# Solute Geochemistry and Arsenic Fate in the Aquifers of Central Gangetic Basin, India

*Thesis submitted to Jawaharlal Nehru University*
*for the award of the degree of*

**DOCTOR OF PHILOSOPHY**

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## Certificate

This is to certify that the research work embodied in this thesis entitled **"Solute Geochemistry and Arsenic Fate in the Aquifers of Central Gangetic Basin, India"** has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. This work is original and has not been submitted in part or full for any other degree or diploma to any university or institute.

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*To my*

*Beloved Parents and*

*Guru Prof. AL. Ramanathan*

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Manoj Kumar

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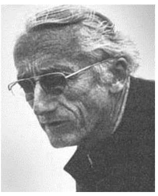
# Chapter 1

# Introduction

*"The ocean is regarded as a sort of bargain basement... People don't realize that water in the liquid state is very rare in the universe. Away from earth it is usually a gas. This moisture is blessed treasure, and it is our basic duty, if we don't want to commit suicide, to preserve it".*



**Jacques-Yves Costeau**

### 1.1. Water, related issues and contaminations

Water resources of any nation constitute one of its fundamental assets. A small fraction of the available water on earth can be considered potable, which can be either surface (e.g. rivers, lakes etc.) and or groundwater sources (Mukherjee et al., 2008). Groundwater is assumed to be less vulnerable to the pollution in comparison to the surface waters (Konikow and Kendy, 2005). With the rapid enhancement in industrialization, boom in the agricultural sector and urbanization in the last few decades, the demand for groundwater has increased. Groundwater depletion is a causation which is expected from the extraction of water from the aquifer in an unbalanced manner (Konikow and Kendy, 2005). The countries facing groundwater depletion worldwide includes major regions of North Africa, the Middle East, North China, North America, Australia, South and central Asia and other localised areas throughout the world (Konikow and Kendy, 2005).

In the context of India, the primary recharge source of the aquifers is known to be monsoonal rainfall, but due to its high uncertainty with respect to time and place, it can raise the problems of flood or drought throughout the country. Due to the rapid growing population and improving standards of life exerting pressure on our water resources, the per capita availability of water resources has been reducing day by day. The contamination of groundwater is mostly attributed to anthropogenic pollution by both microorganisms and chemicals. Studies have revealed that groundwater contamination occurs due to the municipal, agricultural and industrial waste-water discharges (Chan et al., 1998; Ternes, 1998; Heberer, 2002; Khanal et al., 2006; Ghiselli and Jardim, 2007). Besides anthropogenic sources, there is also a geogenic source of the contamination which includes arsenic (As), selenium (Se), fluoride (F), kuranium (U), iron (Fe) and manganese (Mn) which has also been spreading around the world and threatening human lives. There could be some other local source of contamination of Pb (lead) and Cu (copper) from plumbing and the back-flow from treatment plants in case of improper connections and management (Fawell and Nieuwenhuijsen, 2003). To judge the quality and safety of drinking water, international guidelines and national standards are being used.

## 1.2. Geogenic contamination of groundwater and human health: Arsenic, a known major anxiety

The deficiency and/or excess of a particular chemical entity to a certain level caused by a natural geochemical process are considered to be geogenic contamination. Arsenic and $F^-$ are typical examples of the geogenic contamination. High concentration of $F^-$ in the groundwater of twenty-five nations has been the cause of health risks to~200 million people (Ayoob and Gupta, 2006). Currently in India, 20 out of the total 29 states are contaminated with groundwater $F^-$ and the number is likely to increase (Chakraborty et al., 2010). At present 411 million people are living in 20 of the $F^-$ affected states in which 66 million people are suffering from fluorosis (Chakraborty et al., 2016). The remaining population is also at a risk of toxicity. A high groundwater Se concentration has been reported in many parts of the world especially in areas where saline soils and groundwater are common (Deverel and MIllard, 1988). Uranium is found in groundwater associated with granitic rocks and other mineral deposits. Both Fe and Mn can occur at high concentrations in some source water that are anaerobic (Fawell and Nieuwenhuijsen, 2003).

Geogenic or non-point source As contamination of groundwater is widespread in South-East Asian countries. It is not only is it a threat to human health, but also poses a challenge to water supply in the affected areas. It was estimated that the natural As contamination currently affects more that 150 million people in 70 countries (Ravenscroft, 2009). The threat of As is mainly associated with the fluvial and fluvio-deltaic regions viz. Ganga-Brahmaputra-Meghna river system in parts of West Bengal, India and Bangladesh, the Indus River in Pakistan, the Red River in Vietnam, the Irrawaddy River in Myanmar, the Mekong River in Laos and Cambodia and the Yellow River in China. (Acharya et al., 1999; Berg et al., 2001; Iqbal, 2001; Poyla et al., 2005; World Bank, 2005; Saha and Sahu, 2016). Other than the South-East Asian countries, As has been reported in some parts of the countries such as Mexico, Argentina, Chile, Poland, USA and Canada (Chen et al., 2006). The level of the As contamination in the Bengal basin (the lower region of Ganga-Brahmaputra-Meghna) has been well documented and is known as the most severely affected area of the world (Nickson et al., 1998; Burgess et al., 2010). It has been estimated that in 6 states of the Ganga-Brahmaputra plain, 70.4 million people are potentially at risk from groundwater As toxicity (Chakraborty et al., 2016). This has received significant attention in the last three decades due to its serious health effects on millions of people and has been termed “the biggest As calamity in the world” (Smith et al., 2000).

It is hypothesised that the higher concentration of geogenic As is associated with the Holocene shallow aquifers, which has possibly been mobilized from sediments by redox reactions mediated with bacterial activities (Bhattacharya et al., 1997; CGWB, 1997; Nickson et al., 1998; Mukherjee et al., 2006; Kumar et al., 2010a; Kumar et al., 2016). The As contamination in different regions has been reported at different time frames. For instance, the contamination of As in groundwater was noticed in the year 1983 in West Bengal (Garai et al., 1984), in the central Gangetic basin (CGB) in 2002 at the Semaria Ojha Patti village of the Bhojpur district of the state of Bihar (Chakraborti et al., 2003), and in Nepal (Tarai region) in the Gangetic basin in 2003 (Shreshtha et al., 2003).

Even a low dose of As on a long-term exposure can lead to a range of medical complications termed "Arsenicosis" (McCarty et al., 2011). Further consequences of chronic higher As consumption can lead to cancer in the skin, kidneys, liver, bladder, lungs and prostate. Furthermore, it is clearly evident that *in utero* exposure to As can induce epigenetic problems and increase susceptibility to disease later in life (Sanz et al., 2007; Abdul et al., 2015). The groundwater is not only the source of the exposure to people living in the As affected area. Crops irrigated with the As contaminated water, also used as food, can also be sources of the exposure. Arsenic in low concentration can stimulate plant growth but in higher concentration, it can be accumulated above the WHO threshold concentrations for safe ingestion of food crops (Rahman and Naidu, 2009). Recently, the World Health Organisation's Codex Alimentarius has established the maximum limits for inorganic As in rice. Limits of 200 µg/kg for white rice, 250 µg/kg for brown rice and 100 µg/kg for rice destined for the production of foods for infants and young children has been set as the standard (https://www.food.gov.uk/science/arsenic-in-rice). As a consequence, food crops which accumulate elevated As pose serious risks to the health of the local residing population (Dudka and Miller, 1999). In CGB, an amount of 24 and 11 µg/kg of dry weight of As has been reported in the crops of wheat and maize respectively (Singh and Ghosh, 2011).

### 1.3. Mechanisms behind As mobilization

It is justified now to state that high concentration of As can be associated with the reducing aquifer conditions in deltaic and alluvial regions (Smedley and Kinniburgh, 2002). So far four probable mechanisms/chemical associations have been postulated behind the mobilization of As, which have been described below in order of decreasing importance:

*1. Reductive dissolution:* The most common and widely acceptable theory in the alluvial and deltaic plains is that when Fe-oxides, onto which As has been adsorbed/coated, break down because of the decaying of organic matter (which consumes oxygen ($O_2$) sources) and dissolve, they release As in the aqueous solution. In this mechanism, Fe-reducing bacteria such as *Geobacter* reduces Fe(III) to Fe(II) and liberate As(V) directly to a solution where it is converted to As(III) by biotic or abiotic ways. The evolving groundwater from these processes is always strongly reducing in nature, containing high concentrations of bicarbonate ($HCO_3^-$) and Fe, while nitrate ($NO_3^-$) and sulphate ($SO_4^{2-}$) are absent. The process of Fe reduction regulated by decaying of organic matter may be represented by the following equation:

$$8\ FeOOH + CH_3COOH + 14\ H_2CO_3 \longrightarrow 8\ Fe^{2+} + 16\ HCO_3^- + 12\ H_2O$$

*2. Alkali desorption*: The second most common chemical association which forms the mobilization of As, takes place at a higher pH (≥8.0) and in the presence of dissolved $O_2$, $NO_3^-$ or $SO_4^{2-}$, with the evolving water called as 'alkali-oxic' with low concentrations of Fe and Mn. It has been observed that maximum adsorption of As(V) occur at pH 5 and of As(III) at pH 8–9. Sorption of As depends strongly on the pH value and, to a lesser degree, on the presence of competing ions. The Basin-and-Range Province of the USA and the Pampean plains of Argentina are the best examples of alkali desorption of As (Bexfield and Plummer, 2003).

*3. Sulphide oxidation*: This occurs where sulphide minerals such as pyrite or arsenopyrite are exposed to $O_2$, often near a water table, to produce waters that are typically both acidic (pH 1–6) and $SO_4^{2-}$-rich, but not necessarily high in Fe concentration. The equation of the mobilization of As due to oxidation of As-bearing pyrite minerals can be represented as (NIH, 2010):

$$FeAsS + 13\ Fe^{3+} + 8\ H_2O \longrightarrow 14\ Fe^{2+} + SO_4^{2-} + 13\ H^+ + H_3AsO_4\ (aq.)$$

Shallow wells having high water table coupled with over extraction are predominantly susceptible to pollution due to sulphide oxidation chemical complex, as in Washington State (USA), Nova Scotia, France, Ghana and central India (Ravenscroft et al., 2009).

*4. Geothermal*: The waters from deep aquifers, sometimes volcanic, leach As from the country rocks. The evolving water from this process can be distinguished primarily by elevated temperature and usually also by a correlation of As with chloride. It is usually seen in active and former continental-volcanic settings such as New Zealand, the Andes, Southern Italy and the Rockies, and to a lesser extent in the oceanic-volcanic terrains.

Acharyya et al. (1999, 2000) suggested that phosphate fertilizers might be a cause of As contamination in the groundwaters of the Bengal basin, which was later questioned as a significant cause of As mobilization by Ravenscroft et al. (2001).

## 1.4. Arsenic contamination variability in different geomorphic setups

The Ganges plain foreland basin is a repository of sediments originating from the Himalayas and the Peninsular Craton (Acharyya and Shah, 2007). The geomorphology of the Gangetic basin has been documented previously on a broader level (Ahamed et al., 2006; Acharyya and Shah, 2007; Saha and Shukla, 2013). The geomorphic surfaces identified in the regional mapping of the Quaternary deposits of the Ganges plain consist of an active floodplain (T0), river valley terrace surface (T1) and upland interfluves surface (T2). A significant feature of these surfaces is that all of them are depositional surfaces, having a succession of overlying sediments of Holocene over Pleistocene. A study from the

Bengal basin characterized the different gomorphological classification based on the LANDSAT-TM band mosaic and found a large difference in the As concentration in groundwater among all the geomorphic units (Ahmed et al., 2004). The variation in the As concentration has also been observed in CGB and a very high As concentration has been found in Piedmont and Younger Alluvium rather than the Older Alluvium (Mukherjee et al., 2012). In a study, the spatial variability of As in the groundwater of the Ballia district of Uttar Pradesh and the capital city of Bihar, Patna, was conducted on the either sides of the river Ganges. A contrast in the lithological set up was reported with the help of the resistivity survey revealed the results of low resistivity (10–25 Ωm) and high chargeability (5–20 mV/V) for clay deposits between the As contaminated and As free aquifers (Chandra et al., 2011). This was supported by the hydrogeochemical analysis of water samples in CGB, which further revealed the patchy occurrence of As contamination in groundwater with high spatial variability.

### 1.5. Arsenic speciation and its role in mobilisation

Arsenic is a toxic element, known as a class (I) human carcinogen and widely distributed in the environment in both inorganic and organic forms (Hughes et al., 2011). Arsenic behaves distinctly to other oxyanion forming metalloids with respect to its sensitivity to mobilization at a typical pH range (6.5–8.5) of the groundwater (Smedley and Kinniburgh, 2002). Arsenate and most of the other oxyanions have a tendency to become mobile (weakly sorbed), as its pH increases (Dzombak and Morel, 1990). It is noteworthy that the mobility, (phyto)toxicity, potential risk, retention and bioavailability of As in the environment depend on the form in which they enter and the final form in which they are present (Sanz et al., 2007). In well drained and oxygenated soils, As(V) is present as the dominant species. The areas where reducing circumstances are observed include regularly flooded soils or organic matter rich areas. Under these conditions, As(+III), elemental As and arsine(-III) are also present (Van Herreweghe et al., 2003). In the case of As, the inorganic forms are more toxic. Once the inorganic As enters the body, it remains longer than the organic As and furthermore, the process of excreting inorganic As is longer (Abdul et al., 2015).

However, arsenites, is ten times more soluble, mobile (weakly adsorbed) and toxic than As(V) (Mandal and Suzuki, 2002; Van Herreweghe et al., 2003; Chandrasekharam et al., 2007). Hence, determining the total As concentration alone is insufficient for many environmental exposure scenarios. Nonetheless, As speciation analysis is a powerful tool that can generate accurate assessments of environmental impact and risks to human health (Vassileva et al., 2001; Sanz et al., 2007; Rahman et al., 2009; Abdulrahman et al., 2012). The toxicity and bioavailability of As compounds depend on the chemical form in which the As is present (Gong et al., 2002); and secondly, the recycling of As occurs in different environmental scenarios such as swamps, etc. (Zheng et al., 2003). Arsenic remedial action strongly depends on As speciation, the presence of other possible contaminants, and the water chemical composition (Katsoyiannis et al., 2007). The forms of As present in soils depend on the type and amounts of sorbing components available in the soil, pH and redox potential (Mandal and Suzuki, 2002). A study of Ganges River, in Bihar, revealed that fluvial point bars adjacent to the oxbow lakes act as stratigraphic traps for the As-enriched groundwater (Donselaar et al., 2013). These studies address the variation in As concentration occurring in different geomorphologic setups in the CGB.

### 1.6. Stable isotopes applications in studies of As

Stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) are known as ideal tracers and are very useful as a tool to understand the subsurface hydrology and flow paths of groundwater in a better way (Soulsby et al., 2000; Saha et al., 2011; Thilagvathi et al., 2016). Many studies have used stable isotopes of H and O as a proxy to identify the source of the natural recharge of groundwater including the upper Ganges basin and CGB (Saha et al., 2011; Samadder et al., 2011; Mukherjee et al., 2012). The lower Gangetic basin has also been studied extensively with the application of stable isotopic compositions to understand the groundwater dynamics, recharge mechanism and its geochemical behaviour (Agrawal et al, 2000; Harvey et al., 2002; Mukherjee et al., 2007; Mukherjee and Fryar, 2008; Sikdar and Sahu, 2009). It is a well-documented fact that the dissolved organic carbon is known as the primary factor for the reducing conditions in the Gangetic basin which fuel the microbial activities and play a crucial role in the cycling and transport of the carbon and metals including mobilization of As in groundwater. The ($\delta^{13}C$) abundance in the natural carbon is one percent as compared to $^{12}C$. The alteration in the abundance of this ratio can be attributed to the environmental history of carbon and can help in tracing the source of the DOC in the natural system (Vogel, 1959).

### 1.7. Geogenic As contamination in the central Gangetic basin

The CGB is located in the states of Uttar Pradesh and Bihar in India. Geogenic As contamination of tubewells in the CGB was first reported in 2002 at the Semria Ojha Patti village (area 4 km$^2$), Sahapur block in the Bhojpur district of Bihar, India (Chakraborti et al., 2003). Since then, several studies have confirmed a very high level of As and evaluated the situation of groundwater in the CGB (Chakraborti et al., 2003; Chauhan et al., 2009; Kumar et al., 2010a, 2010b; Mukherjee et al., 2012; Saha and Shukla, 2013; Saha and Sahu, 2016). Earlier it was reported that the As spreads were mainly found on both the banks of the river Ganges (Saha, 2009), but currently, new areas are also being reported as having higher As concentration beyond these boundaries. The CGB made up of alluvial deposits of the Ganges and its tributaries, is divided into the upper newer Alluvium known as the Holocene deposits and the lower Older Alluvium also known as the Pleistocene deposits (Acharya, 2005). The hot-spots of As contamination in the CGB is limited to the top 30–40 m bgl of the sequence which is predominately fine-grained, made up of clay/sandy clay with thin (5–10 m) lenses of fine micaceous grey sand enriched with biotite (Saha, 2013; Saha and Sahu, 2016). The top fine-grained deposits are reported to be of Holocene age i.e. 3±1 ka (Acharya, 2004; Shah, 2008), while the Older Alluvium has been reported with less contamination of As (Saha et al., 2010a; Saha and Sahu, 2016). The concentration of As can vary significantly between tubewells only in a short distance apart due to the presence of river interfluves (Fawell and Nieuwenhuijsen, 2003). The CGB has more distinctive geological and geomorphological setups than the lower Bengal delta plain. River geomorphology (frequent river meandering and avulsion) has marked relations with high As in groundwater in the CGB. Due to these differentiations, this region has unevenness in the concentration of As in groundwater even within short distances.

## 1.8. Relevance of study

The elevated level of the As contamination in groundwater and sediments has been well documented in the CGB (Chauhan et al., 2009; Saha et al., 2009, 2010a, 2010b; Kumar et al., 2010a, 2010b; Mukherjee et al., 2012; Saha and Shukla, 2013; Saha and Sahu, 2016; Kumar et al., 2016). Very less effort has been devoted to understanding the role of the geochemical processes and their association with subsurface geochemistry in different geomorphic setups of the CGB. There is a need to understand the role of the major ion chemistry of groundwater and subsurface geochemistry and their interdependency towards mobilization and providence of As and other minor elements in the groundwater of the CGB.

To get an insight into the As mobilization in the CGB, only selected studies have been carried out on the application of the stable isotope in the CGB (Saha et al., 2011; Mukherjee et al., 2012). A very petite attention has been taken towards the role of surface water stagnant bodies in groundwater dynamics and recharge processes. However, no study has been conducted to look into the role of the stagnant water bodies in the groundwater recharge and to test the hypothesis of the organic carbon deposits at the bottom of the ponds and its association with the mobilisation of As in CGB. There is an urgent need to focus on the stable isotopic compositions ($\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$) on a basin scale and to delineate the different sources of the groundwater recharge and the source of the dissolved organic carbon in the study area.

Since most of the studies in the CGB are focused on the estimation of the total As in water as well as in the sediment, only a few studies focus on the speciation of As in groundwater (Chandrasekharam et al., 2007; Chauhan et al., 2009; Kumar et al., 2010a, 2010b). Very little attention has been directed to the speciation studies on As in groundwater, agricultural soils and subsurface sediments in the CGB. So it is crucial to fill this gap in our knowledge. Along with this attempt, we made an effort to understand the role of mineralogy in As mobilization in aquifers, and finally to crosscheck the applicability of the four colour codes for sediment in the CGB of India.

Further, very limited efforts have been directed to determine the degree of As contamination in food components and the associated risk to human through consumption of food. No study has reported elemental concentrations in commonly consumed food components from the CGB of Bihar. Therefore, It is necessary to determine the level of As and other toxic elements present in water, vegetables and other food components grown in this particular area. In the current study the total exposure to As and other elements in water, vegetables and other dietary components in the CGB of Bihar, India, has also been attempted. This study focused on the potential health risks due to the consumption of contaminated water and food components and the role of other related elements that may have a synergistic effect on the health of the people living in the study area.

## 1.9. Research objectives/questions

The present study has been undertaken to carry out the hydro-geochemical characterization of groundwater and subsurface sediment from three different locations representing Piedmont, Older Alluvium and Younger Alluvium in the CGB. The aim of this study was also to enhance the knowledge of the major ion chemistry of groundwater and subsurface geochemistry and their interdependency towards mobilization and providence of As and other minor elements in the groundwater of the CGB. Another aim of this study was to analyze the role of the surface rivers and the stagnant water bodies towards aquifer recharge in this area. The purpose of the study will be to extend this knowledge to speciate the inorganic As in groundwater, soil and sediment samples, finally locate the possible source of the contamination in the groundwater and estimate the health risk on the consumption of contaminated groundwater and food. In this connection, a comprehensive study has been conducted with the following objectives and their respective research questions.

### Hypothesis

Geomorphological features play an important role in As distribution and mobilization in aquifers including food chain via irrigation practices

The main question is whether any distinct geomorphological, lithological and geochemical difference exists between areas where As concentration is present in high and low concentrations.

### Objectives

Within the general objectives, few more specific research questions were addressed

### 1. Geochemical and geomorpho-hydrochemical investigations for As provenance and fate

*Questions*

- Role of weathering in solute dynamics and As fate?

- Latitudinal variation of As and other major solutes in groundwater of the CGB
- Association of groundwater and aquifer sediment geochemistry in As liberation

**2. Groundwater dynamics, recharge processes and DOC behaviour using stable isotopes**

*Questions*

- Are perennial ponds and river channels playing a role in recharging the local aquifers in the CGB?
- Does latitude plays a role in groundwater dynamics in the CGB?
- Behavior of DOC in the CGB

**3. Abundance and distribution of As inorganic species in groundwater, aquifer sediment and agricultural soils**

*Questions*

- What is the ratio of As(III) and As(V) in groundwater, agricultural soil and subsurface sediments
- Arsenic speciation and its mobilization in aquifer sediments
- Role of mineralogy on As mobilization
- Is there any association of As inorganic species with the sediment colour and texture as As total have?
- Applicability of four-color code of As in sediment

**4. Source identification and heath risk assessment of As and other trace elements in groundwater and selected dietary components**

*Questions*

- What are the probable source of the trace elements including As in groundwater and food in the CGB?
- Level of health hazard in the CGB on consumption of contaminated food.

**An outline of the rest of the thesis**

*Chapter 2* details the area chosen for this study in concise (further details of the study are given with separate objectives), *chapter 3* discuss objective 1, *chapter 4* discuss objective 2, *chapter 5* discuss objective 3, *chapter 6* discuss objective 4 and *chapter 7* discuss the summary and conclusions. All the cited references have been listed in bibliography, in the end, the thesis.

# Chapter 2

# Study area

## 2.1 Study area details

Central Gangetic basin (CGB), a part of northern Bihar (25.295° to 26.710° N, 85.130° to 86.950° E), India was undertaken for the current study (**Fig. 2.1**). This area is also known for very fertile and densely populated region of the Gangetic basin. The surveyed area encompasses part of floodplain deposits of the river Ganges and its tributaries covering an area of 32743 km$^2$. In the whole region, the uppermost formations are present flood plains, Diara landforms, channel bars and sand dunes. An area of a stretch from the south bank of the river Ganges near the capital city (Patna) of Bihar to the foothills or Piedmont region of the Himalayas near to the Nepal border. The floodplain deposits of the Ganges and its main tributaries in the area, the River Burhi Gandak, Baghmati and Kamla North Bihar Plain aquifers, which is known to sustain a good reservoir of water in the Indian subcontinent. The CGB is manifest with shallow water level (<8.0 m below ground) with plenty of monsoonal recharge (Saha and Sahu, 2016). The area is known for an agricultural based economy. Most of the cultivation activities and cropping depend on the monsoon cycle except for the crops taken in the winter season when the groundwater meets the requirements (Saha et al., 2011).

Studies have been reported unevenly distributed high concentrations of As in the state's groundwater supplies (Saha and Shukla, 2013). The geography and geomorphology of the survey area have been documented previously (Ahamed et al., 2006; Acharyya and Shah, 2007; Saha and Shukla, 2013). The Ganges plain foreland basin is a repository of sediments originating from the Himalayas and Peninsular Craton (Ahamed et al., 2006; Acharyya and Shah, 2007). The geographic surfaces identified in the regional mapping of the Quaternary deposits of the Ganges plain consist of an active floodplain ($T_0$), river valley terrace surface ($T_1$) and upland interfluves surface ($T_2$). A significant feature of these covers is that all of them are depositional surfaces, having a succession of overlying sediments of Holocene over Pleistocene deposited by Ganges (Mahadevan, 2002).

