment (McArthur et al., 2004; Swartz et al., 2004; Nath et al., 2005, 2008c), which has led researchers to conclude that rather than source, the enrichment of As in groundwater is an artifact of groundwater evolution, governed by the interplay of various biogeochemical interactions (Harvey et al., 2006; Bhattacharya et al., 2007).

3.2. As mobilization hypothesis in the aquifers of Bengal Basin

Several hypotheses have been proposed till now to explain the release of As in groundwater.

3.2.1. Oxidation Hypothesis: This was one of the first proposed hypothesis. Arsenic is released in aquifer via oxidation of As-bearing sulfide minerals, like pyrite (Das et al., 1996; Mallick and Rajagopal 1996; Chowdhury et al., 1999; Fazal et al., 2001). Harvey et al. (2002)
further suggested that due to excessive groundwater withdrawal for irrigation purpose in BDP water table going to decrease and consequently aeration of sediment occurs, followed by additional release of As in groundwater. However, the aquifer where dissolved oxygen is absent (especially, where groundwater withdrawal is absent) and in the low redox potential together with prevalence of dissolved Fe(II) and As(III) over Fe(III) and As(V) respectively have discarded this hypothesis. On the other hand $\text{SO}_4^{2-}$ and As do not show any correlation with each other, if As is released in groundwater as a major component during pyrite oxidation (Ahmed et al., 2004).

### 3.2.2. Iron Reduction Hypothesis

However, the most widely accepted mechanism for the release of As into groundwater is the reductive dissolution of As containing different metal oxyhydroxides, especially Fe oxyhydroxides, which are common in the sedimentary environments (Nickson et al., 2000; Dowling et al., 2002; Harvey et al., 2002; Smedley and Kinniburgh, 2002; Stüben et al., 2003; Charlet and Polya, 2006; Biswas et al., 2014). Mobilization of As into the groundwater of shallow aquifer of BDP by reductive dissolution of different Fe oxides in presence of labile organic matter is the widely accepted mechanism now (Nickson et al., 2000; BGS/DPHE, 2001; Dowling et al., 2002; Harvey et al., 2002; Smedley and Kinniburgh, 2002; Stüben et al., 2003; Charlet and Polya, 2006, Biswas et al., 2014). It is further established that reductive dissolution of Fe oxyhydroxides coupled to the degradation of organic matter is catalyzed by certain metal reducing bacteria (Akai et al., 2004; Islam et al., 2004) and this mechanism is currently considered as a most widely accepted mechanism (Fendorf, 2010). However, this reductive process needs strong involvement of labile organic matter and the source of this labile organic matter is still a controversial issue. Some scientists reported that organic matter may be the possible outcome from peat layers (Ravenscroft et al., 2001; Mc Arthur et al., 2008).

### 3.2.3. Competitive Ion Exchange

The competitive exchange model (exchange between $\text{PO}_4^{3-}$ and $\text{AsO}_4^{3-}$) was initially proposed to highlight the high levels of As in groundwater of BDP, when $\text{PO}_4^{3-}$ is also present in groundwater (Acharyya et al., 1999; 2000). The proposed model postulates that there is a good possibility of exchange (competitive exchange) in between $\text{PO}_4^{3-}$ and $\text{AsO}_4^{3-}$. 

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Because they have similar absorptive capacity. The proposed model has been put forward in BDP, where excessive use of fertilizer (use of agricultural inorganic $\text{PO}_4^{3-}$ fertilizer) has been used to increase agricultural output during green revolution (Nath et al., 2007). The competitive exchange model is there by linking release of As from various adsorbed surfaces (clay, organic matter, silicates). When $\text{PO}_4^{3-}$ is chemically exchanging as sorption effect. This model has been further extended by several workers and the several workers and the several competitive exchange (HCO$_3^-$, SiO$_4^{2-}$) has been proposed in similar manner like $\text{PO}_4^{3-}$ (Apollo et al., 2002; Bauer and Blodau et al., 2002)

The above model has been examined and found several lacuna in the proposed mechanism. The major cause for rejection is competitive exchange anion concentrations in a groundwater should increases with depth, where as the reverse has been reported (Jain and Loeppert, 2000; Dixit and Hering, 2003). Furthermore, high concentration of competitive ion should correspond with low HCO$_3^-$. However, in reality the reverse has been reported (Meng et al., 2000; Stachowicz et al., 2007).