The Older Alluvium (also called *Bhangar*) comprises well oxidised reddish brown sand, silt and clay with profuse kankar, calcareous nodules and pisolitic Fe concentrations. In contrary the Younger Alluvium (also called *Khader*) comprising unoxidised pale greyish yellow to brown sand, silt and clay. Present day sediments which are contained unoxidised sand, silt and clay overlie and embay into the Younger Alluvium along stream courses, channels, levees and swamps. Among the still younger sequence, an older floodplain has been distinguished from present day flood plain in several areas, which represent the past and present oscillation limits of the Ganges and its tributaries. The youngest sediments in the Ganges basin are loose or less compact and have a high content of carbonaceous matter that makes them look grey or black and form a more porous and water bearing. The Older Alluvium is placed in the middle Pleistocene, the newer Alluvium in the upper Pleistocene to Holocene and the Older and Younger flood plain in the early Holocene to the present (Mahadevan, 2002).

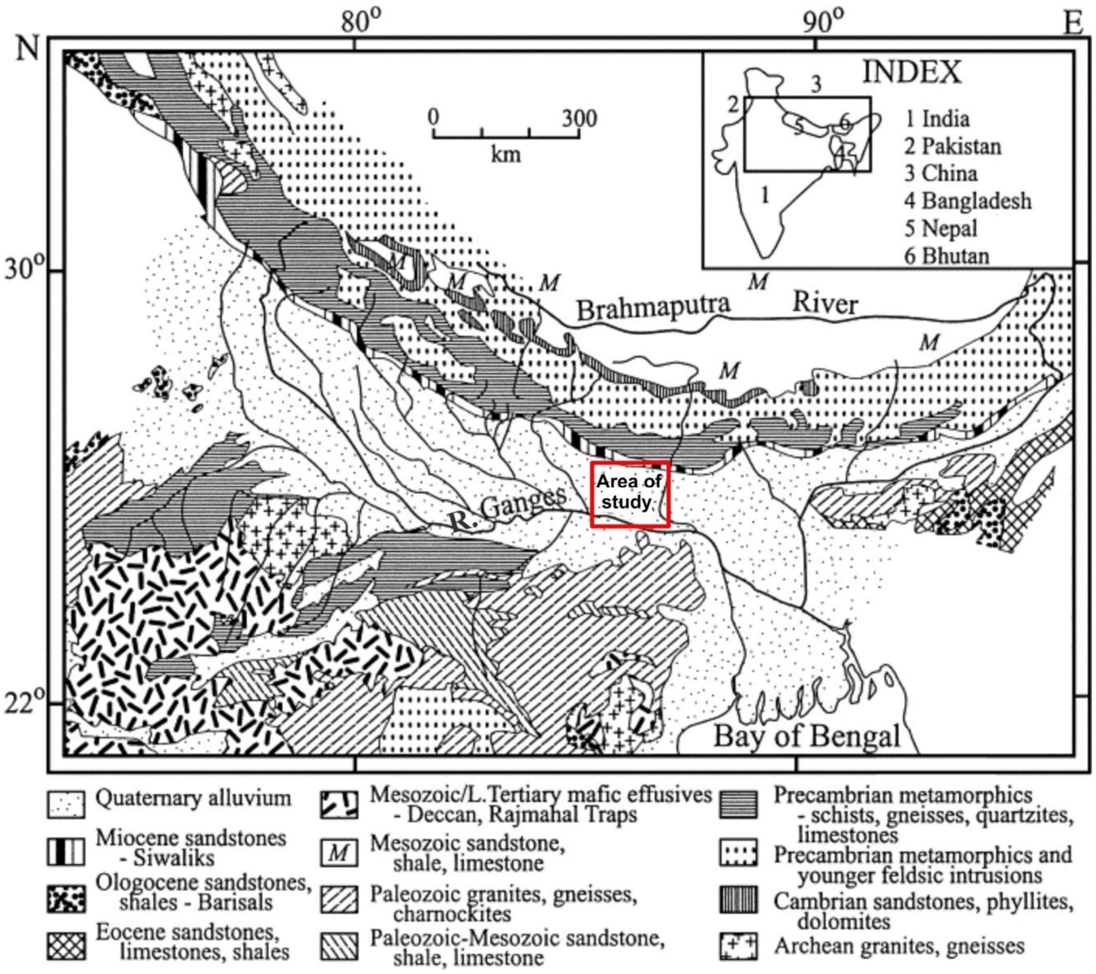


**Fig. 2.1.** Geological map of the Ganges and Brahmaputra drainage basins and surrounding areas (modified from Horey et al., 2003). The red square shape shows the sampling location area

Aquifers of Holocene sandy sediments are unconfined or semi-confined in the CGB, which is mainly used for water extraction. Most of the tubewells extend to shallow aquifers <50 m below ground level (bgl). A two-tier aquifer system (shallow aquifers at a depth of 120–140mbgl and deeper aquifers at 225–240 mbgl) made up of Quaternary sand layers has been identified within 300  m below ground using the drill cut method (Saha and Shukla, 2013). Hand-pumps and tubewells are mainly logged in shallow aquifers (20–60 m) only. Irrigation undertaken in this area relies on the shallow aquifers (Saha and Shukla, 2013).

The area experiences three climatic seasons, March to May experience a hot season; rainy season starts in June beginning with the onset of the South-West monsoon which ends in September. Cold season from November to February, heralded by the retreat of the monsoon in the months of October-November. The average temperature in the cold weather is in the range of 15.5 ºC; December-January is the coldest months, and May-June is the hottest months.

The detailed study area including sampling locations has been given in separate objectives (Chapter 3–6).

# Chapter 3

# Geochemical and geomorpho-hydrochemical investigations for As provenance and fate

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*After*

Hyrdogeochemical triggers for regional scale arsenic release and fate in the central Gangetic Basin, India

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**Research highlights**

- Groundwater As distribution is geochemically and geomorphlogically dependent
- Groundwater As more pervasive in Piedmont and Younger than Older Alluvium aquifers
- Older Alluvium is chemically equilibrated exhibit low As
- Silicate weathering and ion-exchange regulate solute composition in Older Alluvium

## Abstract

Geochmical triggers for regional scale groundwater and sediments on As and other solutes and their fate along regional groundwater flowpath through different geomorphic terrain were inferred in parts of the central Gangetic Basin. Geomorphology and position in the flowpath seem to have a substantial influence on solute chemistry and As distribution. The major groundwater type was Ca-$HCO_3^-$ rich with near to neutral pH in the Piedmont area, while in Younger and Older Alluvium water type ranged from Ca-$HCO_3^-$ to Na-$HCO_3^-$ with slightly alkaline pH. The median concentration of As in Piedmont was 0.2 µM, 0.12 µM in Younger Alluvium and 0.02 µM in Older Alluvium. The median As concentration in core sediments of Piedmont (up to 57mbgl), Older Alluvium (upto 42.6 mbgl) and Younger Alluvium (33.5mbgl) was observed as 0.07, 0.15 and 0.15 molal concentrations, respectively. Aquifers indicated an anoxic to a post-oxic condition in all three geomorphic units. Approximately 70% of the samples fell in $As(OH)_3$ or As(III) field and 30% samples fell in $HAsO_4^{2-}$ or field of As(V). In contrast~60% of the samples fell in the FeOOH field and 40% in Fe(II) field in the Eh-pH plots. Cation exchange plays an important role in Piedmont and Older Alluvium while carbonate dissolution in Younger Alluvium appears to control the groundwater solute chemistry. The groundwater was found be to equilibrium with kaolinite, Ca-smectite, Na-smectite and orthoclase but shows disequilibrium with anorthite and albite. This could be the major source of $Ca^{2+}$ and $K^+$ to the groundwater's solute via silicate weathering. Redox controlled dissolution of Fe-Mn(oxyhydr)oxide was suggested as the probable mechanism for As liberation/ mobilization in Piedmont, while different processes control the mobilization and presence of As in the Younger Alluvium.

## Keywords

Geochemical weathering, Geomorphological setups, Central Gangetic Basin, Oxi-anions

## 3. 1. Introduction

Geogenic or non-point source arsenic (As) contamination of groundwater is widespread in South and South-East Asian countries. It poses a significant threat to human health and a massive challenge to clean water supplies in the affected areas. This threat is mainly associated with the fluvial and fluvio-deltaic regions viz. Ganga-Brahmaputra-Meghna river system in parts of West Bengal, India and Bangladesh, the Indus River in Pakistan, the Red River in Vietnam, the Irrawaddy River in Myanmar, the Mekong River in Laos and Cambodia and finally, the Yellow River in China (Acharya et al., 1999; Berg et al., 2001; Iqbal, 2001; Polya et al., 2005; World Bank, 2005). The level of As contamination in the Bengal Basin (the lower region of Ganga-Brahmaputra-Meghna) has been well documented, and it is now recognized as the world's most severely As affected region (Nickson et al., 1998; Burgess et al., 2010). The level of As contamination in the impacted regions has been reported over the decades. For instance, As contamination in West Bengal was detected in 1983 (Garai et al., 1984), in the Central Gangetic Basin (CGB) in 2002 at Semaria Ojha Patti in Bihar state's Bhojpur district. (Chakraborti et al., 2003). Furthermore, As contamination was reported in 2003 in the Tarai zone in Nepal, at the northern end of the Gangetic Basin (Shreshtha et al., 2003).

The CGB, located in the states of Uttar Pradesh and Bihar in India, is a highly populated and extremely fertile area (Saha and Sahu, 2016). The area of central and upper Gangetic Basin (~0.25 million km$^2$), ranges from the Garo-Rajmahal Hills in the south to the Tarai zone in the north, covers much of Bihar and Uttar Pradesh (population:~303.9 million, Census of India, 2011). A preliminary survey found that ~59% of the hand pumps used in the villages (20–40 m depth) had As greater than 0.66 µM (50 µg/L) (Chakraborti et al., 2003). The sediment in the CGB differentiates into Holocene and Pleistocene depositions and appears to have a grey and brown colour. It was hypothesised that the higher concentration of geogenic As is associated with Holocene shallow aquifers, and probably has been mobilized from sediments via redox reactions mediated with bacterial activity (Bhattacharya et al., 1997; CGWB, 1997; Nickson et al., 1998; McArthur et al., 2004; Mukherjee and Fryar, 2008).

The level of As contamination in groundwater and sediments is well documented in CGB in several studies (Chauhan et al., 2009; Saha et al., 2009, 2010a, 2010b; Mukherjee et al., 2012; Saha and Shukla, 2013; Chakraborti et al., 2016; Kumar et al., 2016; Saha and Sahu, 2016). Only a limited effort has been made to understand the role of geochemical processes and their relationship with subsurface geochemistry in different geomorphic setups of CGB. The central part of the Gangetic Basin has a distinctive geomorphology due to the juxtaposed formation and avulsion of several channels belongs to the river Ganges and its tributaries (Mukherjee et al., 2009, 2012). This paper reports the role of major ion chemistry and subsurface geochemistry and their role in the mobilization and fate of As and other elements (major and minor) in the groundwater of CGB.

## 3.2. Material and methods

### *3.2.1. Background of the study area*

The area undertaken for the study is known as CGB, which forms part of the flood plain of the Ganges and its tributaries, is located in the state of Bihar and covers an area of 32743.1 km$^2$. This area extends from the banks of the Ganges near Patna, the capital city of Bihar in the south to the Terai zone of Nepal in the north (**Fig. 3.1**). The alluvial sediment deposition of the Ganges and its main tributaries, the River Burhi Gandak, Baghmati and Kamla located in the North Bihar Plain, contains a high yield capacity of the groundwater in the Indian subcontinent. The area is regarded as a repository of sediments originating from the Himalayas and Peninsular Craton (Ahamed et al., 2006; Acharyya and Shah, 2007). The CGB does contain a shallow water level (<8.0 m below ground) with ample monsoonal recharge (Saha and Sahu, 2016).

### *3.2.2. Remote sensing and geomorphological investigations*

Identification of the geomorphological features was conducted with the help of a satellite image obtained from the USGS (www.earthexplorer.usgs.gov) based on digital image processing. The image ranged from 25º30'– 26º30' N to 85º30'–86 º 30' N. The image was acquired by Landsat 8 carried by an Operational Land Imager (OLI) sensor on 9 May 2015. The image's pixel size was a 30m resolution for multispectral band sharpened by a 15m panchromatic band. The false colour composite (FCC) band combination 5, 4 and 3 (near-infrared, red and green) was used to differentiate the various geomorphological features. The image was collected on datum WGS 84, projected on UTM 45 and interpolated by resampling –nearest neighbour method. The landforms and features were identified by remote sensing and confirmed by two field visits and were compared with the available previous studies on this area's geomorphology (Saha and Shukla, 2013; Singh and Pandey, 2014; Saha and Sahu, 2016).

### *3.2.3. Study area geomorphology*

The area chosen for this study is located on the northern side of the river Ganges and is one of the most dynamic in the world (Wells and Dorr, 1987; Gole and Chitale, 1996; Jain and Sinha2003; Singh and Pandey, 2014). **Fig. 3.1** illustrates the geomorphological features present including the Younger Alluvial plain (further categorized into the active flood plain and channel depositions), Older Alluvial plain (also known as the interfluves area) and finally the Piedmont Terrain located down to Himalayan foothills. Stagnant surface water bodies, meander scars, active river channels and paleochannels were also found in the area. The active floodplains of the Ganges and its northern tributaries are dotted with numerous stagnant water bodies, meander scars and abandoned channels.

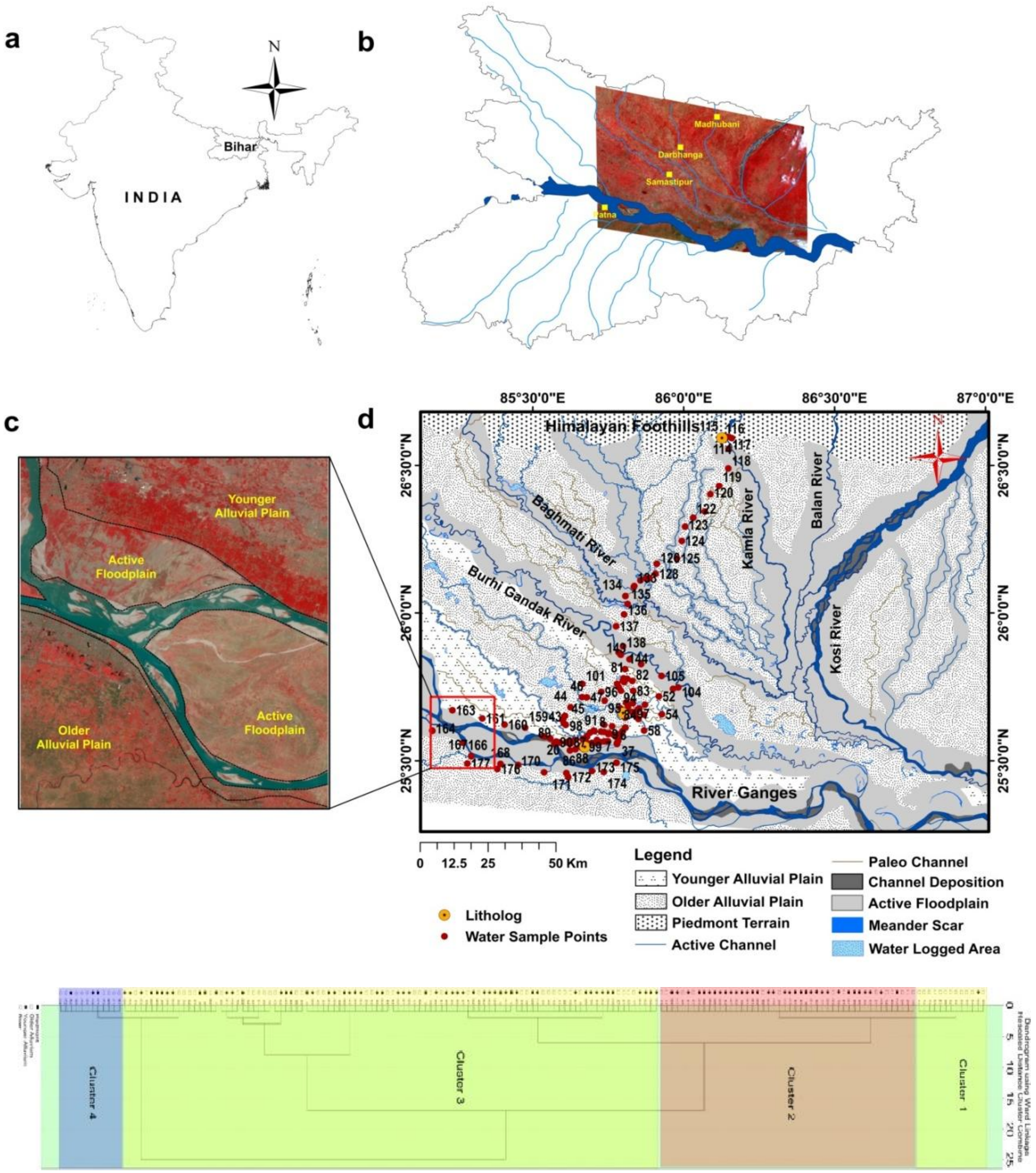

**Fig. 3.1.** Map of the study area (**a**) India (**b**) district Bihar (**c**) geological and geomorphological study area prepared by remote sensing and extensive field survey (**d**) The false color composite (FCC) band combination (band combination 5, 4 and 3) of the given part of the study area image used to distinguished the different geomorphological features. The boundaries of the Younger Alluvial plain, Active floodplain and Older Alluvial plain justify the classification that was undertaken in the study area. Below to study area map (cluster plot for groundwater samples)

The tributaries (such as Kamla, Balan and Baghmati) originated from the Himalayas and carried a heavy amount of sediments and deposits in this area. Some key features were used for the identification of Older and Younger Alluvial plain during the field survey. The Younger Alluvial plain and active flood plains are regularly flooded areas and in general, contain high moisture in their sediments which gives high spectral resolution in satellite image in FCC. The grey colour of the Younger Alluvial plain reveals the presence of reduced metal Fe(II) (oxy) hydroxide minerals (von Bromssen et al., 2007). In contrast, the Older Alluvial plain contains less moisture and enriched with calcite hence give blurred appearance in the satellite image in FCC. Identification of the samples of the Piedmont aquifer is evident from outcrops and the presence of large, round cobblestones in the area's subsurface. The presence of these markers was confirmed during subsurface core sediment collection in Jainagar, city of Madhubani district. For surrounding area, the data were obtained from the local drillers.

### *3.2.4. Sample collection, preservation and transport*

Groundwater (n=164) and river water (n=10) samples were collected from a broad transect following the standard method during 2013–15. The transect extend~ 150km north-south from the Himalayan Piedmont and it crosses the three main tributaries of the Ganges (viz. Kamla, Baghmati and Burhi Gandak) till it reaches Bihar's capital city, Patna. On the basis of geomorphological features of the study area (as above said) the groundwater samples were further categorized into three parts i.e. Piedmont (*n*=8), Older Alluvium (*n*=68), Younger Alluvium (*n*=88). The groundwater samples were also collected from both banks of the River Ganges. Both private tubewells and those installed by the government were selected for collecting water samples from. The depth of the tubewells ranged from 10.6 to 136 mbgl. Most of the tubewells were found at a depth of <50m. The age of the installed tubewells varied from 1 to 52 years. A large number of tubewells were installed 10 years ago. Their locations were reported using portable global positioning (GPS) (Garmin etrex30) device. Water samples of the rivers were collected from the River Ganges (*n*=2), Bya River (*n*=1), Burhi Gandak River (*n*=2), Kamla River (*n*=1), Baghmati River (*n*=1), Santi River (*n*=1), Balan River (*n*=1), and Punpun River (n=1), henceforth, river water will be used for all these river water samples.

Before taking any measurement and samples, the tubewells were purged for 5 min to remove standing water. The measurement of the field parameters, for example, EC, pH and ORP was done *in situ* with the help of a portable multi-parameter HANNA (HI 9828) using a cell flow method to minimize contact with the atmosphere. For As speciation analysis, 50 ml of the water sample was filtered through a disposable cartridge (Metal Soft Center, PA, USA). The cartridge allows the water to pass through and absorb As(V), also permits As(III) to pass through it. In order to minimize chemical alteration, the samples were stored in a portable ice-box. For total As a measurement, 50 ml water sample was passed through a 0.45µm filter with the help of a hand operated vacuum pump followed by adding 2–3 drops of 7M nitric acid ($HNO_3$) as a preservative. Samples for anions study were collected and stored in a 50ml pre-washed plastic container without any preservative added.

Subsurface sediment was collected from three geomorphologically different sites, specifically a Piedmont region, Younger Alluvium plain (also known as the Diara formation) and Older Alluvium plain (also known as the Vaishali formation). It has been categorized in recent studies (Saha and

Shukla, 2013; Singh and Pandey, 2014). A commonly used hand-flapper drilling method was applied to collect the core up to a depth of 57, 42.6 and 33.5 mbgl at Jainagar city, Methrapur and Haral Chapar, respectively. Samples were picked from depths of 1.5, 9.0, 30.0, 36.0, 43.5, 54, 57 mbgl at Jainagar city (Madhubani district), 1.5, 4.5, 9.1, 21.3, 36.6 and 42.6 mbgl at Methrapur village of Dal Singh Sarai block (Samastipur district), while the sediment samples at depths of 1.5, 9.1, 18.3, 24.4 and 33.5 mbgl were collected at Harail Chapar village of Mohiudin Nagar Block (Samastipur district). The above depth samples were screened on the basis of the sediment's grain size and colour. The samples were collected in double zip lock bags and transported to the laboratory. The samples were then dried in the open air in the laboratory for 24 hours and then oven dried at 50 ºC for 72 hours. Finally, the samples were reduced to powder form using an agate and mortar. They were stored in a cool and dry place till further processing.

### *3.2.5. Sediment preparation and digestion*

Samples were digested using a microwave digester (CEM, MARS 6). Approximately 0.5g of the finely powdered sediment sample was weighed directly into a Teflon vessel. An aliquot of 5 ml of separately prepared aqua regia was added into each vessel and allowed to predigest for 30 minutes before sealing the vessels. After 30 minutes each vessel was sealed and loaded into a rotor. After digestion and cooling, the solution was transferred to a 50 ml plastic centrifuge tube, and 20 ml of Milli-Q water was added to dilute it. In order to remove the suspended particles, the digested solution was filtered through syringe filters (PTFE 0.45 µm) and either analysed on the same day or stored in a refrigerator at 4 °C.

### *3.2.6 Instrumentation*

The analysis of the As and other major and minor cations was conducted using inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies, Japan 7500ce). The ICP-MS operating conditions of the analysis have been described previously (Rahman et al., 2015). A Laser Diffraction Particle Size Analyzer (Microtrac, S3500 coupled with Microtrac SDC unit) served to fractionate grain size. Anions estimation was done with the help of IC (DIONEX ICS-2000). DOC analysis was done with the assistance of a total organic carbon analyzer (TOC) SHIMADZU (TOC-L-CSH). The concentrations of $NH_4^+$ and $NO_3^-$ were determined with the help of Skalar Plus Analyzer (SAN++ system 3000). All the analysis was conducted in the Centre for Environmental Risk Assessment and Remediation (CERAR), which is located at the University of South Australia.

### *3.2.7. Hydrogeochemical modelling and Statistical work*

To understand the status of the different phases of the minerals underground, saturation indices (SI) were calculated for the median concentration of the selected elements of the groundwater. Speciation analyses for the mineral phases currently present in the groundwater of the study area were calculated with the aqueous geochemical modelling program PHREEQC by David Parkhurst of the United States Geological Survey (U.S.G.S.) using Geochemist's Workbench (v. 10.0) software. The map was created in ArcMap version 9.3. Statistical evaluation of groundwater data was done through the application of cluster analysis (CA) so that the relationships between the samples could be understood. For this purpose SPSS version, 19 software was employed.

### *3.2.8. Data analyses*

The relationships among the samples and the hydrogeochemical grouping was employed on the basis of distribution of As, Fe, Mn, Zn and major cations and anions. The significance of the method (multivariate) used in this study has been described elsewhere (Davis, 1986; Rock, 1988). The cluster analysis relies on discriminate analysis to check if the groups are statistically significant and whether the variables significantly discriminate between the groups. Cluster analysis shows an association among the groundwater of the different geomorphic units (i.e. Piedmont, Older and Younger Alluvium) as shown in (**Fig. 3.1**). Cluster 1 represents only Older Alluvium except for one sample; cluster 2 denotes the group of Younger Alluvium having~70% of the samples. Cluster 3 is a mixed group including Piedmont, Older and Younger Alluvium while cluster 4 represents purely river water samples.

## 3.3. Results and discussion

### *3.3.1. Groundwater and river water chemistry and hydrochemical facies*

The pH of the Piedmont region (ranges 6.80–7.33) was near to neutral but for Older Alluvium (6.99–7.88) and Younger Alluvium (6.90–7.91), showed slightly alkaline nature (**Table 3.1**). Calcium was the dominant cation in all different geomorphological setups, i.e. Piedmont (55%), Older Alluvium (61%), and Younger Alluvium (67%). The highest median concentration of $Ca^{2+}$ (2482 µM) was observed in Older Alluvium followed by the Younger Alluvium (2441 µM). Potassium was the lowest in concentration among the cations in all setups, but concentrations of $Na^{+}$ and $Mg^{2+}$ were almost comparable for Piedmont, Older and Younger Alluvium. Referring to the anions, $HCO_3^-$ was dominant for all different geomorphic setups. The median concentration of $HCO_3^-$ was virtually the same in the Piedmont, Older Alluvium and Younger Alluvium, and comprised 95–97% of the total anions. The higher median $HCO_3^-$ concentration was observed in Piedmont (8290 µM) followed by Older Alluvium (7357 µM). The highest median concentration of dissolved organic carbon (DOC) was observed in Piedmont (1.78 mg/L) followed by Older Alluvium (0.25 mg/L). The presence of relatively refractory organic matter or limited microbial activity may be responsible for the presence of DOC in the Older Alluvium (Chapelle, 2001).

A lower concentration of DOC (median 0.18 mg/L) in Younger Alluvium indicates more microbial activity in the aquifers. A larger concentration of Si was observed in Older and Younger Alluvium compared to Piedmont (525 µM) and river water (median 319.6 µM). A median $SO_4^{2-}$ concentration was reported to be larger in Older Alluvium (median 274 µM) followed by Younger Alluvium (median 262.7 µM), while it was low in Piedmont having a median concentration of 55.7 µM. The concentration of $NH_4^+$ ranged from 0.31–0.38 µM in Older Alluvium but 0.05–0.95 µM in Younger Alluvium and this signified that reducing conditions are prevailing in Younger Alluvium. The median $NO_3^-$ concentration was reported as 13.6, 29.7, 31.0 µM for Piedmont, Older and Younger Alluvium, respectively.

The median Mn concentration was lowest in river water (1.0 µM) followed by Older Alluvium (2.3 µM). Piedmont and Younger Alluvium contain comparatively higher median Mn concentrations of 5.9 and 5.7 µM, respectively. Median total Fe concentration was higher in Piedmont (17.2 µM) followed by river water (10.9 µM). The median concentration of Fe was 6.6 µM and 4.7 µM in Younger Alluvium and Older Alluvium, respectively. Higher concentration of As was observed in Piedmont followed by Younger Alluvium having median values of 0.2 and 0.07 µM, respectively and lowest in Older Alluvium (median 0.02 µM). A considerable concentration of As was also observed in the river water samples, mainly in the seasonal river channels or tributaries of the Ganges. The concentration of As varied between the Ganges and its tributaries as follows: Ganges (0.02–0.05 µg/L); Bya (0.30 µM); Burhi Gandak (0.22–0.32 µM); Kamla (0.007 µM); Baghmati (0.18 µM); Santi (0.06 µM); Balan (0.16 µM); and Punpun (0.07 µM). Higher As concentration has not been observed in most studies on the central and lower Gangetic Basin. However, an elevated concentration of As (0.27– 0.30 µM) has been reported in a small stream (River Gobra) in Murshidabad (Stuben et al., 2003) and River Jalangi and upper Ichamati (range 0.49–1.35 µM) of West Bengal (Mukherjee et al., 2009). It has been suggested that the reduction of Mn in the Gobra while the groundwater discharge served as a source of As in River Jalangi and upper Ichamati is due to elevated As concentrations. In the current study, it was observed that the river or channels which are small and locally recharged (Burhi Gandak, Bya, Baghmati and Balan) contain high levels of As while the River Ganges and its channels contain much fewer concentrations. The probable reason for higher concentrations of As may be lean flow into the channels and recharge from the adjacent aquifers. The river Kamla originates in the Himalayas and contains much less As concentration in its upper reaches near Jainagar city of Madhubani district in Bihar state.

**Table 3.1**
Statistical summary of the solute chemistry of the groundwater

| Parameter | Piedmont (n=8) | | | Older Alluvium (n=67) | | | Younger Alluvium (n=88) | | | River (n=10) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Median | Range | Mean | Median | Range | Mean | Median | Range | Mean | Median | Range | Mean |
| TW depth (m) | 51 | 12–121 | 48 | 30 | 12–121 | 35 | 24 | 10–136 | 31 | – | – | – |
| pH | 6.97 | 6.80–7.33 | 7.02 | 7.39 | 6.99–7.88 | 7.42 | 7.44 | 6.90–7.91 | 7.46 | 7.67 | 7.51–7.95 | 7.70 |
| EC (µS) | 796 | 429–1325 | 809 | 627 | 361–1927 | 687 | 530 | 252–1858 | 670 | 414 | 176–1078 | 478 |
| pe | 0.07 | -0.22–0.17 | 0.00 | -0.85 | -3.07–1.70 | -1.05 | -1.53 | -3.14–1.61 | -1.34 | – | – | – |
| DOC (mg/L) | 1.78 | 1.37–4.72 | 2.11 | 0.25 | 0.1–3.50 | 0.58 | 0.18 | 0–1.77 | 0.40 | 0.12 | 0.11–0.12 | 0.12 |
| $HCO_3^-$ (µM) | 8290 | 4597–13351 | 7599 | 7357 | 4872–11618 | 7590 | 7240 | 4004–11475 | 7444 | 3712 | 2211–5089 | 3584 |
| $F^-$ (µM) | 23.9 | 11.1–37.6 | 23.2 | 21.1 | bdl–45.2 | 21.6 | 17.0 | 0.0–148.7 | 19.4 | 17.3 | 12.0–31.9 | 20.2 |
| $Cl^-$ (µM) | 49.1 | 13.2–2218 | 606.8 | 434 | 19.9–6601.1 | 988.5 | 379.4 | 0.00–7088.1 | 835.4 | 298.4 | 75.9–2170.1 | 618.9 |
| $NO_3^-$ (µM) | 13.6 | 11.0–15.3 | 13.7 | 29.7 | 3.1–2453.6 | 189.4 | 31.0 | 7.8–1654 | 142.0 | 27.2 | 9.8–1173 | 143.6 |
| $SO_4^{--}$ (µM) | 55.7 | 3.5–531 | 134.8 | 274 | 3.7–1676.8 | 415.9 | 262.7 | 3.8–2310.6 | 388 | 177.7 | 86.9–313.4 | 182.4 |
| $PO_4^{---}$ (µM) | 5.5 | 0.00–8.4 | 4.6 | 6.0 | 4.0–6.5 | 5.6 | 8.0 | 5.9–10.1 | 8.0 | 28.9 | 5.7–52.1 | 28.9 |
| $NH_4^+$ (µM) | – | – | – | 0.02 | 0.31–0.38 | 0.03 | 0.01 | 0.05–0.95 | 0.05 | 0.03 | 0.04–0.01 | 0.02 |
| Si (µM) | 525 | 404.5–597.6 | 518 | 647 | 453–788.2 | 651 | 657 | 419–794.8 | 663.6 | 319.6 | 154–762 | 390 |
| $Na^+$ (µM) | 1343 | 787.7–3936 | 1836.9 | 1285.8 | bdl–3893.5 | 1529 | 805 | 228.8–7094.5 | 1233.4 | 822.9 | 193–3289.7 | 1128.4 |
| $K^+$ (µM) | 51.1 | 35.2–596.5 | 187.3 | 44.4 | 14–2890 | 113.7 | 81.1 | 20.1–882.4 | 97.1 | 132.3 | 53.4–416.1 | 175.5 |
| $Mg^{++}$ (µM) | 582.2 | 364.2–1853.1 | 757.6 | 1247 | 147–4435 | 1377.6 | 1071 | 279.2–3562 | 1210 | 419.4 | 288.9–917.9 | 509.6 |
| $Ca^{++}$ (µM) | 1357 | 955–2192 | 1410 | 2482 | 456–4811 | 2409 | 2441 | 760–4841 | 2483 | 794 | 407–1566 | 834 |
| $Mn^{++}$ (µM) | 5.9 | 3.7–10.1 | 6.6 | 2.3 | bdl–27.9 | 4.3 | 5.7 | 0.2–22.4 | 7.0 | 1.0 | 0.2–4.0 | 1.3 |
| Fe (total) (µM) | 17.2 | 8.1–148.3 | 51.3 | 4.7 | 0.1–81.8 | 10.5 | 6.6 | 1.5–169.2 | 16.5 | 10.9 | 1.0–48.3 | 14.1 |
| Fe(II) (µM) | 1.8 | 0.9–6.6 | 3.0 | 5.7 | 2.4–25.3 | 8.1 | 11.4 | 8.4–30.6 | 15.4 | – | – | – |
| Fe(III) (µM) | 16.9 | 6.9–125.6 | 44.8 | 2.7 | 0.1–67.1 | 12.8 | 24.9 | 1.0–118.7 | 38.9 | – | – | – |
| Fe(II)/ Fe(III) | 0.13 | 0.01–0.9 | 0.21 | 4.54 | 0.18–37.2 | 7.23 | 0.43 | 0.15–25.08 | 4 | – | – | – |
| As(total) (µM) | 0.2 | 0.1–0.7 | 0.3 | 0.02 | bdl–0.9 | 0.06 | 0.07 | bdl–1.8 | 0.2 | 0.12 | 0.01–0.32 | 0.14 |
| As(III) (µM) | 0.07 | 0.03–0.12 | 0.07 | bdl | bdl–0.33 | 0.05 | 0.05 | bdl–0.95 | 0.11 | – | – | – |
| As(V) (µM) | 0.28 | 0.06–0.50 | 0.28 | 0.03 | 0.01–0.57 | 0.11 | 0.03 | bdl–1.11 | 0.11 | – | – | – |
| As(III)/ As(V) | 0.42 | 0.23–0.57 | 0.41 | bdl | bdl–0.17 | 0.03 | 0.87 | bdl–61.42 | 6.17 | – | – | – |

*bdl = below detection limit

Piper plot shows that Piedmont and river water is of Ca-$HCO_3$ type, and only one river water sample fell in mixed Ca-Na-$HCO_3$ type (see **Fig 3.2**). In Older Alluvium~88% of the samples were Ca-$HCO_3$ type, 9% were Na-$HCO_3$ type while one sample from each (Older and Younger Alluvium) were of Ca-Cl and Ca-Mg-Cl type. Approximately 94% of the samples in Younger Alluvium were found to be Ca-$HCO_3$ water type, while the remaining 6% ranged from the Ca-Na-Cl-$HCO_3$ to Na-$HCO_3$ types. An evolutionary flowpath of the groundwater was depicted in the Piper plot which indicates that aquifers of Younger Alluvium are receiving some water from the aquifers of Older Alluvium. The source of the recharge to the Piedmont may probably be rainwater. The individual piper plots for Piedmont, Older Alluvium and Younger Alluvium and river water are shown in **Fig. 3.2** (**a**), (**b**), (**c**) and (**d**).

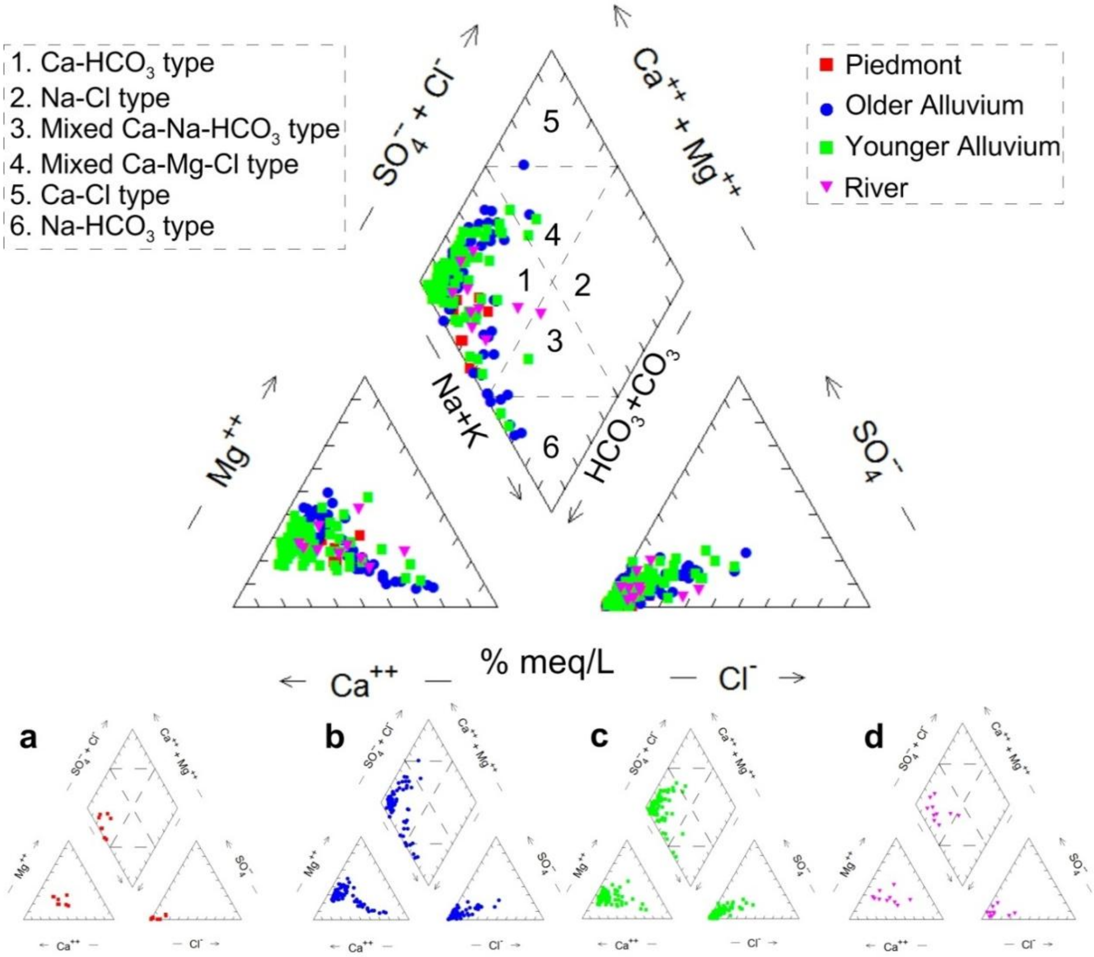

**Fig. 3.2.** Piper plots representing the study area's major solute chemistry

*3.3.2. Geochemistry of the subsurface sediment*

**Table 3.2** shows the subsurface geochemistry of the three main geomorphic setups (i.e. Piedmont, Older Alluvium and Younger Alluvium) of the CGB. Depth profiles of the major cations in subsurface sediments are shown in **Fig. 3.3**. The median concentration of alkali metal; Na in

Piedmont and Younger Alluvium was 1.32 and 0.63 µM, respectively while in Piedmont it was 5.30 µM (**Table 3.2**). The variation in Na concentration in the subsurface sediment of Older and Younger Alluvium below the surface (42.6 and 33.5 mgbl, respectively) was very low, but the concentration of Na was higher throughout the core (upto 57mbgl) in the Piedmont. The trend was the same as Na for K and Mg attributing the presence of minerals like albite, biotite and Na-smectite for Na and K, while dolomite could be responsible for the higher concentration of Mg. The concentration of Ca below the surface was higher in Older Alluvium (median 296.42 µM) due to existence of calcium carbonate as *kankar* formation and lowest in Piedmont (47.99 µM) due to the absence of *kankar* in this area. The concentration of Ca in Younger Alluvium ranged in between the concentration reported in Piedmont and Older Alluvium. **Fig. 3.4** shows the metals present in the representative core sediments of all three alluvial setups.

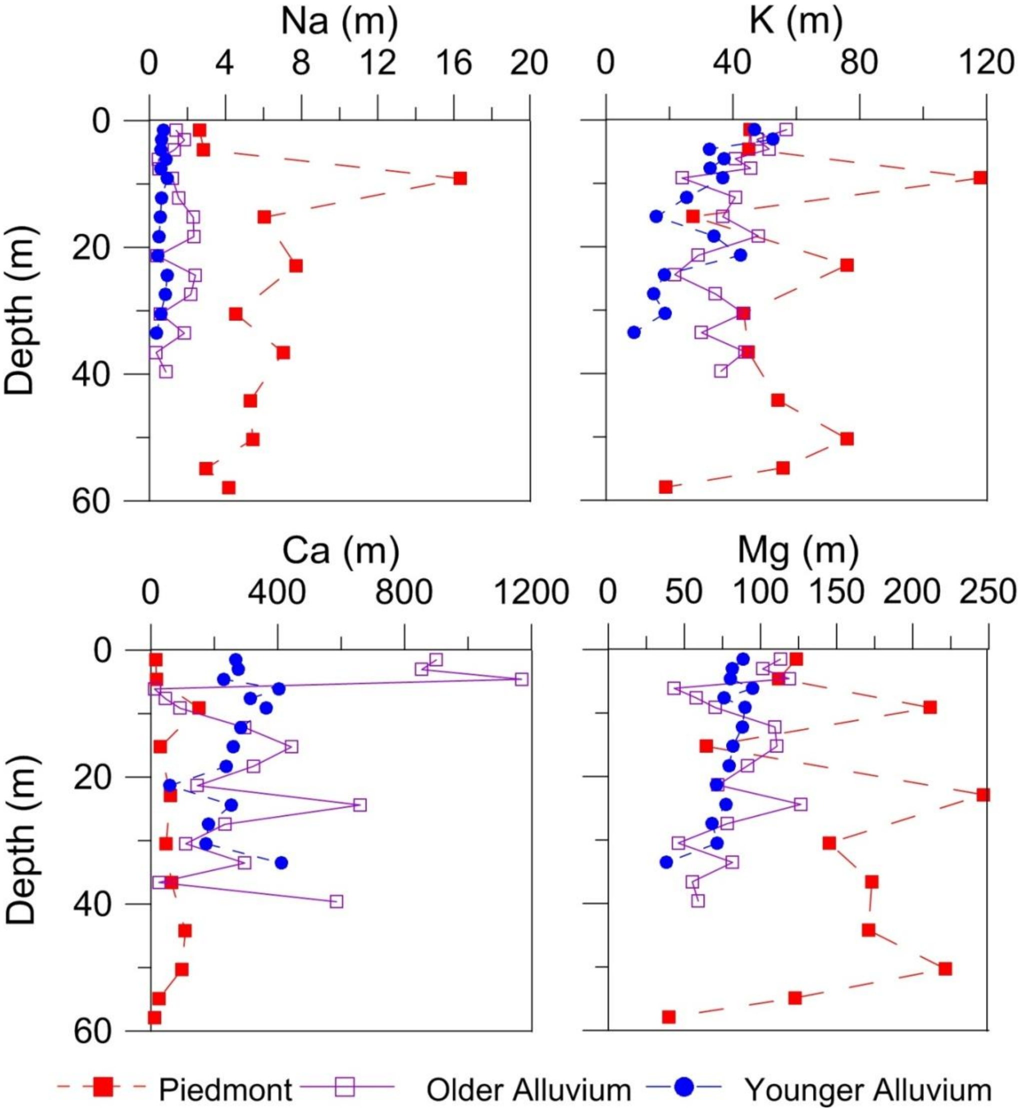

**Fig. 3.3.** Comparative depth profile of alkali and alkaline earth metals in representative core sediments of Piedmont (Jainagar), Older Alluvium (Methrapur) and Younger Alluvium (Harail Chapar)

**Table 3.2**
Statistical summary of sediment geochemistry from the study area

| Elements m, molal conc. | Piedmont (n=11) | | | Older Alluvium (n=17) | | | Younger Alluvium (n=14) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Median | Range | Mean | Median | Range | Mean | Median | Range | Mean |
| Na | 5.30 | 2.64–16.34 | 5.91 | 1.32 | 0.35–2.42 | 1.33 | 0.63 | 0.39– | 0.67 |
| K | 45.46 | 18.75–117.99 | 54.98 | 40.71 | 21.66–56.88 | 38.75 | 32.67 | 8.71–52.50 | 29.78 |
| Mg | 145.12 | 39.80–246.30 | 148.28 | 78.03 | 43.27–126.54 | 81.72 | 79.74 | 38.29–94.73 | 77.63 |
| Ca | 47.99 | 12.25–151.94 | 57.43 | 296.42 | 11.16–1168.77 | 392.48 | 263.63 | 60.31–410.71 | 265.36 |
| Al | 378.32 | 91.65–675.69 | 402.61 | 82.93 | 56.70–112.88 | 84.81 | 87.26 | 34.45–96.33 | 77.67 |
| Fe | 453.90 | 90.75–682.23 | 422.06 | 206.80 | 20.71–433.81 | 183.98 | 192.68 | 81.27–373.44 | 216.49 |
| Mn | 6.96 | 1.09–18.20 | 8.10 | 5.48 | 3.04–14.69 | 6.71 | 7.29 | 2.30–21.90 | 7.43 |
| Cu | 0.23 | 0.06–0.54 | 0.29 | 0.23 | 0.05–0.56 | 0.28 | 0.25 | 0.04–0.45 | 0.24 |
| Zn | 0.62 | 0.16–1.21 | 0.72 | 0.88 | 0.33–2.91 | 1.01 | 0.67 | 0.21–1.15 | 0.61 |
| Cr | 0.36 | 0.08–0.74 | 0.41 | 0.36 | 0.17–0.65 | 0.43 | 0.42 | 0.10–0.56 | 0.35 |
| Co | 0.33 | 0.06–0.54 | 0.33 | 0.29 | 0.12–0.56 | 0.34 | 0.35 | 0.07—0.63 | 0.30 |
| Ni | 0.30 | 0.09–0.64 | 0.35 | 0.31 | 0.12–0.57 | 0.35 | 0.38 | 0.06–0.53 | 0.30 |
| Pb | 0.06 | 0.01–0.11 | 0.07 | 0.08 | 0.02–0.14 | 0.08 | 0.06 | 0.02–0.11 | 0.06 |
| As | 0.07 | 0.03–0.13 | 0.07 | 0.15 | 0.05–0.34 | 0.17 | 0.15 | 0.06–0.26 | 0.14 |

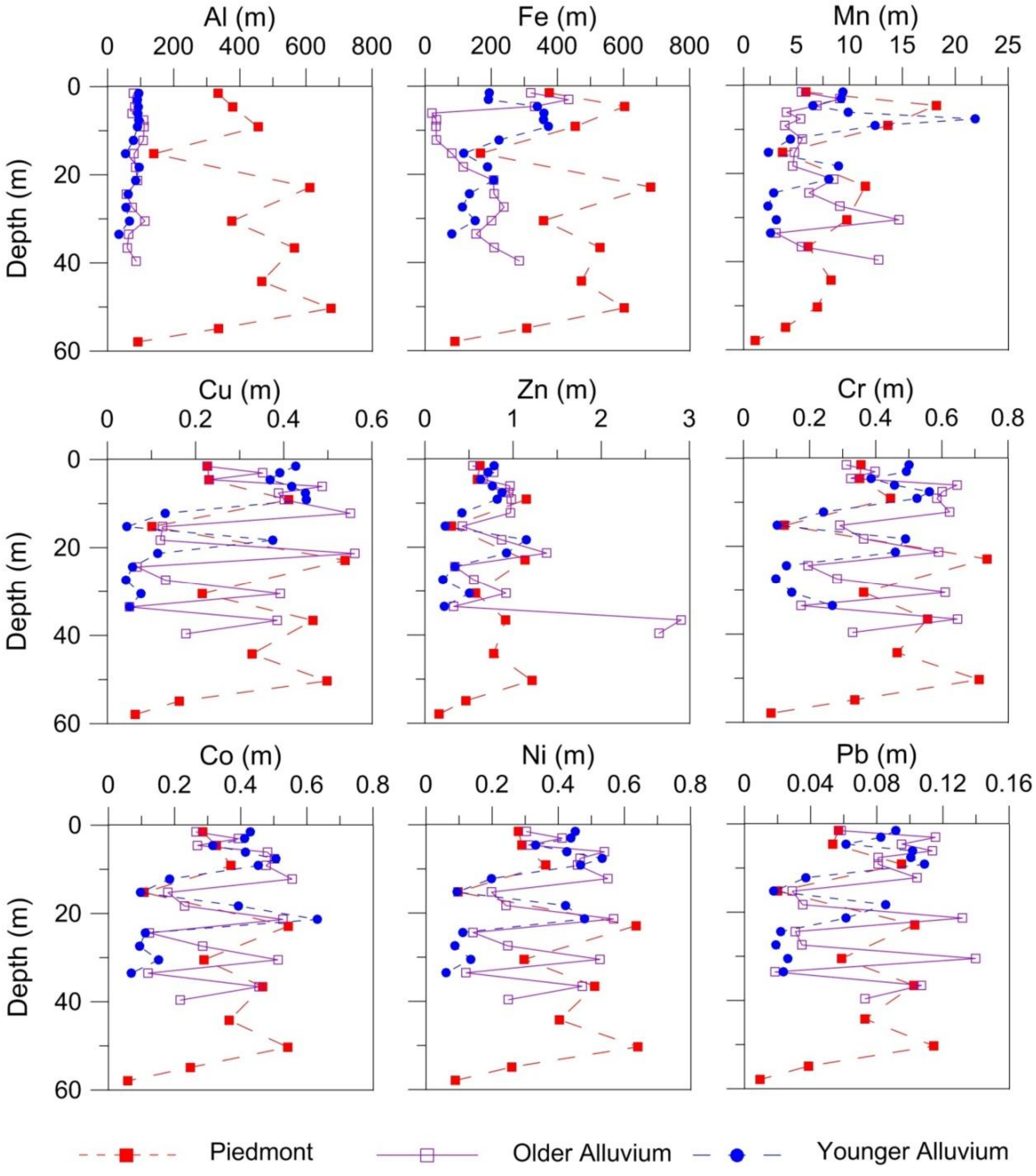

**Fig. 3.4.** Comparative depth profile of the metals present in representative core sediments of Piedmont (Jainagar), Older Alluvium (Methrapur) and Younger Alluvium (Harail Chapar)

The concentration of Al in Older and Younger Alluvium was almost comparable throughout the core below the surface, but it was higher in Piedmont, the reason could be the presence of silicate minerals like albite and orthoclase. Concentrations of Fe in Older Alluvium (median 206.8 µM) and Younger Alluvium (median 192.68 µM) were almost similar and revealed a zig zag trend in Piedmont with the highest median concentration of 453.9 µM. The concentration of Fe was higher throughout the core below the surface in Piedmont area could be due to the availability of mineral biotite. The median concentrations of Mn in Piedmont, Older and Younger Alluvium, were 6.96, 5.48 and 7.29 µM, respectively. For Mn, Piedmont and Younger Alluvium show a decreasing trend while in Older Alluvium it first decreases and then increases. Zinc shows a similar trend for all three cores except for

Older Alluvium, which has a higher concentration range (2.91–2.65) at a depth of 35–40 m below the surface. Median Cu concentration in all three setups varied as 0.23, 0.23 and 025 µM. The median concentration of Cr in Piedmont and Older Alluvium was same (0.36 µM) while the median concentration of Cr in Younger Alluvium was slightly higher (0.42 µM).