3.3. Influence of Anthropogenic activity

Many hypothesis have been put forward to explain/understand the As release mechanism in groundwater. The most accepted mechanism is the reductive dissolution of different Fe oxides, which are common in sedimentary environments, is a key process for the release of As into groundwater (Nickson et al., 2000; Dowling et al., 2002; Harvey et al., 2002; Stüben et al., 2003; Charlet and Polya, 2006, Farooq et al., 2010). But this reductive process needs strong involvement of labile organic matter and the source of this labile organic matter is still a controversial issue. Some scientists reported that organic matter may be the possible outcome from peat layers (Mc Arthur et al., 2008; Ravenscroft et al 2001). However Harvey et al. (2005) suggested that reduction of different Fe oxides can triggered by surface derived organic carbon from local pond, which is drawn into the aquifer by irrigational pumping, continuous pumping of community water wells/ public water wells. Recently researchers have reported that human activities like land use pattern, large scale groundwater development for irrigation, sanitation installation and local recharge from degraded eco-systems can have significant impact. The reaction time between sediment and groundwater is very crucial for kinetically controlled hydro chemical balance chemical reactions like, competitive surface exchange and dissolution of mineral phases (Harvey et al., 2005; Stute et al., 2007). From the time period of Indian “Green Revolution” massive use of
groundwater withdrawal through irrigation pumping is very popular and regular practice, which affects the regional hydrology (Harvey et al., 2005). At the dry period due to the huge groundwater abstraction with the progressive lowering of the head of local groundwater head O$_2$ fronts enter into the aquifer and causing oxidation of reduced sediment and as a consequence As release in to the aquifer according to Oxidation hypothesis.

![Fig.3.1. Schematic cross-sections illustrating hypotheses A and B, which both link the distribution of As in the aquifer to groundwater pumping for irrigation purposes. Hypothesis A suggests that As is mobilized by re-infiltrated irrigation water which has high concentrations of young organic carbon. Hypothesis B proposes that the decrease in groundwater residence time in the upper part of the Holocene aquifer causes As to be flushed out of it. The pumping of large water volumes increases the rate of groundwater regeneration, and hence the distinct peak-shape of profile (2) develops from profile (1). Both hypotheses present a conceptual elucidation for the peak-shaped vertical As concentration profile practical at the Bengal Basin Note that hypotheses A and B are not mutually exclusive. (source: Klump et al., 2006)](image)

![Fig.3.2. Conceptual model of sources and pathways for the introduction of modern and young organic matter to shallow arsenic-prone aquifers in BDP. Transportation of modern DOC from surface ponds to the aquifer even in the absence of huge groundwater pumping. Groundwater pumping may decrease the travel time of young DOC to greater depths within the aquifer system. Anthropogenic activities, such as the excavation of surficial clays or extensive groundwater pumping, are likely to result in changes to the relative proportions of different organic matter sources present in groundwaters, which may ultimately influence the arsenic hazard in shallow groundwaters of this region. [source: Lawson et al., 2013)](image)
3.4. Role of Organic matter

In BDP the geomicrobiological release mechanism is a recent argument. The basic important issue is the role of organic matter, which is playing key role with the help of bacteria (mostly metal reducing bacteria) to mobilize As from solid to aqueous phase (Akai et al., 2004; Islam et al., 2004; Oremland et al., 2005). The natural process is complex and controlled under local situation, which is varies from place to place and unique in active deltas and flood plain. In the sedimentary environment where often oxygen along with sunlight (energy source) is generally lacking which impedes reducing nature of the bacteria, where organic matter plays important role (see Fig. 3.3) (Oremland et al., 2005). In fact the nature, type, characteristic and quality of the organic matter is important and playing crucial role to maintain reducing environment, where high As groundwater is common (Biswas et al., 2014; Majumder et al., 2016). Moreover, labile, reactive, easily degradable and fresh small organic molecules (with short aliphatic chain) are playing crucial role, which can be accepted and as well as mediated by a wide range of bacteria like, FeRB, arsenate reducing prokaryotes (DARP’s) (Mailloux et al., 2003; Knapett et al., 2011)

![Fig. 3.3. Three possible mechanism of As mobilization in BDP groundwater in anoxic environment. The reactions are carried out by metal reducing bacteria with the help of organic matter and by using Fe(III) and As(V) as terminal electron acceptor. (source: Oremland et al., 2005)](image)
It is further important to note that their concentration and distribution is another important factor which is regulating the system, including As release in groundwater. It has been already found that their concentration are decreasing with depth in aquifer sediments (notably, in BDP). This could be one of the possible explanation to explain the ‘bell shaped’ vertical profile As distribution in BDP aquifer (Harvey et al., 2005; Polizotto et al., 2008). In age old worked and reworked sediments (often mature) where recalcitrant organic matter, mostly plant fibre, long chain soil based organic (humic and fulvic acid) are preserved during depositional environment (Roland et al., 2006). However, the reduction process of various organic matter (long chain to short chain) is an important issue, because they helps electron shuttling reaction and and also provide large fraction of long life span organic carbon fraction (Lovley et al., 1996; Straub et al., 2001; Kappler et al., 2004). These dissolve organic carbon fraction is often known as DOC (dissolved organic carbon). It has been noted that the level of DOC is often high in shallow As contaminated aquifer of BDP (Bhattacharyya et al., 2003; Polizotto et al., 2005; Neumann et al., 2010). The role of DOC is important and often dual in character, which means that the degradability, labiality, reactivity are significant signature of those DOC's which plays crucial role in electron donation (supply of electron in microbial respiration processes). On the other hand persisting humic substances are often carrying out electron shuttling reaction, where Fe(III) reduction is a common phenomenon. The possible mechanism of As mobilization in groundwater in reducing condition as mediated by metal reducing bacteria are already reported (Islam et al., 2004; Oremland et al., 2005).