The maximum median concentrations of Co (0.35 µM) and Ni (0.38 µM) were observed in Younger Alluvium. The concentration of Pb in Piedmont and Younger Alluvium was almost comparable having a median value of 0.06 µM, but it was comparatively higher in Older Alluvium (median 0.08 µM). No distinct trends were observed for Cr, Co, Ni and Pb in core sediments of Piedmont, Older and Younger Alluvium below the surface. All cores showed very similar median concentrations as well. The median concentration of As was same in cores of Younger and Older Alluvium having 0.15µM, but the median concentration in Piedmont was half to that. A litholog was constructed from the core sediment collected from three different locations. **Fig. 3.5** illustrates the comparative As concentration in groundwater and sediments below the surface and there was a peak of As concentration in groundwater samples at a depth of 10–30 mbgl in Piedmont and Younger Alluvium. The concentration of As decreased below the surface. A higher concentration was associated with fine and grey sediment in Piedmont and Younger Alluvium, respectively.

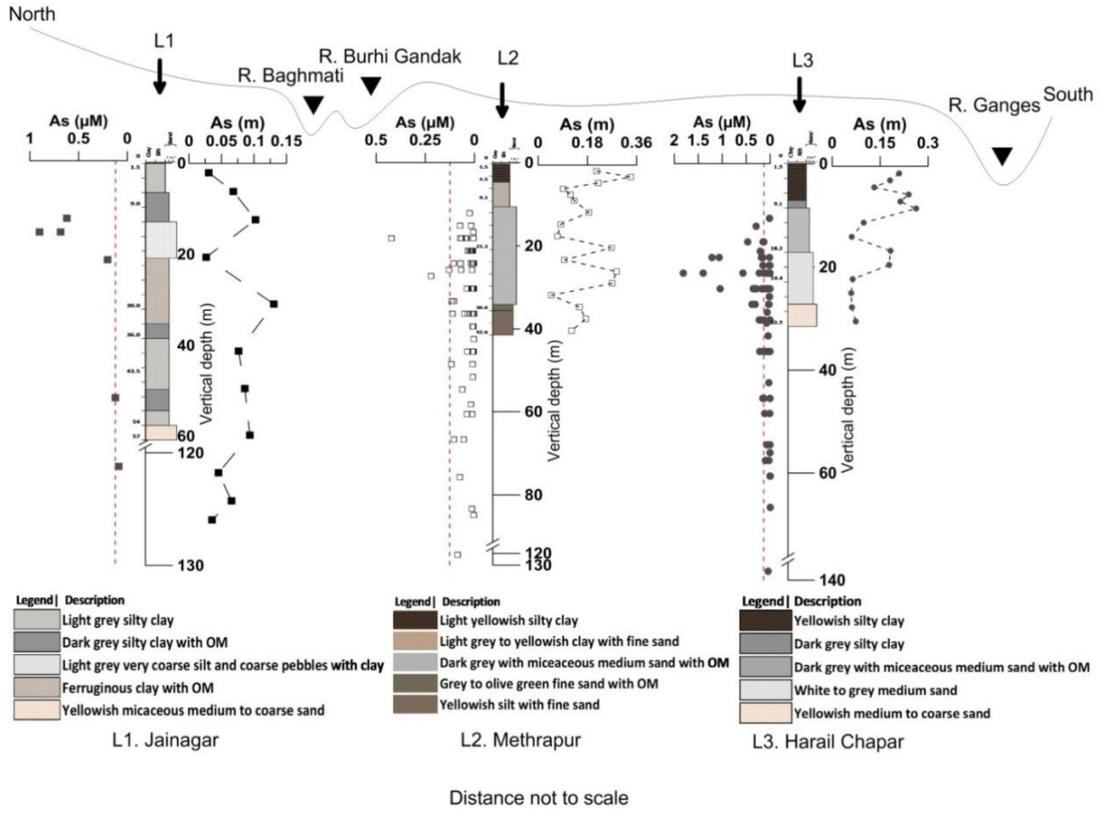

**Fig. 3.5.** Lithologs of the study area along with the estimated As concentration in groundwater of the localized tubewells (to the right of each litholog) and sediment (to the left of each litholog). Red dashed vertical line represents the (WHO, 2011) guideline and (BIS, 2012) standards

The concentration of As was also higher in sediments having a dark grey colour with micaceous medium sand containing organic matter.

### *3.3.3. Redox conditions, arsenic speciation and other trace elements in groundwater*

The redox conditions of aquifers were classified on the basis of the equilibrium *pe* values (Parkhurst et al., 1996). The median values of *pe* for Piedmont, Older Alluvium and Younger Alluvium were observed as 0.07, -0.85 and -1.53, respectively (**Table 3.1**). Piedmont shows a narrow range of *pe* (-0.22–0.17) and this indicates an anoxic condition. Older Alluvium shows a range of *pe* (-3.07–1.70) anoxic to post-oxic, while Younger Alluvium reveals a wide spectrum of the redox conditions and range (-3.14–1.61), thus suggesting highly anoxic to post-oxic conditions. The median *pe* value ranged from As(III)-As(V) transition and extended to V(VI)-V(III) in Older Alluvium and Younger Alluvium. Median $As_{total}$ concentration in Piedmont was estimated as 0.2 µM which is higher than the WHO guideline value of 0.13 µM (10 µg/L). Meanwhile the median concentration of $As_{total}$ in Older Alluvium was observed as 0.02 µM. Arsenic ranged from below detection limit (bdl) to 1.8 µM was observed in Younger Alluvium with the mean $A_{stotal}$ concentration of 0.2 µM. The detection limit of the instrument was 0.01 µg/L. Arsenic(III) ranged from 0.03–0.12 µM in Piedmont and bdl –0.95µM in Younger Alluvium. The ratio of the median As(III) to the median As(V) concentrations in groundwater of Younger Alluvium was 0.87 and for Piedmont, it was 0.42, which indicated reducing environmental conditions existed in the aquifers. *pe*-pH plot (**Fig. 3.6**) was constructed in order to understand the species distribution in all three geomorphic setups. It emerged that~ 75% of the samples fell in the $As(OH)_3$, i.e. (AsIII) field and remaining samples fell in $HAsO_4^{2-}$ i.e. (AsV) due to reducing conditions of the aquifers. Box-Whisker Plots in **Fig. 3.7** show the variation in concentrations of trace elements in the study area including river water samples. The concentration of Pb ranged between bdl–0.3 µM. This indicates a decreasing trend for Older Alluvium, Younger Alluvium and river water samples. A higher concentration of U and Sr were observed in Older Alluvium whilst the Al, Cr, Ni, Co and V concentrations were higher in the river water samples.

### *3.3.4. Evolution and source of major solutes*

Mineralogy of any terrain plays an important role in understanding the source mineral and weathering reactions. The presence of a common mineral assemblage in this area has been observed which defines gross lithology of the region (**Table 3.3**). A common mineral assemblage: quartz, albite, muscovite, orthoclase, mica, illite were observed in all three geomorphic units. It was noticed that $Ca^{2+}$ containing mineral was not traced by XRD in Piedmont and biotite was traced in Piedmont and Younger Alluvium in a minor amount. Mineral siderite was also traced in the deeper sections of the cores in Younger and Older Alluvium, while the magnetite was observed in the upper layer of core sediments in Younger Alluvium only.

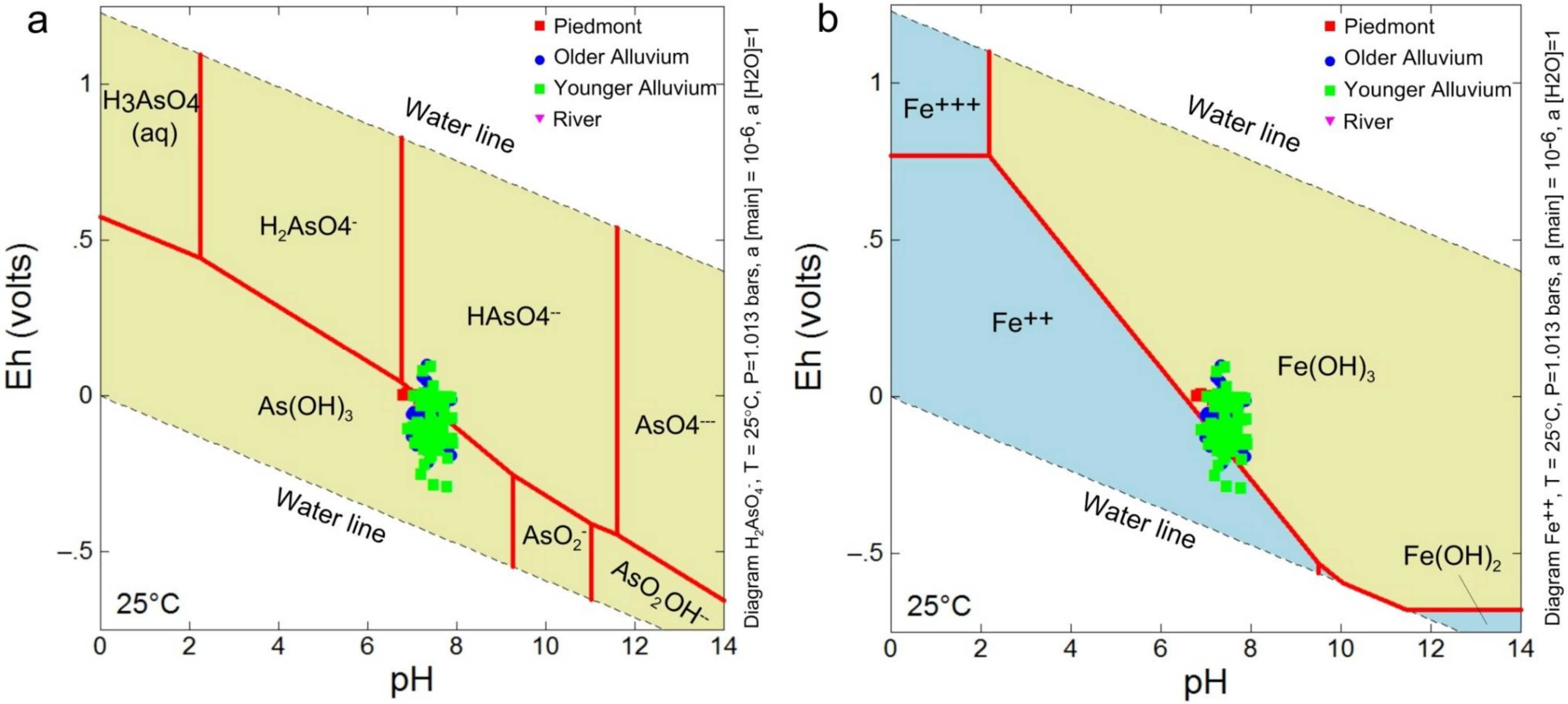

**Fig. 3.6.** Eh-pH diagram for groundwater (**a**) As and (**b**) Fe species existing in the study area

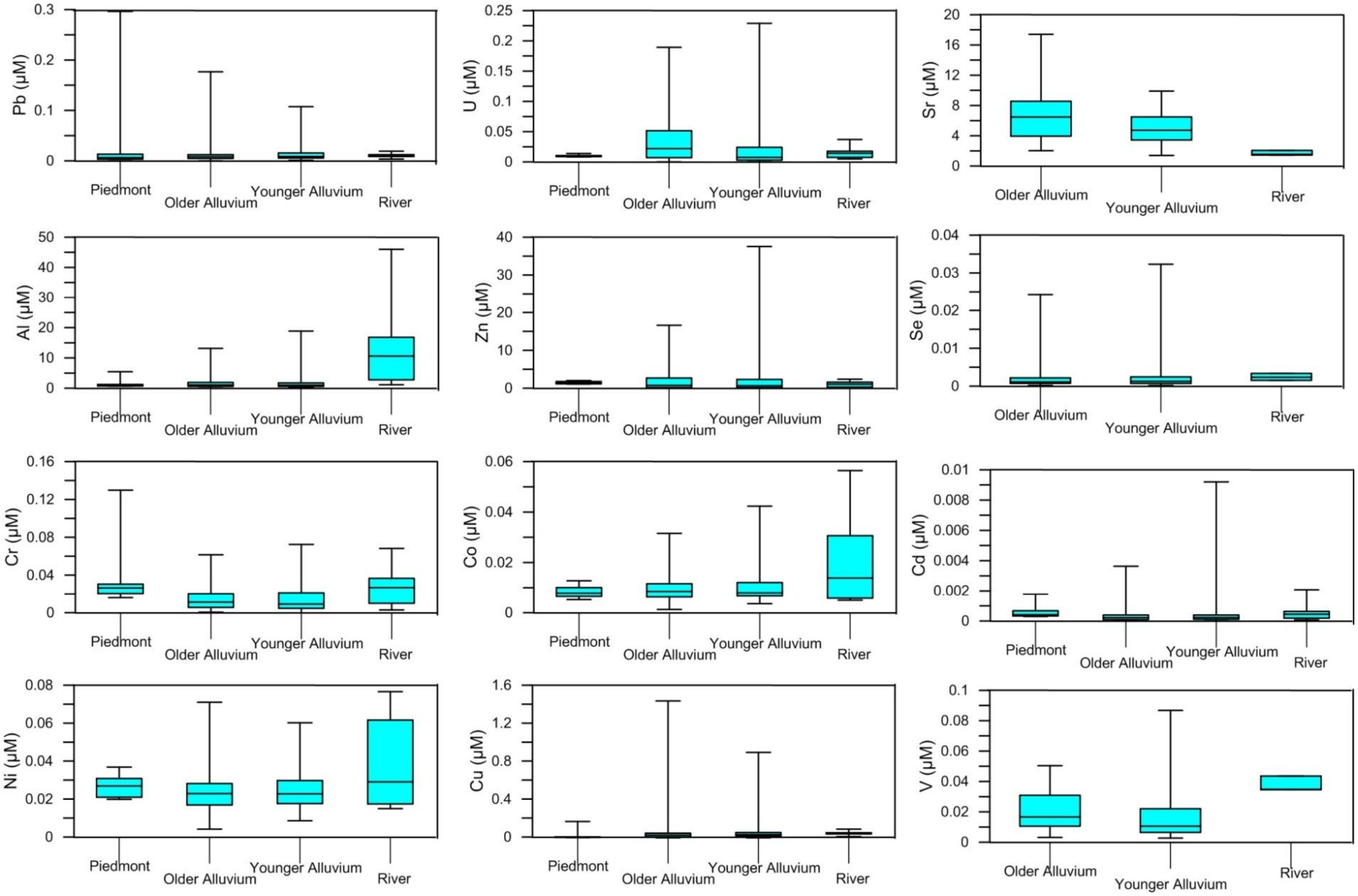

**Fig. 3.7.** Box-Whisker plots of the trace elements present in the groundwater of the study area

Siderite is known as a sink for As in alluvial regions. A previous study documented the presence of minerals viz. quartz, chlorite, muscovite, montmorillonite, feldspar, kaolinite, amphibole and goethite; however, pyrite mineral was absent from the CGB of Uttar Pradesh and Bihar (Shah, 2008). A similar mineralogy has also been observed in the sediment core of Chakda and Baruipur in West Bengal, which revealed an assemblage of iron-oxide-coated quartz and clay (illite) grains, Fe-Mn-siderite, magnetite and biotite/ chlorite (Acharyya and Shah, 2007). Three processes (evaporite dissolution, carbonate dissolution and silicate weathering) contribute the major solutes in the groundwater. The load of the dissolved major cations ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$ and $K^{+}$) and anions ($Cl^{-}$, $SO_4^{2-}$ and $HCO_3^{-}$) in groundwater can be modelled regarding the weathering of various minerals located in the parental material along with the rate of weathering. Due to their faster rate than silicate weathering; the evaporite dissolution and carbonate dissolution, a relatively minor proportion can significantly influence the water chemistry (Meybeck, 1987). Simple representative reactions of weathering of the common minerals via calcite dissolution, silicates weathering and cation exchange, respectively involved here (Garerels and Mackenzie, 1971; Sarin et al., 1989) can be written as follows:

**Table 3.3**

Mineralogy of sediments collected from three geomorphic units

| Piedmont | Older Alluvium | Younger Alluvium |
|---|---|---|
| – | Quartz | Anorthite |
| Quartz | Calcite (5–7%) | Quartz |
| Albite | Albite | Calcite (5–6%) |
| Muscovite | Pyroxene | Dolomite (1–3%) |
| Orthoclase | Orthoclase | Albite |
| Anorthite | Muscovite | Orthoclase |
| Biotite | Goethite | Muscovite |
| Mica | Hematite | Pyroxene |
| Illite | Pyroxene | Magnetite |
| Goethite | – | Goethite |
| Dolomite (1–2%) | – | Siderite |

*minerals like siderite, goethite, hematite, and magnetite were detected in minor amounts

$$\mathrm{CaCO_3 + H_2CO_3 = Ca + 2HCO_3}$$

$$\mathrm{(Na, K, Mg, Ca)silicate +\ H_2CO_3 = H_4SiO_4 + HCO_3 + Na + K + Mg + Ca + solid\ products}$$

$$\mathrm{0.5\ Ca^{2+} + Na - clay = 0.5Ca - clay + Na^{+}}$$

Groundwater chemical composition may also be altered by the mixing of recharging water, residence time of the groundwater and aquifers' water-sediment interaction (cation exchange). To understand the contribution of the evaporite dissolution, silicate weathering and carbonate dissolution, a bivariate mixing diagram of Na-normalized Ca versus Na-normalized Mg and $HCO_3$ was plotted in **Fig. 3.8**.

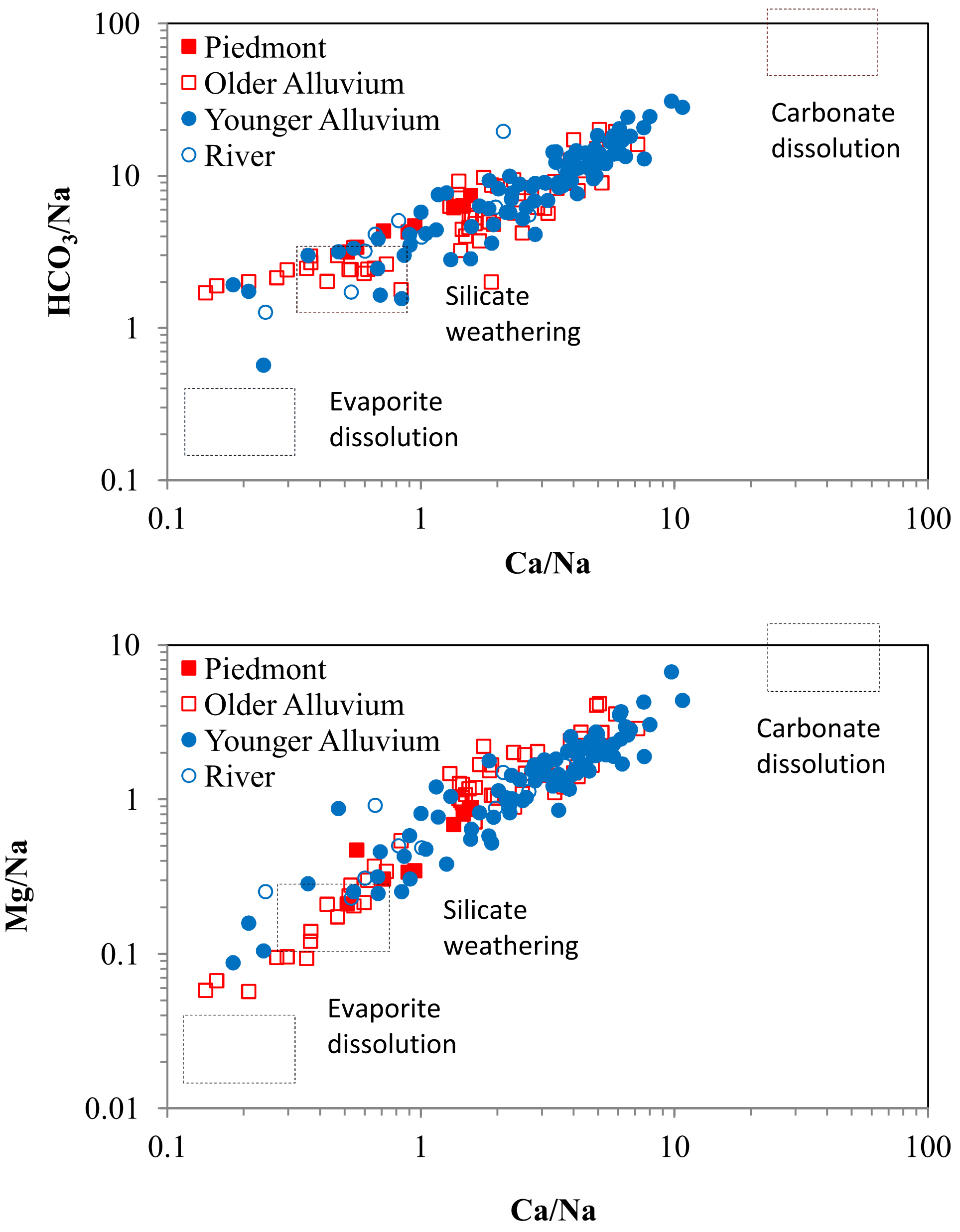

Fig. 3.8. Bivariate plot of Na-normalized (µM/µM) versus Ca and Mg versus Ca showing the weathering trend. The dashed rectangular area demonstrates global average composition of groundwater with respect to evaporite dissolution, while the dashed oval area shows the global average composition of the groundwater with respect to silicate weathering and carbonate dissolution without mixing (Gaillardet et al., 1999)

One-third of the groundwater samples from Older Alluvium and half of the groundwater samples from Piedmont fell close to global average silicate weathering remaining groundwater samples fell between silicate weathering and carbonate dissolution. Samples from Younger Alluvium tend to be closer to the global average carbonate dissolution than to silicate weathering. The solute load's contribution to the groundwater of the CGB via cation exchange was evaluated using an equivalent bivariate plot along with the slope values (see **Fig. 3.9**) of corrected bivalent cations ($Ca^{2+}$ and $Mg^{2+}$) that may have been involved in exchange reactions. These were corrected by subtracting the equivalent concentrations of associated anions ($HCO_3^-$ and $SO_4^{2-}$) that would be derived from other processes (carbonate dissolution and silicate weathering). Likewise, the concentration of $Na^+$ that may result from water-sediment interactions in the aquifer can be accounted for by assuming that the $Na^+$ of meteorite origin would be balanced by an equivalent concentration of $Cl^-$ (McLean and Jankowski, 2000; Mukherjee et al., 2009). It is assumed that for active cation exchange to take place in the aquifer, the slope of this bivariate plot should be~-1 (i.e. y=-x) (Jankowski et al., 1998).