Oremland and Stolz have already mentioned the various reaction where oxidation of organic matter has been carried out by the microbes in presence of various metal oxide, these metal oxide are generally terminal electron acceptor (TEA), on the other hand DARP’s are also important and they are releasing adsorbed As from the surface of various metal oxide, that has been often reported in various part of BDP (Fendorf et al., 2010; Neumann et al., 2010).

Recently researchers have reported that human activities like land use pattern, large scale groundwater development for irrigation, sanitation installation and local recharge from degraded eco-systems can also have significant impact on As release processes (Harvey et al., 2002; Neumann et al., 2009; Sutton et al., 2009; Biswas et al., 2014; Majumder et al., 2016). For example, in the area, where surface aquitard is thin (≤3 m), local pond can be hydraulically connected with the underlying shallow aquifers and can act as a potential contributor to the groundwater recharge (Biswas et al., 2014). Especially during monsoon
rain, when the surface recharge increases, pond and wetland can serve as a potential source of infiltrating dissolved organic carbon (DOC), (Kocar et al., 2008; Polizzotto et al., 2008; Lawson et al., 2013; 2016; Mailloux et al., 2013). In a recent study of 20 months long hydrogeochemical monitoring we have hypothesized the continuous seepage of organic rich water from a nearby pond as responsible for the gradual development of anoxia at the uppermost part of the shallow aquifer causing continuous release of As into the groundwater over the monitoring period at this depth (Lawson et al., 2013; Biswas et al., 2014). Nevertheless, the potential influence of ponds as a source of organics to the shallow aquifers is still a matter of debate (Harvey et al., 2006; Sengupta et al., 2008; Neumann et al., 2010; Datta et al., 2011; McArthur et al., 2011) and it needs further investigations.

3.5. As distribution in Vertical and temporal pattern in the aquifers of Bengal Basin BDP

Several studies on BDP clearly indicate that the occurrence of dissolved As is primarily in shallow aquifer. Whereas deeper aquifers are often free from As (safe) and usually used for drinking water supply (Charlet et al., 2006; Burgess et al., 2010). Researchers are also been reported that As distribution in BDP is patchy in nature (spar and unspar) which is often changing in narrow scale (up to 10 to 100 m) (Nath et al., 2008a). The BDP ground water flow system is recently influenced by large scale ground water development, notably for irrigation purposes, which may have cause cross-contamination in between shallow-medium-deep aquifers (Harvey et al., 2005). Such cross contamination also have some influence on spatial vertical and temporal distribution pattern of As in BDP. In BDP, the enrichment of As in Shallow aquifer is important and serious. This enrichment is also representing in spatial distribution pattern which spar-inter spar in nature. Such patchy distribution of As often provide safe as well as unsafe aquifer, even in small distances. This typical behavior of lateral As distribution pattern (generally spatial in nature) is the most debatable and encouraging scientific investigation in the As affected areas (van Geen et al., 2008a). Several attempts have been made to explain the hydrological aspect of such spatial heterogeneity. However, the findings are often contradictory. Studies, which was conducted in the north eastern part of BDP (Bangladesh) reveals that large scale ground water flow system is mostly controlled by local scale flow under flat basical topography. This local ground water flow pattern is often influenced by huge groundwater development which is often changing recharge and discharge areas of ground water local flow pattern. Such local
scale behavior of ground water flow pattern may have some influence on spatial, and vertical heterogeneity of As distribution which is often reported in the shallow (<50m). This huge ground water development pattern can often bring fresh organic matter to the shallow aquifer. The nature, type and characteristics of such organic matter is important, because they are easily biodegradable and can be utilized by the natural, bacterial, consortium of the shallow aquifer (Harvey et al., 2005; Lawson et al., 2013). On the contrary researchers are reported that history of aquifer flushing and their seasonal changes under the influence of sub surface geology may cause local as well as regional scale (depending on rate of aquifer flushing and their quantum) of spatial As distribution pattern. These phenomenon are often becoming more conspicuous in nature when aquitards are often beneath the shallow aquifers where such flushings are common. (van Geen et al., 2008a)