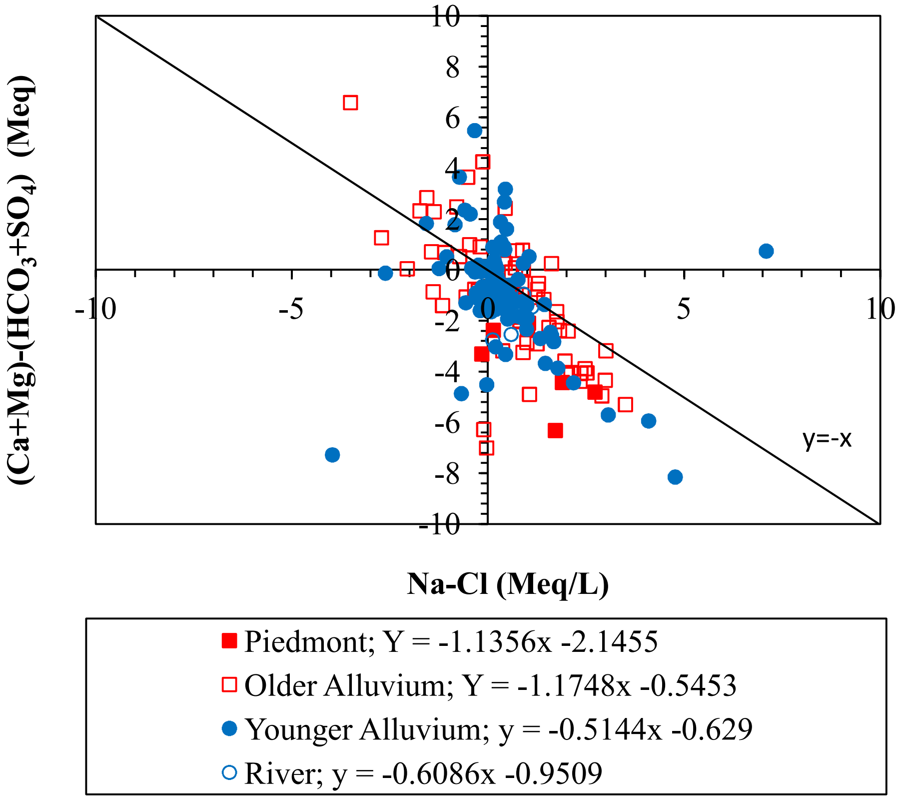

**Fig. 3.9.** (Ca and Mg) less ($HCO_3^-$ and $SO_4^{2-}$) against Na less Cl to indicate cation exchange reaction in the groundwater samples

It can be seen from **Fig. 3.9** that groundwater samples from Piedmont and Older Alluvium have slopes of -1.1356 and -1.1748, respectively, thus supporting the active cation exchange processes in these aquifers. In Younger Alluvium the slope is -0.5144, and this is the same for the river water (-0.6086), indicating the cation exchange is having no or much less influence of in both waters.

A plot of $Ca^{2+}$+$Mg^{2+}$ and $N^+$+$K^+$ against total cation concentration (**Fig. 3.10** (**a**) and (**b**)) was plotted to prove the sources of the major cations in the groundwater of the study area. The median of the ratio of the $Ca^{2+}$+$Mg^{2+}$ to total cations followed the order as Younger Alluvium (0.81; range 0.21–0.92) > Older Alluvium (0.74) > River (0.57) > Piedmont (0.55). The silicate weathering's influence in Piedmont was also supported by the global average silicate weathering plot (**Fig. 3.8**). The median of the ratio of the $N^+$+$K^+$ to the total cations followed a reverse order: Piedmont (0.45)> River (0.43)>

Older Alluvium (0.26)> Younger Alluvium (0.19). The abundance of $Ca^{2+}$ and $Mg^{2+}$ in Piedmont and Older Alluvium could be primarily due to silicate weathering of the sediment enriched with alkaline earth silicates (Sarin et al., 1989). The probable source of $Na^+$ and $K^+$ could be the dissolution of orthoclase or albite since the mineralogy shows the presence of these minerals in the study area. A significant contribution could be assumed from the carbonate dissolution. For Younger Alluvium it is evident that silicate weathering did not have much impact on carbonate dissolution. **Fig. 3.10** (**c**) and (**d**) are plots of $Ca^{2+}+Mg^{2+}$ versus $HCO_3^-$ and $Na^++K^+$ versus $HCO_3^-$. All the samples except for a few from Older Alluvium fell to along a 1:2 aquiline on a bivariate plot of $Ca^{2+}+Mg^{2+}$ versus $HCO_3^-$ support the calcite dissolution by carbonic acid, in which two $HCO_3^-$ molecules generate a $Ca^{2+}$ (Mukherjee et al., 2009). A few samples from Older Alluvium $Ca^{2+}$ and $Mg^{2+}$ could have been contributed by silicate weathering.

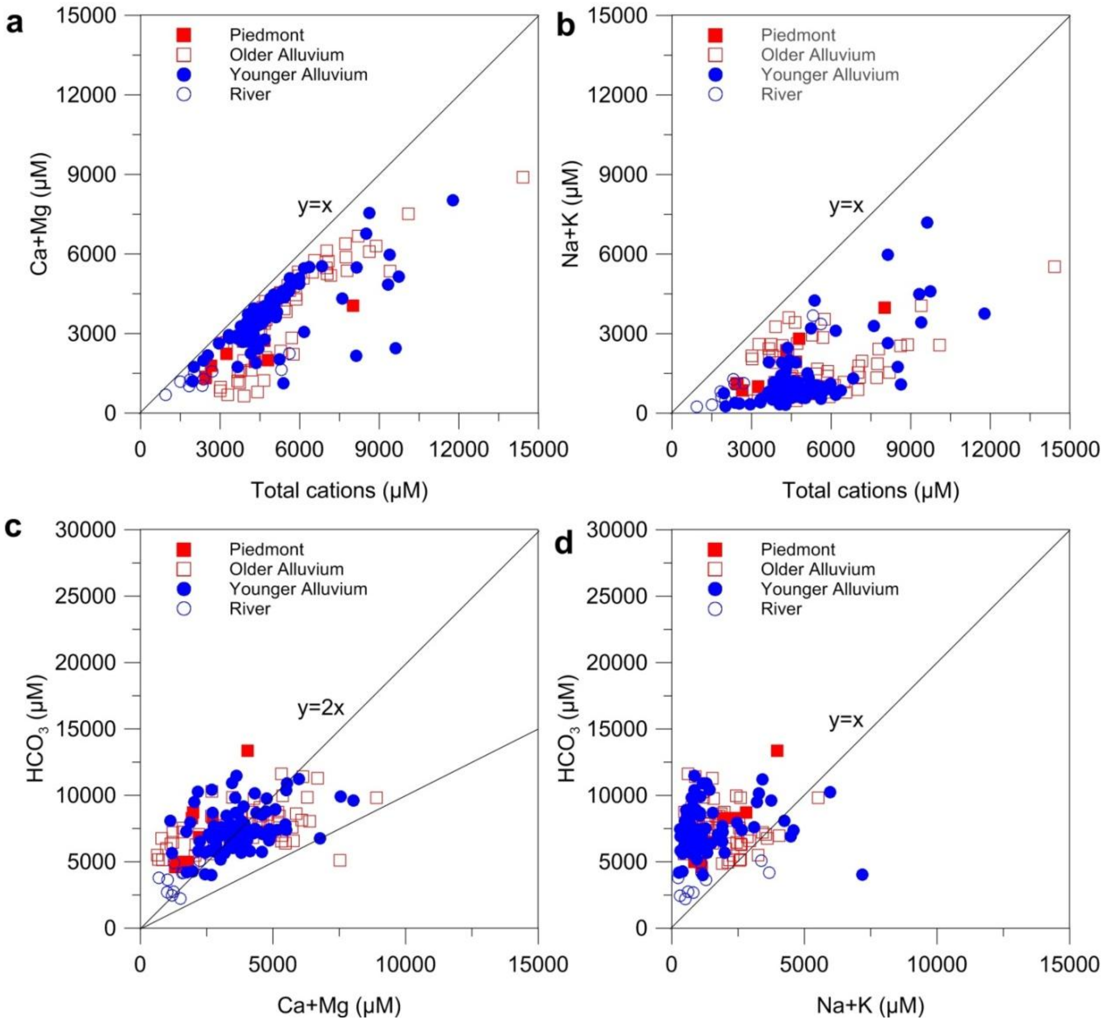

**Fig. 3.10.** Bivariate plots of (**a**) Ca and Mg and (**b**) Na and K versus total cation concentration (**c**) Bivariate plot HCO3- versus Ca and Mg (**d**) Na and K concentration in the groundwater samples

In the plot of $Na^++K^+$ versus $HCO_3^-$ (**Fig. 3.10** (**d**)) all the samples tend to be closely clustered, and they attained a much higher ratio of $HCO_3^-$ to $Na^++K^+$. This indicated their weak relationship with silicate weathering. In all three setups including river water the median $Cl^-/SO_4^{2-}$ ranged between 2–3. The median values of $Na^++K^+$: $Cl^- + SO_4^{2-}$ for Piedmont were higher (median: 6) than the others which ranged from 1.37–1.51. Samples which fell below the 1:1 of $Na^++K^+$: $Cl^-+SO_4^{2-}$ (**Fig. 3.11**) may have resulted from cation exchange (Mukherjee et al., 2009).

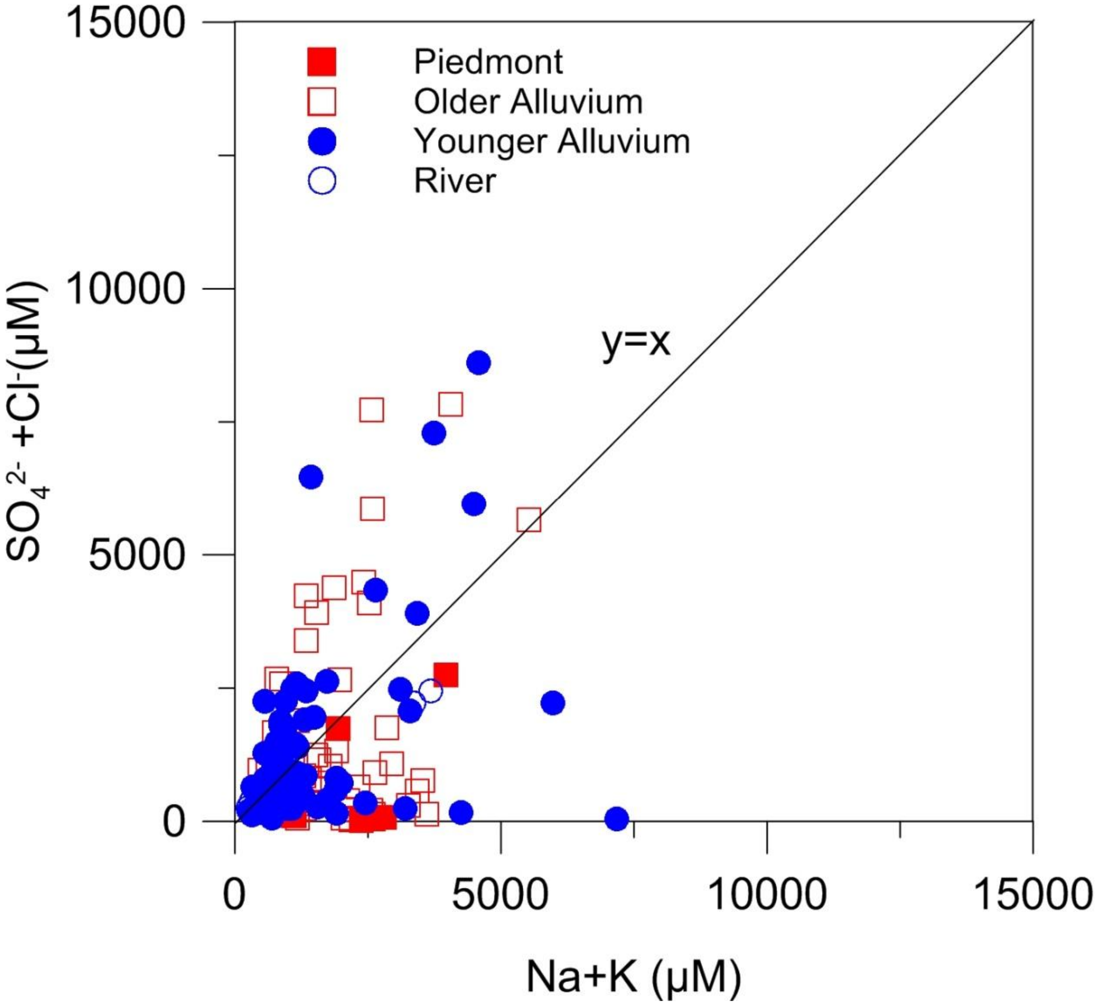

**Fig. 3.11.** Bivariate plot of Cl and $SO_4^{2-}$ versus Na and K concentration

The stability diagrams based on the solute activities calculated using Geochemist Workbench software (version 10.0) assuming end-members compositions using the equilibrium relationships of Tardy (1971) and Drever (1997) for standard temperature (25 ºC) and pressure (1 atm), by plotting log $[H_4SiO_4^0]$ versus log $([Ca^{2+}]/[H^+]^2)$, log $([Na^+]/[H^+])$ and log $([K^+]/[H^+])$, respectively (**Fig. 3.12** (**a**, **b** and **c**)). Plots show that: firstly, all the samples from the study area fell in the kaolinite stability field; and secondly, are in equilibrium with the Ca-Na smectite. Samples from all the geomorphic setups along with river water samples indicate equilibrium with orthoclase. In contrast, weathering in CGB is very complex and dominated by monosialltization and bisiallitization in which the formation of kaolinite and smectite and orthoclase took place. Anorthite and albite seem to be in disequilibrium, and this finding supports active feldspathic weathering. These results were also supported by saturation indices calculated for the groundwater of all three setups (**Fig. 3.12**). Furthermore, it was observed that minerals like kaolinite, muscovite and orthoclase were supersaturated and albite was near to equilibrium and slightly saturated, while anorthite was undersaturated having an SI value that ranged from 4.1-4.7 with respect to the groundwater.

### *3.3.5. Hydrogeochemical evolution of groundwater in central Gangetic Basin*

The mineral dissolution will be more prominent in the zone of recharge due to the water aquifer matrix reactions. Conversely, cation exchange will dominate more in the zone of discharge (Drever, 1997; Mukherjee et al., 2012). Toth (1963) has stated that local topography plays a key role in controlling gravity-driven flow groundwater and influence the chemical composition of local groundwater. A topography-driven flow system with local to regional flow paths was assumed to exist for this study area (Toth, 1963). The Piedmont in the Himalayan foothills may act as the recharge zone while the discharge zone may be located in the active floodplains of the River Ganges. Surface water bodies are the signature of the joining of the flow systems (Toth, 1963). Several surface water bodies created from River Gange's channels are existing in the study area. The River Ganges forms a major hydrological boundary and the regional discharge point (Mukherjee et al., 2012). A sluggish movement of the groundwater has been observed (Saha et al., 2009) in Younger Alluvium or the vicinity of the River Ganges (hydraulic gradient 1:1700–1:5750). The movement of groundwater may be higher (Saha and Shukla, 2013) in Older Alluvium (hydraulic gradient 1:900).

The groundwater chemistry of Piedmont, Older Alluvium and Younger Alluvium differed from each other. Some noticeable trends were observed in the study area with respect to the regional hydraulic gradient Piedmont (North) to Younger Alluvium (South). These trends in solutes' for selected parameters with latitude worked as a proxy for tracing the regional evolutionary flowpaths for groundwater (**Fig. 3.13**). The concentration of $Ca^{2+}$+$Mg^{2+}$, $HCO_3^-$ and Si were lower in the vicinity of the Kamla and Baghmati, but there was a peak for these elements in the concentration between two river channels. As the water evolves from the piedmont towards southern path, it is dominated by an increase in the concentration of $Na^+$ and decrease in the concentration of $Ca^{2+}$ indicating the dissolution of $Na^+$ phases and precipitation of $Ca^{2+}$ bearing phases. Piedmont was dominated by $HCO_3^-$ with the relatively larger amount of $Ca^{2+}$ compared to $Na^+$. The Older Alluvium exhibited two distinct clusters for the water concentrations indicating two different possible sources for the two different clusters or two different types of evolution in the Older Alluvium region (**Fig. 3.2**). Towards the north in between Kamla and Baghmati of Younger Alluvium the groundwater chemistry is similar to the Older Alluvium in the less evolved part indicating the evolution possibility due to water-rock

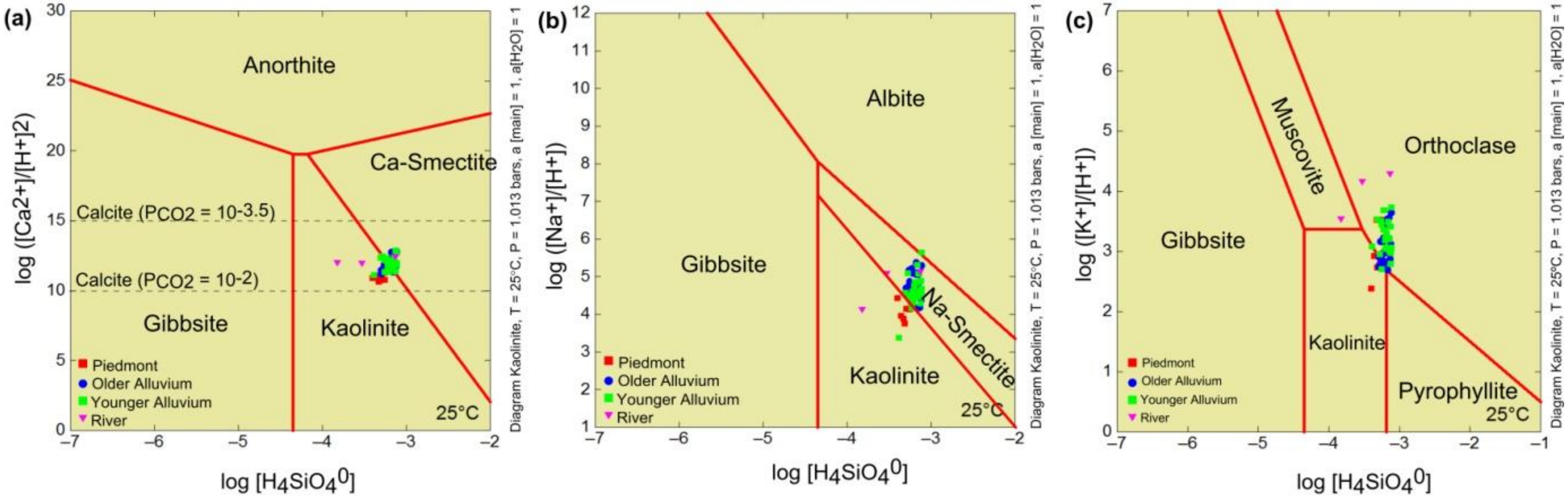

**Fig. 3.12.** Plots showing minerals expected to be in equilibrium with the groundwater samples. The diagram was generated assuming end-member compositions using the equilibrium relationships documented in Tardy (1971) and Drever (1997) for standard temperature (25ºC) and pressure (1 atm)

interaction and mixing with river water. The south side of Younger alluvium in between Burhi Gandak and River Ganges groundwater chemistry indicatd the evolution from the different cluster of the Older Alluvium and river water mixing. Piedmont and Older Alluvium are dominant with $HCO_3^-$, but the majority of the samples from Younger Alluvium and all river water samples contains low $HCO_3^-$. In Piedmont, silicate weathering was dominant (**Fig. 3.8**). In the aquifers between Baghmat and Burhi Gandak $Ca^{2+}+Mg^{2+}$, $HCO_3^-$ and Si shows increasing while for $Na^++K^+$ has a decreased trend that indicates carbonate dissolution is dominating over silicate weathering in this area. These trends were further increasing towards the river Ganges.

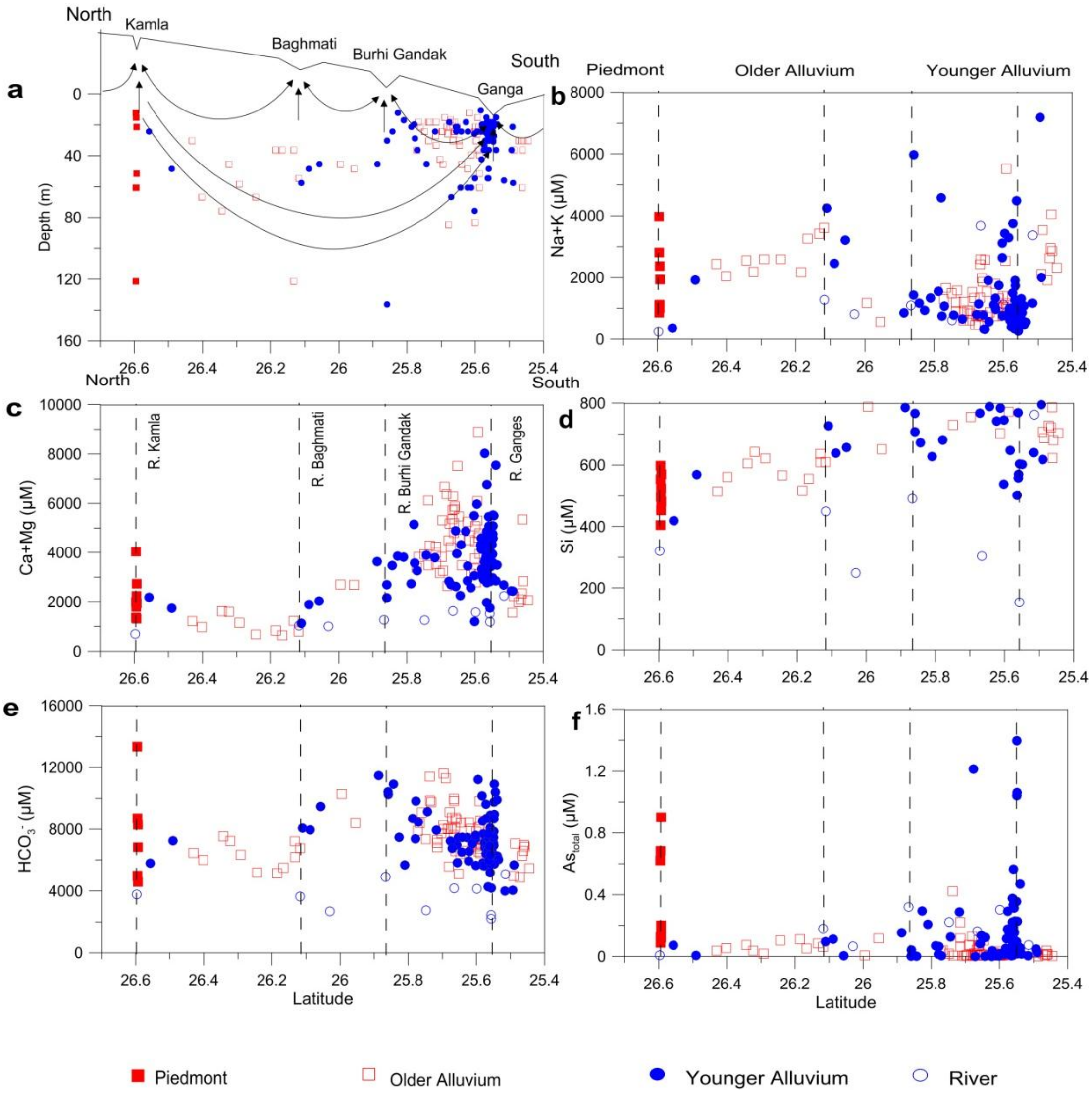

**Fig. 3.13.** Distance (with latitude) plots of groundwater quality parameters (**a**) Groundwater samples depth and flowpath (**b**) Na+K (**c**) Ca+Mg (**d**) Si (**e**) $HCO_3^-$ (**f**) $As_{total}$

The decreasing trend of $Ca^{2+}+Mg^{2+}$ and inverse trend of $Na^++K^+$ in Piedmont and Older Alluvium are supporting cation exchange in these geomorphic units. An increase in $Ca^{2+}+Mg^{2+}$ and $Na^++K^+$ towards Younger Alluvium suggests that there was carbonate and silicate weathering prominent in this area.

These results were also supported by **Fig. 3.9** having (y=-x >1) for Piedmont and Older Alluvium, while it was -0.51 for Younger Alluvium. The concentration of $HCO_3$- showed a slight increasing trend from north to south with a slight decrease in Older Alluvium, Si also followed the same trend indicating the contribution of $HCO_3^-$ from silicate weathering. The increasing trend of the $SO_4^{2-}$ coupled with high anoxic conditions (maximum *pe* -3.14) in Younger Alluvium indicates that the groundwater of the aquifer did not reach the sulfidic environment. Higher As concentration was observed in Piedmont (North) and Younger Alluvium (South), while it was much less in Older alluvium (the middle part of the stretch).

### *3.3.6. Geochemical speciation modelling in solution*

Saturation indices illustrate about saturated and undersaturated mineral phase which refers to minerals having a tendency to remain in dissolved form or being precipitated once it enters the groundwater. **Fig. 3.14** illustrates the SI values which are important and may exert a major influence on the groundwater chemistry in different geomorphic setups. Some important minerals like arsenolite, Ca-Al-pyroxene, anorthite and corundum are undersaturated and tend to remain in dissolved form once these enter the groundwater.

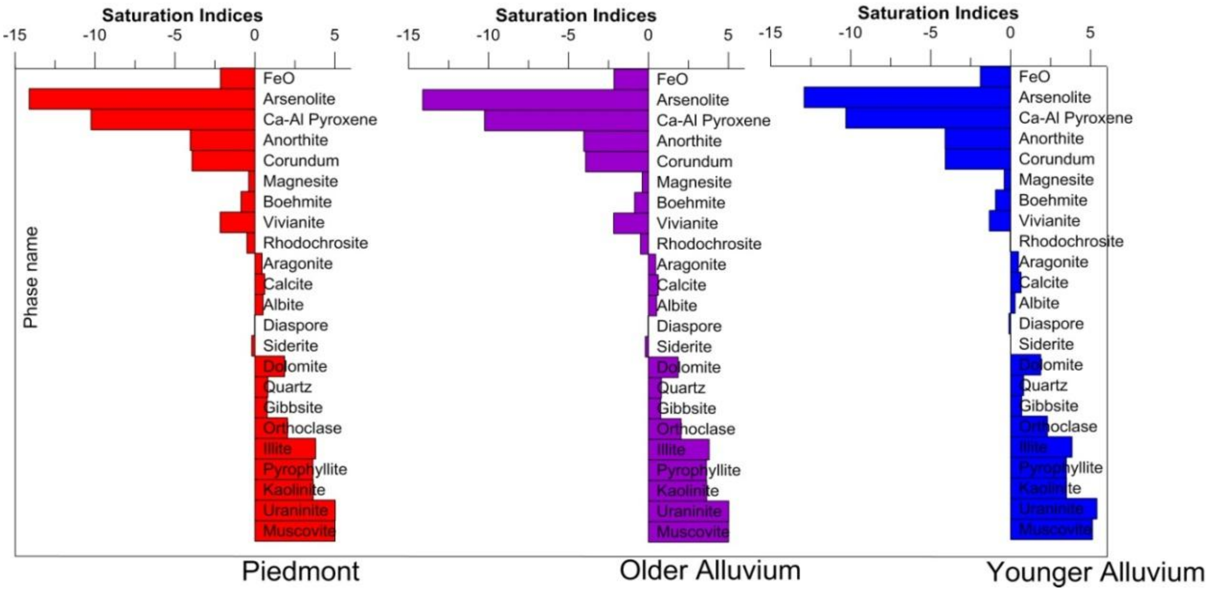

**Fig. 3.14.** Plot of saturation indices (SI) calculated by Geochemist Workbench (v. 10.0) for some mineral phases possibly occurring in groundwater of all three geomorphic areas

The presence of FeO indicates the reducing conditions of the aquifers in all three setups. Groundwater in all three geomorphic setups is slightly supersaturated with respect to Fe- and Mn-bearing minerals like siderite and rhodochrosite in the groundwater. This suggests favourable conditions for potential As adsorption (sink) onto the surfaces of Fe-Mn-bearing oxides and carbonates formed under oxidizing and reducing conditions, respectively. It is well known that As strongly sorbs onto

Fe(III)oxide surfaces (Dixit and Hering, 2003; McArthur et al., 2010). The groundwater was slightly saturated with respect to calcite and dolomite. Groundwater was supersaturated with some common minerals, for example, albite, gibbsite, orthoclase illite pyrophyllie, kaolinite and muscovite. This indicated their stability in groundwater.

### *3.37. Inverse Geochemical Modeling*

The results of the successful models of the different hypothetical geochemical flow paths (local and regional) using inverse modeling along predicted groundwater flow directions in the study area are summarized in **Table 3.4**. All of the modeled reaction flow paths include a combination of silicate weathering, carbonate weathering and cation exchange. However, the predictive results obtained from these models are only indicative of general hydrogeochemical reactions (suiting our hypotheses) in the aquifers of the central Gangetic Basin. Following the model design based on our hypothesis of hydrogeochemical evolution along the reaction flow paths, the representative down-gradient groundwaters can be explained by (I) mixing of fresh groundwaters with river waters (II) aquifer matrix/ sediment-groundwater interactions (dissolution/ precipitation reaction) and ion exchange reactions, (III) ion exchange reactions and (IV) both mixing and reactions.

**Table 3.4**
Details of reaction path models

| Model | Flowpath | Mixing With | No of Minimal Modes | Carbonate Weathering | Silicate Weathering | Ion Exchange |
|---|---|---|---|---|---|---|
| A | 108-109 | N | 2 | N | Y | N |
| B | 109-113 | N | 5 | N | Y | N |
| C | 113-113 | N | 3 | N | Y | N |
| D | 113-119 | N | 6 | N | Y | N |
| E | 119-126 | N | 8 | Y | Y | Y |
| F | 137-139 | N | 5 | Y | Y | Y |
| G | 139-143 | N | 7 | Y | Y | Y |
| H | 143-150 | N | 9 | Y | Y | Y |
| I | 116-136 | Y | 2 | N | Y | N |
| J | 116-137 | Y | 1 | N | Y | N |
| K | 116-118-119 | Y | 4 | Y | Y | Y |
| L | 119-140-137 | Y | 2 | Y | Y | Y |

Several of these flowpath models converged successfully without treating Si as a conservative solute, which indicate that there can be dissolution input and/or precipitation of silicates along the flow paths. Models A, B, C and D (**Table 3.4**) support silicate weathering as contributing to the evolution of groundwater compositions along the respective flow paths, which suggests mixing water-rock interactions leading to higher concentrations of $Na^+$ localities. On the other hand, Models, E, F, G, H (Type II, **Table 3.4**) explain both carbonate and silicate weathering in the groundwaters along the respective flow paths as a consequence of the dissolution of calcite, anorthite along with silicate mineral weathering and probable ion exchange. Flow paths in the Models I and J can be only explained by regional flow path evolution of the piedmont water. The predictive outputs of these models are in congruence.

### *3.3.8. Mobilization and fate of arsenic in groundwater and river water*

Bivariate correlation plots (**Fig. 3.15**) of As with various redox-sensitive species and solutes for the groundwater in the study area suggested that As mobilization does not follow any single reaction or pathway. Correlation of As follows for Piedmont e.g. with ORP ($r^2$=0.43), Fe ($r^2$=0.44) and Mn ($r^2$=0.88). Correlation of As with other redox sensitive species and solutes is weak or absent (see **Fig. 3.15**). In order to know the correlation between As a Fe-Mn-Al in subsurface sediments of Piedmont, Older Alluvium and Younger Alluvium, bivariate correlation plots were made (**Fig. 3.16**). The plot shows that $As_{total}$ has a correlation, but it was not very highly significant ($r^2$=0.42). The correlation of $A_{total}$ with Mn and Al was also not significant. The correlation matrix of As with various parameters in water and sediments suggested Fe-Mn (oxyhydr)oxides and competitive exchange could be the favourable mechanism for As liberation. The concentration of As in solid phase of the CGB is similar to the range present in the Bengal Basin (Saha and Sahu, 2016). Various studies have hypothesized that reductive dissolution of the Fe-Mn(oxyhydr)oxides coating over the sediment grains such as muscovite, feldspar, quartz and chlorite (Harvey et al., 2006; Mukherjee et al., 2008) rich in adsorbed As, is mediated by the consumption of organic carbon by bacteria (Saha and Sahu, 2016). Another study done in the Kosi Basin revealed the competitive exchange with anions (e.g. $HCO_3^-$) derived from water-rock interaction, and could be the probable mechanism for As mobilization near the Himalayas (Mukherjee et al., 2012).

Bivariate correlations of As with various redox-sensitive species for Younger Alluvium are very weak or absent in groundwater but in sediments, $As_{total}$ has a significant correlation with Fe (r2=0.60), Mn ($r^2$=0.66) and Al ($r^2$=0.66). The above said chemical associations are suggesting that in Younger Alluvium reduction of Fe-Mn-Al(oxyhydr)oxides mediated with microbial activity could be the probable mechanism. Strong positive correlation of Al with As indicates a significant contribution of Al-oxy(hydr)oxides. It is likely that hydrated Al oxides (HAO)/ amorphous $Al(OH)_3$, clay minerals and other phyllosilicates may act as a potential sink for As species (Manning and Goldberg, 1997; Yan et al., 2000; Stollenwerk, 2003; Hasan et al., 2009). In groundwater, the reason for poor correlation of As with Fe-Mn could be the precipitation of these elements due to the supersaturation as indicated from **Fig. 3.13**. However, the concentration of As in Older Alluvium was very small and consequently there is no concern for the controlling factors concerning As. Mukherjee et al. (2009) observed a similar pattern in the correlation in Bengal Basin, and stated several factors were responsible for As mobilization and its fate rather than any single reaction. The groundwater of CGB was characterized by anionic dominance with $HCO_3^-$ and cationic dominance with $Ca^{2+}$ and mildly alkaline pH (Saha and Sahu, 2016).

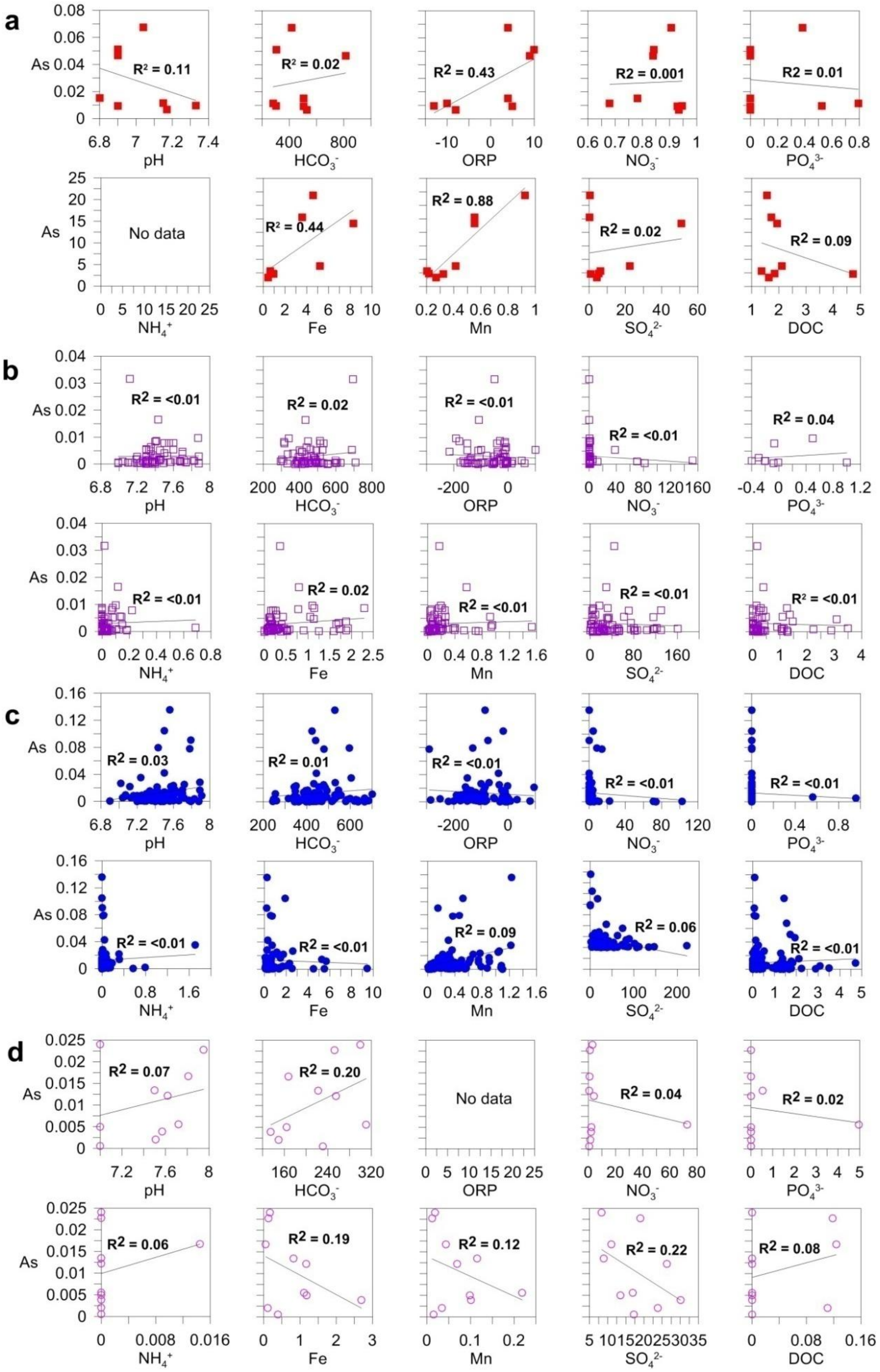

**Fig. 3.15.** Bivariate plots of As with various redox-sensitive species and solutes, for example, pH, $HCO_3^-$, OPR (Eh), $NO_3^-$, $PO_4^{3-}$, $NH_4^+$, Fe, Mn, $SO_4^{2-}$ and DOC for Piedmont (**a**), Older Alluvium (**b**), Younger Alluvium (**c**) and river water samples

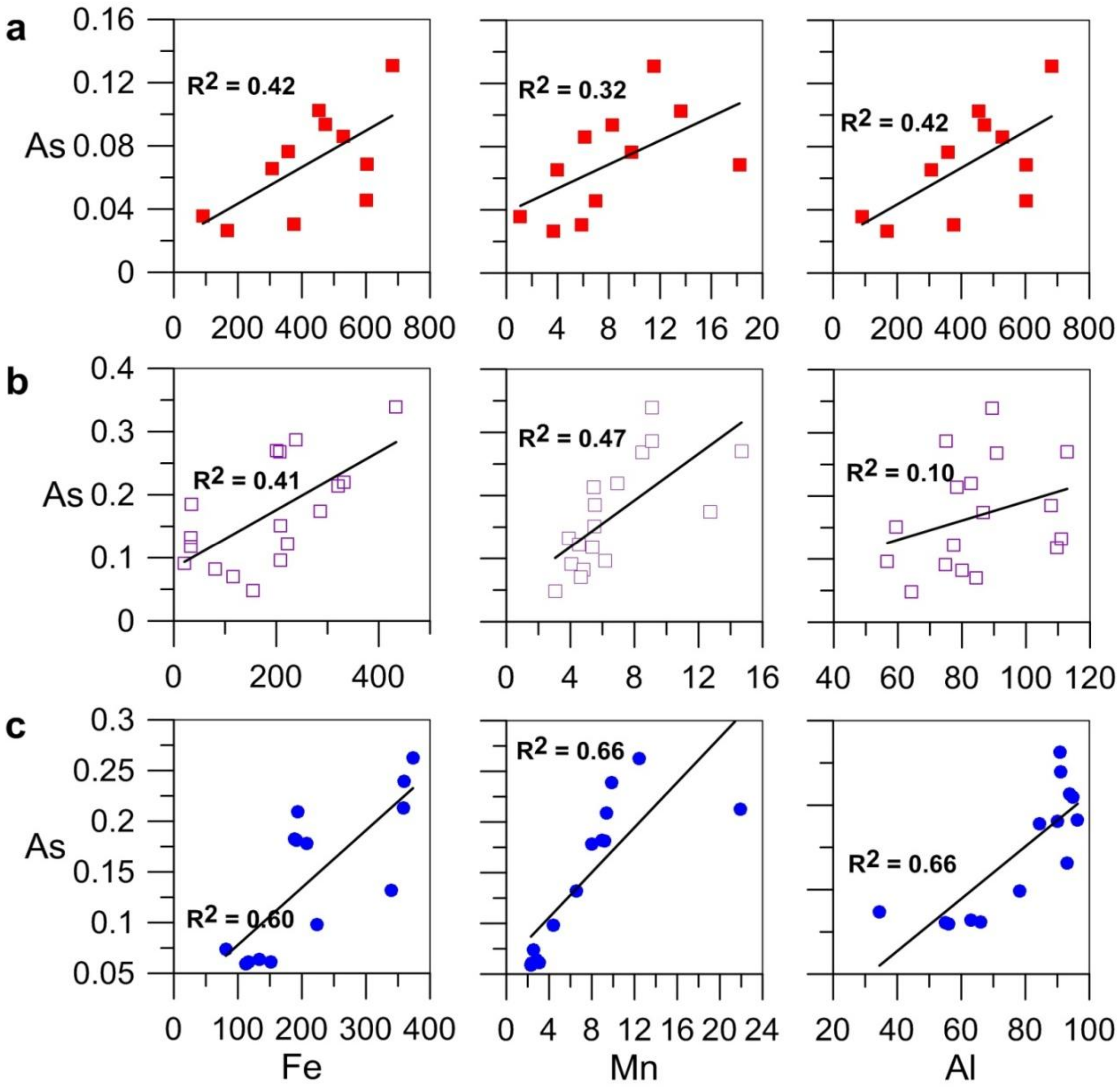

**Fig. 3.16.** Bivariate plots of $As_{total}$ with Fe, Mn and Al for (**a**) Piedmont (**b**) Older Alluvium (**c**) Younger Alluvium

A correlation of As with redox-sensitive species with Fe ($r^2$=0.43) and $NH_4^+$ ($r^2$=0.46) was observed, but there was no correlation with $SO_4^{2-}$ and $NO_3^-$ in the Ballia district of Uttar Pradesh. The authors concluded the reduction dissolution is the most likely mechanism for As mobilization (Chauhan et al., 2009). Poor correlation ($r^2$=0.17) (Shah, 2013) and good correlation ($r^2$=0.67) (Saha et al., 2010) of As with Fe were observed in CGB. Arsenic did not demonstrate a good correlation with $HCO_3^-$ in CGB (Saha et al., 2010). There was no significant correlation of As with other redox-sensitive species except a slight positive correlation with $HCO_3^-$ ($r^2$= 0.20) and a negative correlation with Fe and $SO_4^{2-}$ indicating that these channels are receiving As contaminated water from the adjacent aquifers only.

## 3.4. Conclusions

This study investigated the three major geomorphic units (Piedmont, Older Alluvium and Younger Alluvium) in the central Gangetic Basin in India. Extensive field observations and remote sensing were employed for this task. The groundwater of Piedmont was nearly neutral having Ca-$HCO_3^-$ water types, while in Younger and Older Alluvium type of water ranged from Ca-$HCO_3^-$ to Na-$HCO_3^-$. Furthermore, Ca-Mg-Cl type had slightly alkaline pH. A median concentration of As 0.2 and 0.12 µM were observed in Piedmont and Younger Alluvium, respectively, while 0.02 µM was evident in Older Alluvium. The median concentrations of As in the core sediments of Piedmont (up to 57mbgl), Older Alluvium (up to 42.6 mbgl) and Younger Alluvium (33.5mbgl) were observed; these were 0.07, 0.15 and 0.15 molal concentrations, respectively. Aquifers indicated anoxic to post-oxic conditions in all three geomorphic units.~70% of the groundwater samples fell in $As(OH)_3$/ As(III) field and reaming (30%) in field of $HAsO_4^{2-}$AsV. In pe-pH plot~60% of the samples fell in FeOOH field and 40% fell in $Fe^{2+}$ field.

Cation exchange played an important role in Piedmont and Older Alluvium, while carbonate dissolution in Younger Alluvium served to control the groundwater solute chemistry. The groundwater was in the equilibrium with kaolinite, Ca-smectite, Na-smectite and orthoclase but showed disequilibrium with anorthite and albite, which could be the major source of $Ca^{2+}$ and $K^+$ to the solute in the groundwater via silicate weathering. The inverse grochemical modelling results indicated that water in different geomorphic units i.e. Piedmont, Older and Younger Alluvium evolved by different processes. The groundwater is governing by silicate weathering and carbonate dissolution and the evolution was also affected by local and regional flowpath followed by the groundwater along with mixing and other ion exchange reactions. Dissolution of Fe-Mn (oxyhydr)oxide and competitive exchange were suggested as the most likely mechanism for As liberation in Piedmont while different processes controlled the mobilization and of As in Younger Alluvium.

## Acknowledgements

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# Chapter 4

# Groundwater dynamics, recharge processes and DOC behavior using stable isotopes

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*After*

Basin-scale stable isotopic study on groundwater recharge and dissolved organic carbon behaviour in an arsenic contaminated province of central Gangetic basin, Bihar, India

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**Research highlights**

- Significantly evaporated water had recharged aquifers in Older and Younger Alluvium
- Good connectivity of shallow to deeper aquifers in Older and Younger Alluvium
- A little recharge from River Ganges and its tributaries to the adjacent aquifers
- Ponds are playing no role in recharging and DOC leaching into the aquifers
- Active floodplains of the river Ganges are exhibiting higher microbial activity

## Abstract

The geomorphological units of the study area were broadly classified as Piedmont, Older and Younger Alluvium using remote sensing and field investigations. Water samples (n=105) were collected in which 88 were groundwater and 17 from the surface (river Ganges and its tributaries) and pond water for the analysis of stable isotopes ($\delta^{2}H$, $\delta^{18}O$ and $\delta^{13}C$) and dissolved organic carbon (DOC). Stable isotopes ($\delta^{2}H$ and $\delta^{18}O$) record revealed that groundwater of Piedmont had been recharged by meteoric origin before evaporation while aquifers of Older and Younger Alluvium had been recharged with water which has undergone little evaporation loss. River Ganges and its tributaries passing through this area have a little contribution in recharging while ponds are playing no role in recharging the adjoining aquifers. Shallow aquifer of Piedmont has very less connectivity with the deeper aquifer. The connectivity of the shallow aquifers of aquitard formation (25–60m bgl) with the main upper aquifer at the depth of (> 120m bgl) was found to be higher in Older and Younger Alluvium. Depleted $\delta^{13}C$ (median -9.57‰; range -13.21 to -5.4) and low DOC (median 1.35 mg/L; range 0.99–1.77mg/L) indicated acceleration in microbial activity in the Younger Alluvium especially in the active floodplain of the river Ganges and its proximity. In deeper aquifers (> 120m bgl,) of Younger Alluvium and both shallow and deeper aquifers of Older Alluvium the groundwater was found to be enriched with $\delta^{13}C$ and the significant concentration of DOC which indicated the limited microbial activity in these formations.

## Keywords

Stable isotopes, dissolved organic carbon, meteoric water, refractory organic matter, significant evaporation

## 4. 1 Introduction

Upper shallow aquifers are most contaminated with Arsenic (As), in contrary to the subsequent lower aquifers which contain low As in Younger Alluvium of the central Gangetic basin (CGB) (Saha et al., 2011; Saha and Sahu, 2016). The Older Alluvium wasfound to be As free. A study has been reported a two-tier main aquifer system (upper aquifer and lower aquifer) within 300m bgl in Samastipur district of Bihar in this study area (Saha and Shukla, 2013). The study revealed that upper aquifer is 85–110 m thick while the lower aquifer is thinner (20–25 m). The existence of a Himalayan origin thin aquifer has also been described which is present in upper aquitard zone. Most of the tubewells are tapped in this upper aquifer of up to 25–60 m depth, this formation is made up of clay/ sandy clay with thin (5–10 m thickness) patches of fine grey sand. Many studies have been reported a very high level of As upto 331 µg/L (Chauhan et al., 2009; Saha et al., 2009; Chandra et al., 2011; Kumar et al., 2016) in this aquifer compared to the shallow main aquifer of a higher depth (<2 and 8 µg/L at 219 and 222m bgl respectively) in Samastipur district (Saha and Shukla, 2013) of CGB. The deeper aquifer was found free from As contamination. A study from the south side of the river Ganges in Bhojpur district using stable isotopes revealed that there is a connectivity between upper Himalayan origin aquifer and thick shallow aquifers. It may pose a threat to the As free groundwater reservoir of lower depth (Saha et al., 2011) if water is extracted in an unsustainable way. The hydraulic connectivity of main upper aquifer with the lower aquifer was not observed due to the presence of thick (13–29 m) clay layer.

Application of the stable isotope is importantin the study of groundwater to investigate the origin, age and type of water. If the isotopic composition changes along a flow path, it will reflect the history of water like mixing, mineralization and discharge (Thilagavati et al., 2016). DOC which is known as the main constituent of the carbon cycle, food web and energy balance in aquatic food web also fuels microbial respiration (Datta et al., 2011) and regulate biogeochemical cycling of the elements due to its high susceptibility to leaching. The source of the DOC in groundwater and other systems like river and lake water can be traced using stable carbon isotope ($\delta^{13}C$) (Murphy et al., 1989; Wassenaar et al., 1991). The origin and consumption of DOC also can be traced with the study of $\delta^{13}C$.

Many studies focussed on As assessment and mobilization (Chauhan et al., 2009; Saha et al., 2009, 2010a, 2010b; Saha and Shukla, 2013) and health risk assessment (Singh and Ghosh, 2012; Kumar et al., 2016; Chakraborti et al., 2016) which has been carried out in the CGB. The lower Gangetic basin has been studied extensively with the application of stable isotopic compositions to understand the groundwater dynamics, recharge mechanism and its geochemical behaviour (Agrawal et al., 2000; Harvey et al., 2002; Mukherjee et al., 2007; Mukherjee and Fryar, 2008; Sikdar and Sahu, 2009). Only selected studies have been carried out on the application of the stable isotope in CGB (Saha et al., 2011; Mukherjee et al., 2012). There is a paucity regarding the various recharge sources to the local aquifers in CGB on the major river (Ganges) and its tributaries (Kamla, Baghmati and Burhi Gandak), surface stagnant water reservoir. Very little attention has been taken towards the role of surface water on groundwater dynamics and recharge processes. No study has been conducted to investigate the role of stagnant water bodies in groundwater recharge and to test the hypothesis of the DOC deposits at the bottom of the ponds and its role in mobilization in aquifers of the CGB. The current study has been carried out with the following objectives 1. To understand the sources of recharge in relation to meteoric circulation/ rainfall, 2. To evaluate the isotopic signature of recharging shallow groundwater and its interaction with deep groundwater 3. To investigate the source/ transport of DOC and its relation with recharging water.

## 4. 2 Material and methods

### *4.2.1. Study area*

The CGB covers the major part of Uttar Pradesh and Bihar. The Northern part of Bihar was selected for this study since this is very fertile and densely populated region of the Gangetic basin ranging 25º30’– 26º30’ N and 85º30’–86 º 30’ N (**Fig. 4.1**). Major tributaries of the Ganges (Kamla, Baghmati and Burhi Gandak) flowing from north to south-east are passing through this area, depositing their sediment load and forming active flood plain. This area has been demarked into Piedmont, Older and Younger Alluvium (Saha and Shukla, 2013; Singh and Pandey, 2014)**.** The area is known for an agricultural based economy. Most of the cultivation activities and cropping depend on the monsoon cycle except for the crops grown during in the winter season when groundwater meets its requirements (Saha et al., 2011).

### *4.2.2. Sample collection and analysis*

Total one hundred and five water samples (n=105) were collected for the current study. In which 88 were from groundwater and further categorised into different geomorphic regions like Piedmont (n=8), Older Alluvium (n=40), Younger Alluvium (n=40). Along with these (n=11) were collected river Ganges and its tributaries; river henceforth and (n=6) from surface ponds during 2013–15. The tubewell was purged for 10–15 minutes before taking any measurement and samples, to drive out the standing water from the casing. The field parameters i.e. pH and oxidation-reduction potential (ORP) were measured *in situ* using cell flow method to limit the atmospheric contact in the field with HANNA (HI 9828) multi- parameter. For the analysis of $\delta^{2}$H and $\delta^{18}$O, unfiltered water samples were collected in 15 ml HDPE plastic bottle without headspace from tubewells of various depths, river and ponds. Samples for $\delta^{13}$C analysis from groundwater collection were stored in 2 L plastic bottles and the pH was raised to 10–11 by adding NaOH drop by drop followed by 10 ml saturated $BaCl_2$.

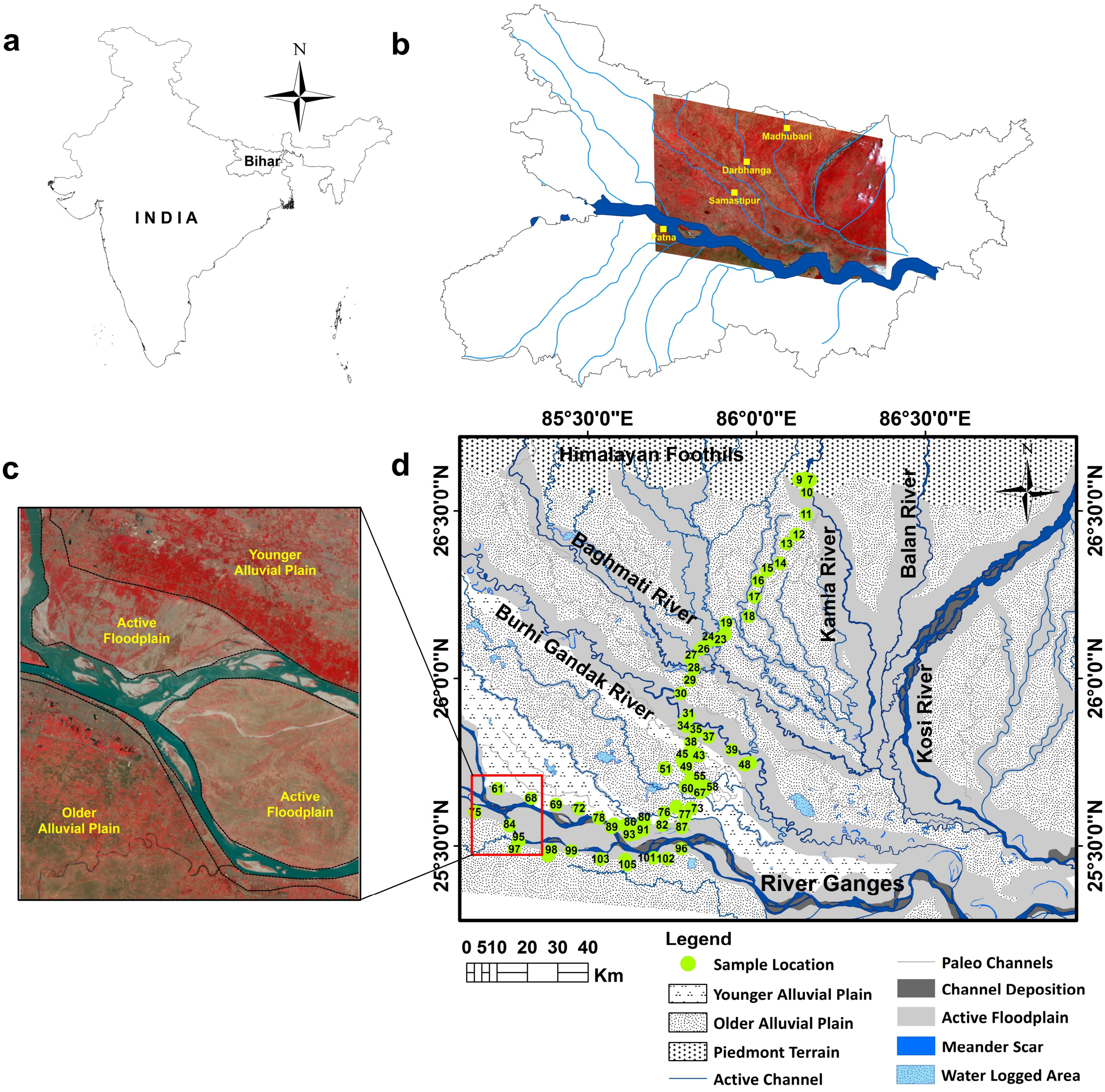

**Fig. 4.1.** Map of the study area (a) India (b) Bihar state (c) tool used for identification of different geomorphic features

The samples were kept until the precipitate appeared. The precipitate was collected after drying in wide mouth plastic bottles. The location of the samples was marked using a GPS portable device, and the details associated with tubewells depth and age was sourced by interviewing the owners. DOC analysis was done with the help of total organic carbon analyzer (TOC) SHIMADZU (TOC-L-CSH) in CERAR, University of South Australia, Australia. The stable isotopes ($\delta^2$H and $\delta^{18}$O) were estimated using PICARRO (L2140-i Analyzer) cavity ring-down spectroscopy (CRDS) in SES, JNU, India. The estimation of the bicarbonate ($HCO_3^-$) was also carried out in the SES, JNU using Metrohm (877 Titrino plus). The obtained analytical precision for $\delta^2$H and $\delta^{18}$O were observed as 0.24‰ and 0.07‰ respectively. A very small aliquot of sample (2.0 µL) was required for optimum precision. Each sample was repeated five times where the value of the 1st sample was excluded to improve the precision of the result. Three international standards (VSMOW, GISP and SLAP) were used for normalization of the isotopic records. The estimation of $\delta^{13}C$ was done in Radio and Atmospheric Sciences Division (RASD) of CSIR-National Physical Laboratory, New Delhi, India using isotope ratio mass spectrometer (Isoprime 100, Isoprime UK®) coupled with an elemental analyzer (Pyrocube, Elementar®). The precision of the isotope analysis ($\delta^{13}C$) and total carbon were found to be ±0.2‰ and better below 5% respectively.

### *4.2.3. Statistical analysis*

Origin (v. 6) was used to plot the bivariate graphs. Other bivariate and Box and Whisker plots were plotted in grapher (v. 9.0) software.

### *4.2.4. Identification of different geomorphic units in the study area*

Identification of the geomorphological features was based on remote sensing and digital image processing; a freely available satellite image was obtained from USGS site (www.earthexplorer.usgs.gov). The coverage of the image ranged 25º30'– 26º30' N and 85º30'–86 º 30' N. The image was sourced by Landsat 8 having a sensor Operational Land Imager (OLI) on May 9, 2015. The image was 30m in resolution for the multispectral band which was sharpened by the 15m panchromatic band. In order to distinguish the different geomorphic units in the image, the false colour composite (FCC) band combination 5, 4 and 3 (near-infrared, red and green) was used as shown in figure (**Fig. 4.1c**). The map was prepared in ArcGIS (v. 9.3). The landforms and features identified by the remote sensing were confirmed by field visit for two times and further with the previous available literature on geomorphology for this area (Saha and Sahu, 2015; Saha and Shukla, 2013; Singh and Pandey, 2014).

## 4.3. Result and discussion

### *4.3.1. Solute chemistry and isotope signatures*

Statistics of the physicochemical properties of the groundwater has been shown in **Table 4.1**. Groundwater in Piedmont region shows neutral pH with the mean value of 7 (range 6.8–7.3). The pH of Older and Younger Alluvium was found to be neutral to slightly alkaline having median values of 7.6 and 7.5 respectively river water also shows alkaline pH having a range of 7.5–8.0 (**Fig. 4.2**). Higher $HCO_3^-$ concentration was observed in Younger Alluvium followed by Piedmont and Older Alluvium. Median $HCO_3^-$ concentration in river water was almost half that of the groundwater with the mean concentration 219 mg/L and range (135–310 mg/L) indicating the less geochemical evolution. The trend of calcium ($Ca^{2+}$) concentration was same as $HCO_3^-$ for Piedmont, Older and Younger Alluvium. The DOC concentration was observed higher in Piedmont having median 1.78

mg/L (range 1.37–4.7 mg/L) followed by Younger Alluvium (median 1.35 mg/L), the Older Alluvium, which has low DOC concentration having a median concentration of 1.27 mg/L.

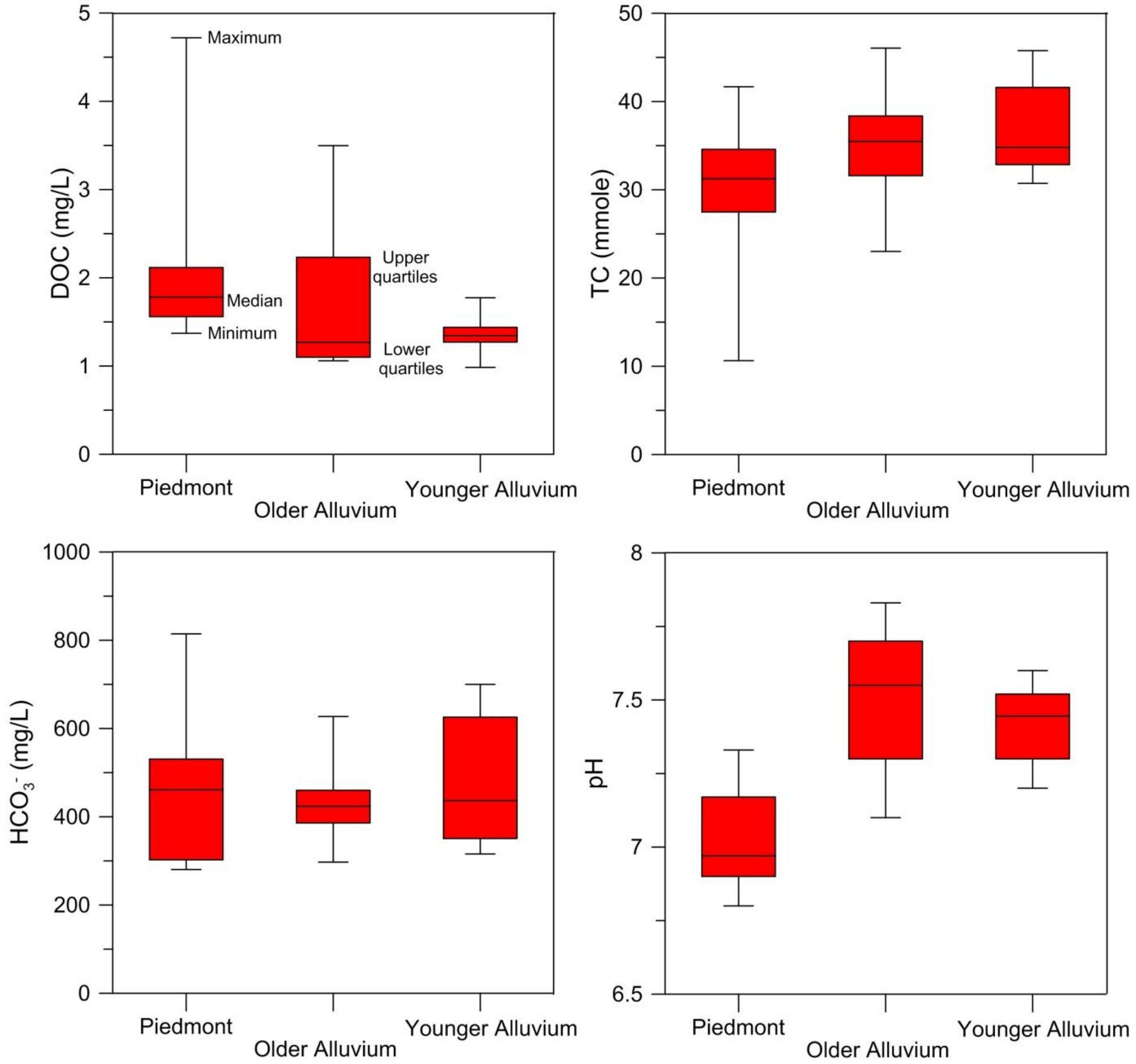

**Fig. 4.2.** Box-Whisker plot of the selected parameters DOC, TC, $HCO_3^-$ and pH of the groundwater of different geomorphic units

Stable isotopic results shows that groundwater samples ranged from -7.90 to -6.05‰ (against VSMOW) for $\delta^{18}O$ (median -7.21‰) for Piedmont region, -7.94 to -2.81‰ (median -6.31‰) for Older Alluvium and -9.43 to -2.81 ‰ (median -6.99 ‰) for Younger Alluvium in the study area. River water samples showed wide range for $\delta^{18}O$ -11.61 to 3.23‰ (median -4.48‰) indicating the enrichment that reflects evaporation effect due to loss of lighter isotopes. The range for $\delta^{2}H$ was observed -47.66 to -36.81‰ median (-45.59‰) for Piedmont region, -55.5 to -28.70‰ (median -46.32‰) for Older Alluvium and -61.83 to -25.43‰ (median -48.90‰) for Younger Alluvium. River water showed a range -76.24 to 25.23‰ median (-33.43‰) for $\delta^{2}H$. The water samples collected from ponds shows highly enrichment of the stable isotopic records of $\delta^{18}O$ having (range 0.5–8.9‰) and

$\delta^2$H (range -2.3–43.2‰). The calculated d-excess for pond water ranged -27.7– (-8.6)‰. The total carbon (TC) estimation in the groundwater was observed to be higher in Older Alluvium with a range 23 to 46 mmole (median 36 mmol) followed by Younger Alluvium (median 35 mmole). The concentration of TC was lower in Piedmont with a range 10.6–42 mmole (median 31 mmole).

**Table. 4.1**

Physicochemical and isotopic compositions of groundwater and River water

| Parameters | Piedmont (*n*=8) | Older Alluvium (*n*=14) | Younger Alluvium (*n*=14) | River (*n*=10) |
|---|---|---|---|---|
| *pH* | | | | |
| Mean | 7.0 | 7.5 | 7.4 | 7.7 |
| Median | 7.0 | 7.6 | 7.5 | 7.6 |
| Range | 6.8–7.3 | 7.1–7.8 | 7.2–7.6 | 7.5–8.0 |
| $HCO_3^-$ *(mg/L)* | | | | |
| Mean | 458 | 432 | 489 | 219 |
| Median | 461 | 424 | 437 | 226 |
| Range | 280–814 | 297–627 | 316–700 | 135–310 |
| $Ca^{2+}$ (mg/L) | | | | |
| Mean | 56.7 | 59.1 | 86.7 | 33.4 |
| Median | 55.4 | 62.9 | 84.7 | 31.8 |
| Range | 38.3–87.8 | 18.3–91.1 | 45.3–148.9 | 16.3–62.8 |
| *DOC (mg/L)* | | | | |
| Mean | 2.11 | 1.70 | 1.38 | 0.12 |
| Median | 1.78 | 1.27 | 1.35 | 0.12 |
| Range | 1.37–4.7 | 1.06–3.5 | 0.99–1.77 | 0.11–0.12 |
| *δD(‰)* | | | | |
| Mean | -43.33 | -44.37 | -47.80 | -39.49 |
| Median | -45.59 | -46.32 | -48.90 | -33.43 |
| Range | -47.66–(-36.81) | -55.53–(-28.70) | -61.83–(-25.43) | -76.24–(25.23) |
| $\delta^{18}O$*(‰)* | | | | |
| Mean | -7.09 | -6.16 | -6.67 | -5.41 |
| Median | -7.21 | -6.31 | -6.99 | -4.48 |
| Range | -7.90–(-6.05) | -7.94–(-2.81) | -9.43–(-2.81) | -11.61–(3.23) |
| $\delta^{13}$ *C* | | | | |
| Mean | -11.69 | -7.79 | -9.51 | |
| Median | -11.67 | -8.07 | -9.57 | |
| Range | -13.13–(-10.82) | -9.76–(-3.11) | -13.21–(-5.4) | – |
| *C( mmole)* | | | | |
| Mean | 30 | 35 | 37 | |
| Median | 31 | 36 | 35 | |
| Range | 10.6–42 | 23–46 | 31–46 | – |

### *4.3.2. Isotopic behaviours in groundwater and surface (river and pond) waters in study area*

Several sources could be responsible for the recharge to the study area viz. modern day precipitation (monsoon source at the Bay of Bengal or local moisture), precipitation in palaeoclimate, surface water infiltration, river or surface water bodies. Similarly, river water also could be influenced by high altitude snow melt, precipitation, groundwater discharge and evaporation (Mukherjee et al., 2012). Bivariate plots of $\delta^2$H and $\delta^{18}$O were constructed to understand the characterization of recharge process in the study area (**Fig. 4.3**). Most of the groundwater samples and river water samples plot along the global meteoric water line (GMWL) and local meteoric water lines (LMWL) of nearby stations from West Bengal (Mukherjee et al., 2007). There is no LMWL derived for Patna or any other place in the CGB. The LMWL of West Bengal is close to the GMWL (**Fig. 4.3**). The samples fell close to and below to the GMWL and LMWL for Older Alluvium and Younger Alluvium while all the samples from Piedmont were falling on LMWL with a trend ($\delta^2$H = 6.0 $\delta^{18}$O - 0.6) indicating that aquifers are getting recharge with modern day precipitation having no evaporation effect. The median value of $\delta^{18}$O for Younger and Older Alluvium were recorded as -6.31 and -6.99‰ correspondingly with a trend line of ($\delta^2$H = 3.3 $\delta^{18}$O-23.9) and ($\delta^2$H = 4.7 $\delta^{18}$O-16.2) respectively. Negative slopes to the GMWL and LMWL depicting that the aquifer has been recharged with water which has undergone for significant evaporation.

In a study from the adjacent area, the isotopic composition of $\delta^{18}$O and $\delta^2$H were recorded for different geomorphic units as -5.5 (-41.5), -6.7 (-44.0) and -5.95 (-35.0) ‰ for Piedmont, Older and Younger Alluvium respectively (Mukherjee et al., 2012). This study revealed recharge of adjacent aquifers from meteoric or surface water which has undergone some evaporation. In the current study,~50% of the samples from Older Alluvium fell on the GMWL and LMWL whilst~50% below to the GMWL and LMWL. In Younger Alluvium 37% of the samples are having enriched $\delta^{18}$O with values higher than the median of -6.99 indicating the evaporation effect on recharging water in these aquifers. Majority of the samples in Piedmont, Older and Younger Alluvium have lighter isotopes and fell very close to LMWLs indicating direct recharge source as precipitation with little evaporation effect. One sample (sample #36) reported with highly enriched $\delta^{18}$O (-2.8‰), this tubewell has good connectivity to the flanking pond (sample #35) having highly enriched $\delta^{18}$O (8.9‰) (**Table 4.2**). In order to know the contribution of the water from river Ganges and its tributaries to the adjacent aquifers, plots of $\delta^{18}$O, $\delta^2$H and d-excess versus latitude for groundwater samples were plotted (**Fig. 4.4 a, b** and **c**). Samples from River Ganges (samples #88 and #89) (**Table 4.1**) recorded with lighter isotopic values ($\delta^{18}$O-8.4 and -11.6‰ respectively and $\delta^2$H were -64.6 and -76.2‰ respectively).

Among river waters, it indicated high altitude source component due to the highly depleted snowmelt from the Himalayas (the origin place of the Ganges) (Ramesh and Sarin, 1992; Stuben et al., 2003). The River Ganges is perennial and flows in a large channel. In another study, slightly enriched values of $\delta^{18}$O (~-4.75) was reported by Saha et al. (2011) in water samples collected from River Ganges in

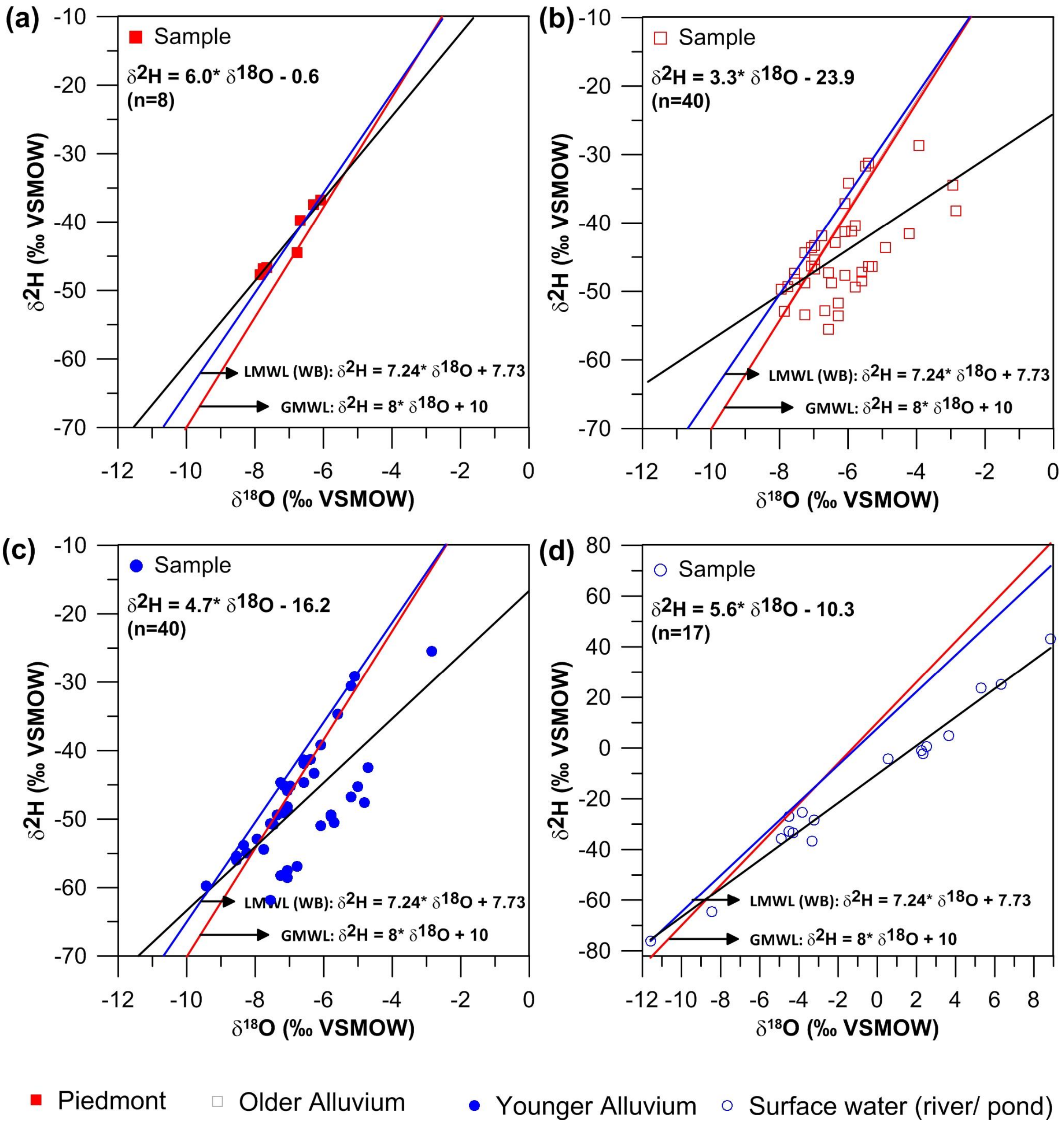

**Fig. 4.3.** Bivariate plot of $\delta^2$H and $\delta^{18}$O separated for Piedmont (**a**), Older Alluvium (**b**), Younger Alluvium (**c**) and River water (**d**). The Global Meteoric Water line (GMWL) of Craig (1961) and Local Meteoric Water Line (LMWL) of West Bengal is provided for reference

the same season indicating local evaporation loss from the surface of the rivers. The samples in the current study were collected from mid of the stream and~1 foot deep from the surface of the water.It was depicted from (**Fig. 4.4a** and **b**) that most of the tributaries having different isotopic signature(enriched) but the surrounding aquifer's water showed depleted $\delta^{18}$O and $\delta^2$H values indicated less hydraulic connectivity and much less recharge from these tributaries. Three groundwater samples (#36, #42 and #44) flanking river Burhi Gandak shows virtually similar isotopic signature indicating good hydraulic connectivity. Hence, these aquifers are getting recharged by that river. The water samples (#64 and #65) which were collected from a seasonal river (name Balan) recorded highly enriched $\delta^{18}$O values (5.4 and 2.3‰ respectively) (**Table 4.2**) indicating evaporation loss heavily due to stagnant water. The water samples collected from other northern tributaries of the river Ganges Baghmati, Kamla, Burhi Gandak and Bya also recorded enriched isotopic compositions with a range -4.9 to -2.3‰ indicating evaporation effect during their course and no or very little connectivity to the local aquifers. A hydrographical study conducted to the south side of the Ganges, in CGB, shows shallow groundwater resource build up mainly from the monsoonal precipitation (Saha et al., 2011). These tributaries carry seasonal flow only. However, the channels are narrow attributing to less flow thus causing higher evaporation. The groundwater isotope ($\delta^{18}$O and $\delta^{2}$H) trend positively in Older and Younger Alluvium from north to south (**Fig. 4.4a** and **b**). Few locations in Younger Alluvium in the proximity of the river Ganges showed similarity in stable isotopic composition indicating the possibility of recharge locally. The lower d-excess (<5) values of the pond (not shown in the figure) and a few river and groundwater samples of Older and Younger Alluvium from north to south indicate significant evaporation (**Fig. 4.4c**).

Highly enriched isotopic composition of O and H for surface stagnant water (samples #25, #35, #51, #52, #59, #73) were reported having $\delta^{18}$O (0.5 – 8.9‰) and $\delta^{2}$H (-4.30 to 43.2‰) (**Table 4.1**) indicating extensive evaporation effect. The samples for the current study were collected in pre-monsoon during peak summer season. Except at one location (sample #36), there is no signature of recharge from these surface water bodies and ponds in this area. Many studies have proven from the stable isotopic record, that the ponds are playing no role in recharging, mixing or providing organic matter to the groundwater in West Bengal (Datta et al., 2011; McArthur et al., 2004; Sengupta et al., 2008). While other studies argue that ponds are recharging the groundwater and contributing DOC to the As affected shallow aquifers waters (Harvey et al., 2006; Neumann et al., 2010). From the isotopic record, it was reported that rainfall recharges the perennial pond of the West Bengal Basin during the height of monsoon and subsequently undergoes substantial enrichment (Dutta et al., 2011). The current study revealed that there is no or very little connectivity of the pond water to the groundwater, hence indicated that there is the very little probability of the migration of the DOC from ponds to the groundwater.

Plots of the depth versus $\delta^{18}$O, $\delta^{2}$H and d-excess (**Fig. 4.5 a, b** and **c**) were plotted in order to examine the interconnectivity of the top 30–50 m shallow aquifers in upper aquitard formation to the upper main aquifer demarcated by Saha and Shukla (2013) in this area. It was noted that in Piedmont region these two aquifers showed different isotopic signature. Deeper aquifer (samples #2, depth 121 m) shows more depleted values of $\delta^{18}$O (-7.8‰) and $\delta^{2}$H (-47‰) than the adjacent shallow tubewell (sample #3, depth 12 m) (**Table 4.1**) where the $\delta^{18}$O and $\delta^{2}$H were recorded as -6.7 and -39.8‰ respectively. This indicates the source of the recharging water from different climatic conditions for shallow and deeper aquifers. It can be reflected from depth versus d-excess plot (**Fig. 4.5c**) that all three deeper tubewells formed a group and exhibited higher d-excess, which indicated that the aquifers were recharged before evaporation mainly during the monsoon period. This fact above also suggests that there is much less hydraulic connectivity of the upper shallow aquifer to the main adjacent deeper aquifer. In Older and Younger Alluvium with $\delta^{18}O$ values of -5.6 and -6.5 for the main shallow aquifer and -5.6 and -6.2 for the upper shallow aquifer shows no or very little difference indicating good connectivity in both the aquifer layers. The same results were observed by Saha et al. (2011) and found that the aquifer of the upper aquitard formation and main shallow aquifer (at depth~ 120 m) have the same $\delta^{18}O$ and $\delta^{2}H$ signature indicating the connectivity of the aquifers. An attempt was also made to investigate the isotopic composition of carbon from north to south (**Fig. 4.4 d**). The $\delta^{13}C$ trended positive from north to south in Older Alluvium indicating enrichment of heavier stable isotope. Enriched $\delta^{13}C$ are generally thought to be related to production of isotopically heavy carbon in relatively high $pCO_2$ in shallow depths due to microbial reactions of methanogenesis in the soils and is driven by the carbonate dissolution (Hackley and Liu, 1996; Smedley et al., 2002). This area is near to the Younger Alluvium hence there may be a transition zone which has appropriate conditions for such activities. On the contrary in Younger Alluvium the trend was opposite and lighter isotopes were increased southwards, also in the proximity to the river Ganges. Lighter isotope of carbon consists with the oxidation of organic matter (Zheng et al., 2004; Thilagvathi et al., 2016).

DOC concentration was also comparatively low (**Fig. 4.2**) in Younger Alluvium due to higher microbial activity in this region. Dissolution of carbonates could be the reason for depleted $\delta^{13}C$ in Younger Alluvium. Carbonate dissolution was observed to be the prominent weathering type in Younger Alluvium (Kumar et al., 2016). Depth plot of $\delta^{13}C$ (**Fig. 4.5d**) shows that the deeper aquifers are enriched with lighter isotopes and the presence of considerable DOC concentration. In three deeper tubewells (>120 m) water samples #2 #20 and #33 DOC concentration was 1.63, 1.36 and 1.27 mg/L respectively. The presence of DOC in deeper aquifers reflects limited microbial activity or the presence of relatively immobile refractory organic matter (Mukherjee et al., 2008). The most enriched $\delta^{13}C$ compositions were found in the shallow aquifer, the reason may be due to the presence of kankar layer in the upper shallow zone in the CGB coupled with high $pCO_2$. The median isotopic composition of $\delta^{13}C$ was -9.6‰ (for all samples); $\delta^{13}C$ ranged (-3.11 to -13.21). The variation of $\delta^{13}C$ (-5 to -11‰) can be inferred as aquifers being dominated by carbonate inputs incorporated with only little influence from respiration of soil organics (Aucour et al., 1999).

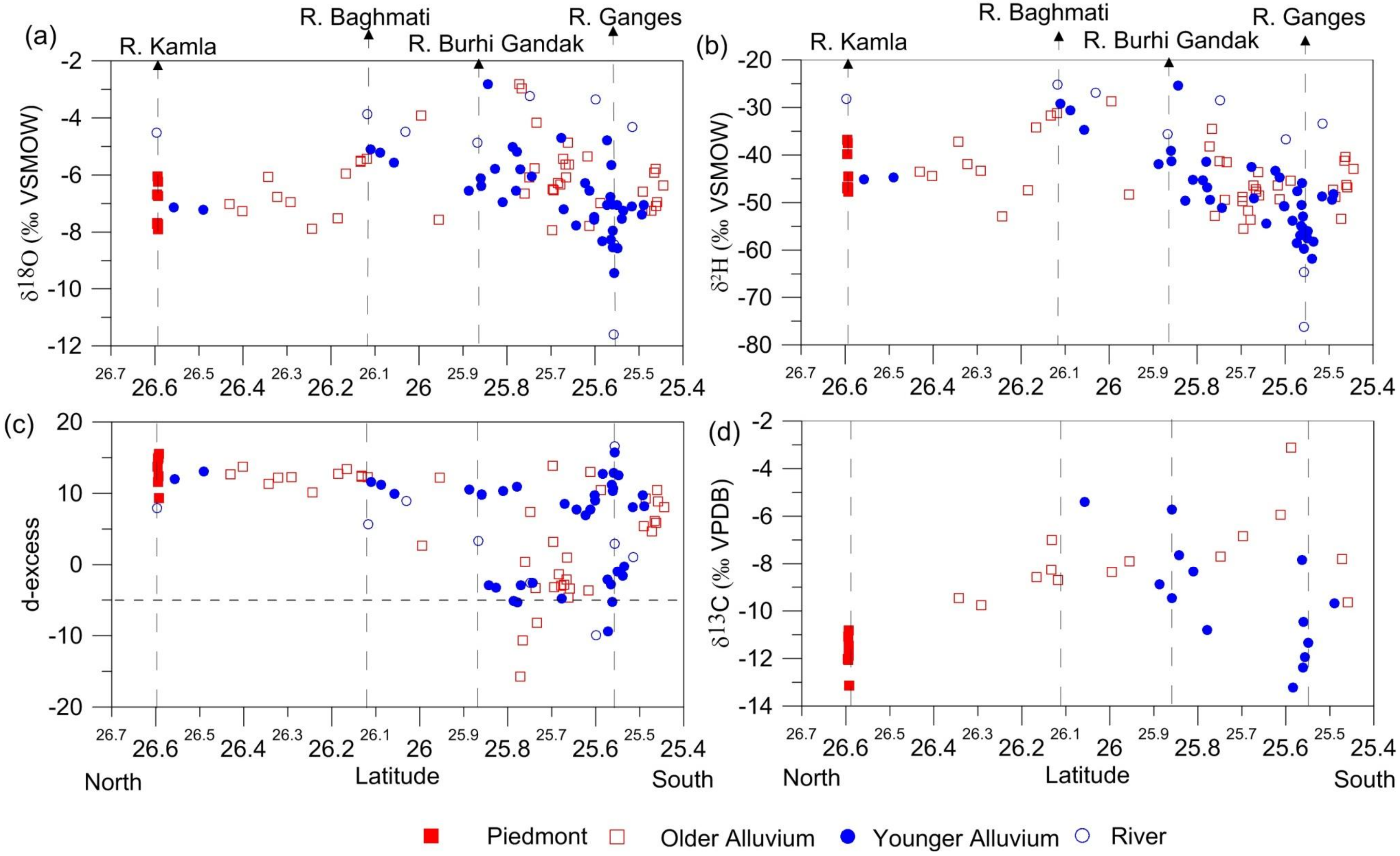

**Fig. 4.4.** Plots $\delta^{18}O$, $\delta^{2}H$, d-excess and $\delta^{13}C$ with latitudes (as proxy of distance from Himalayan foothills to CGB) **a**, **b**, **c** and **d.** Horizontal dashed line shows d-excess (+5) in (**c**)

**Table 4.2**

Sample location (with latitude) for groundwater and surface water; Piedmont (n=8), Older Alluvium (n=40), Younger Alluvium (n=40) and River (n=11) for CGB (calibrated)

| S.No. | Lat | Log | Feature | Village | Block | District | Depth (m) | $HCO_3^-$ | $\delta^{18}O$(‰) | $\delta^{2}H$(‰) | d-excess | TC | $\delta^{13}$ C(‰) | Ca | DOC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | **26.597** | **86.144** | **R. Kamla** | **Bela** | **Jaynagar** | **MD** | **–** | **231** | **-4.5** | **-32.8** | **3.3** | **–** | **–** | **–** | **–** |
| 2 | 26.595 | 86.138 | PD | Bela | Jaynagar | MD | 121 | 531 | -7.8 | -47.0 | 15.0 | 27.9 | -11.1 | 56.5 | 1.63 |
| 3 | 26.595 | 86.137 | PD | Jaynagar | Jaynagar | MD | 12 | 814 | -6.7 | -39.8 | 13.6 | 33.3 | -12 | 87.8 | 1.94 |
| 4 | 26.595 | 86.127 | PD | Pithua Tola | Jaynagar | MD | 15 | 305 | -6.1 | -36.8 | 11.9 | 27.5 | -12.1 | 46.3 | 1.73 |
| 5 | 26.595 | 86.126 | PD | Pithua Tola | Jaynagar | MD | 61 | 303 | -7.7 | -46.7 | 14.6 | 33.6 | -11.1 | 40 | 1.84 |
| 6 | 26.593 | 86.159 | PD | Bela | Jaynagar | MD | 52 | 506 | -7.9 | -47.7 | 15.1 | 10.6 | -11.5 | 54.4 | 4.72 |
| 7 | 26.593 | 86.16 | PD | Bela | Jaynagar | MD | 21 | 506 | -6.8 | -44.5 | 9.7 | 41.7 | -13.1 | 72.4 | 2.12 |
| 8 | 26.593 | 86.126 | PD | Uchchhal Tola | Jaynagar | MD | 61 | 280 | -7.8 | -46.8 | 15.2 | 29.2 | -10.8 | 38.3 | 1.37 |
| 9 | 26.593 | 86.127 | PD | Uchchhal Tola | Jaynagar | MD | 15 | 417 | -6.3 | -37.5 | 12.8 | 34.6 | -11.9 | 57.9 | 1.56 |
| 10 | 26.557 | 86.149 | YAP | Singhgrahi | Jaynagar | MD | 24 | 353 | -7.2 | -45.1 | 12.2 | – | – | – | – |
| 11 | 26.49 | 86.148 | YAP | Datwar | Khajauli | MD | 48 | 442 | -7.3 | -44.7 | 13.4 | – | – | – | – |
| 12 | 26.43 | 86.118 | OAP | Rasheedpur | Khajauli | MD | 30 | 394 | -7.1 | -43.6 | 12.9 | – | – | – | – |
| 13 | 26.402 | 86.089 | OAP | Belhvad | Rajnagar | MD | 67 | 366 | -7.3 | -44.4 | 13.7 | – | – | – | – |
| 14 | 26.343 | 86.071 | OAP | Madhubani | Madhubani | MD | 76 | 460 | -6.1 | -37.2 | 11.5 | 39.2 | -9.5 | 47.2 | 1.10 |
| 15 | 26.322 | 86.032 | OAP | Mangalia | Madhubani | MD | 45 | 441 | -6.8 | -41.9 | 12.3 |  |  |  |  |
| 16 | 26.292 | 86.005 | OAP | Raiam | Madhubani | MD | 58 | 386 | -7.0 | -43.3 | 12.5 | 33.8 | -9.8 | 36.3 | 3.50 |
| 17 | 26.243 | 85.994 | OAP | Kevti | Darbhanga | DB | 67 | 316 | -7.9 | -52.9 | 9.9 | – | – | – | – |
| 18 | 26.185 | 85.978 | OAP | Bhawanipur | Bijli | DB | 36 | 314 | -7.6 | -47.4 | 13.1 | – | – | – | – |
| 19 | 26.166 | 85.911 | OAP | Chuna Bhatti | Sadar | DB | 36 | 336 | -6.0 | -34.2 | 13.7 | 34.6 | -8.6 | 18.3 | 1.47 |
| 20 | 26.133 | 85.907 | OAP | Kapuri Chowk | Laheria Sarai | DB | 121 | 440 | -5.5 | -31.7 | 12.3 | 31.6 | -8.3 | 36.4 | 1.36 |
| 21 | 26.132 | 85.907 | OAP | Kapuri Chowk | Laheria Sarai | DB | 36 | 378 | -5.5 | -31.7 | 12.3 | 38.4 | -7 |  | 1.28 |
| 22 | 26.118 | 85.887 | OAP | Said Nagar | Bahadurpur | DB | 55 | 413 | -5.4 | -31.3 | 11.9 | 23 | -8.7 | 22.4 | 3.08 |
| **23** | **26.117** | **85.876** | **R. Baghmati** | **Dharnipatti** | **Bahadurpur** | **DB** | **–** | **222** | **-3.8** | **-25.3** | **5.3** | **–** | **–** | **–** | **–** |
| 24 | 26.11 | 85.857 | YAP | Taralahi | Bahadurpur | DB | 58 | 492 | -5.1 | -29.2 | 11.6 | – | – | – | – |
| **25** | **26.091** | **85.837** | **Pond** | **Bhajnali Pokhar** | **Bahadurpur** | **DB** | **–** | **227** | **0.5** | **-4.3** | **-8.6** | **–** | **–** | **18.6** | **–** |
| 26 | 26.088 | 85.835 | YAP | Delahi | Hanuman Nagar | DB | 48 | 485 | -5.2 | -30.6 | 11.0 | – | – | – | – |
| 27 | 26.057 | 85.807 | YAP | Bisanpur | Hanuman Nagar | DB | 45 | 578 | -5.6 | -34.7 | 10.1 | 33.8 | -5.4 | 45.3 | 1.43 |
| **28** | **26.03** | **85.815** | **R. Santi** | **Jatmal Pur** | **Hanuman Nagar** | **DB** | **–** | **164** | **-4.5** | **-27.0** | **9.1** | **–** | **–** | **–** | **–** |
| 29 | 25.995 | 85.803 | OAP | Bhattichowk | Kalayanpur | SP | 45 | 627 | -3.9 | -28.7 | 2.7 | 37.3 | -8.4 | 62.9 | 1.26 |
| 30 | 25.955 | 85.776 | OAP | Kalayanpur | Kalayanpur | SP | 48 | 514 | -7.6 | -48.3 | 12.2 | 46.1 | -7.9 | 78.1 | 1.26 |
| 31 | 25.887 | 85.799 | YAP | Sari Tola | Warisnagar | SP | 45 | 700 | -6.6 | -41.9 | 10.7 | 32.8 | -8.9 | 106.2 | 1.77 |
| **32** | **25.867** | **85.785** | **R. B.G.** | **Samastipur** | **Samastipur** | **SP** | **–** | **299** | **-4.9** | **-35.6** | **3.7** | **–** | **–** | **–** | **–** |
| 33 | 25.859 | 85.792 | YAP | Bahadurpur | Samastipur | SP | 136 | 626 | -6.4 | -41.3 | 9.7 | 41.6 | -9.5 | 49.3 | 1.27 |
| 34 | 25.859 | 85.791 | YAP | Bahadurpur | Samastipur | SP | 30 | 636 | -6.1 | -39.2 | 9.5 | 31 | -5.7 | 64.9 | 1.41 |

**Table 4.2** continued

| S.No. | Lat | Log | Feature | Village | Block | District | Depth (m) | $HCO_3^-$ | $\delta^{18}O$(‰) | $\delta^2H$(‰) | d-excess | TC | $\delta^{13}$ C(‰) | Ca | DOC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **35** | **25.843** | **85.821** | **Pond** | **Visanpur** | **Ujiyarpur** | **SP** | **–** | **200** | **8.9** | **43.2** | **-27.7** | **–** | **–** | **37.7** | **–** |
| 36 | 25.843 | 85.822 | YAP | Visanpur | Ujiyarpur | SP | 24 | 666 | -2.8 | -25.5 | -2.7 | 34.4 | -7.6 | 98.3 | 1.67 |
| 37 | 25.827 | 85.859 | YAP | Bhattri Chowk | Bibhutipur | SP | 12 | 455 | -5.8 | -49.6 | -3.3 | – | – | – | – |
| 38 | 25.81 | 85.806 | YAP | Bilari Kachahari | Ujiyarpur | SP | 17 | 347 | -7.0 | -45.2 | 10.6 | 45.8 | -8.3 | 109.8 | 1.37 |
| 39 | 25.787 | 85.927 | YAP | Angar Ghat | Bibhutipur | SP | 21 | 530 | -5.0 | -45.3 | -5.3 | – | – | – | – |
| 40 | 25.779 | 85.801 | YAP | Ujiyarpur | Ujiyarpur | SP | 20 | 450 | -6.6 | -41.4 | 11.2 | 44.1 | -10.8 | 123.9 | 1.32 |
| 41 | 25.777 | 85.813 | YAP | Rampur Iksalla | Ujiyarpur | SP | 29 | 599 | -5.2 | -46.8 | -5.2 | – | – | – | – |
| 42 | 25.771 | 85.798 | OAP | Pakhri | Ujiyarpur | SP | 36 | 483 | -2.8 | -38.2 | -15.4 | – | – | – | – |
| 43 | 25.77 | 85.83 | YAP | Ramchandrapur | Ujiyarpur | SP | 36 | 517 | -5.8 | -49.4 | -3.1 | – | – | – | – |
| 44 | 25.766 | 85.803 | OAP | Raepur Khanua | Ujiyarpur | SP | 18 | 513 | -2.9 | -34.5 | -10.9 | – | – | – | – |
| 45 | 25.76 | 85.78 | OAP | Satanpur Chowk | Ujiyarpur | SP | 21 | 555 | -6.7 | -52.8 | 0.6 | – | – | – | – |
| 46 | 25.749 | 85.785 | OAP | Satnapur | Ujiyarpur | SP | 24 | 449 | -6.1 | -41.3 | 7.4 | 39.1 | -7.7 | 91.1 | 1.13 |
| **47** | **25.748** | **85.982** | **R. B.G.** | **Singhiya Ghat** | **Bibhutipur** | **SP** | **–** | **168** | **-3.2** | **-28.5** | **-2.6** | **–** | **–** | **–** | **–** |
| 48 | 25.743 | 85.965 | YAP | Shiv Nathpur | Bibhutipur | SP | 45 | 558 | -6.1 | -51.0 | -2.3 | – | – | – | – |
| 49 | 25.737 | 85.792 | OAP | Chandi Chaur | Dal Singh Sarai | SP | 18 | 696 | -5.8 | -49.4 | -3.1 | – | – | – | – |
| 50 | 25.733 | 85.727 | OAP | Nargoghi | Sarai Ranjan | SP | 18 | 596 | -4.2 | -41.6 | -7.8 | – | – | – | – |
| **51** | **25.730** | **85.731** | **Pond** | **Nargoghi** | **Sarai Ranjan** | **SP** | **–** | **–** | **2.5** | **0.6** | **-19.6** | **–** | **–** | **–** | **–** |
| **52** | **25.702** | **85.807** | **Pond** | **Chhapkahi** | **Dal Singh Sarai** | **SP** | **–** | **–** | **2.3** | **-2.3** | **-21.1** | **–** | **–** | **–** | **–** |
| 53 | 25.697 | 85.809 | OAP | Basaria | Dal Singh Sarai | SP | 24 | 505 | -8.0 | -49.7 | 13.9 | 30.4 | -6.8 | 81.8 | 1.07 |
| 54 | 25.696 | 85.81 | OAP | Basaria Gomti | Dal Singh Sarai | SP | 24 | 709 | -6.5 | -48.8 | 3.0 | – | – | – | – |
| 55 | 25.694 | 85.832 | OAP | Kamraun chowk | Dal Singh Sarai | SP | 45 | 488 | -6.6 | -55.5 | -2.9 | – | – | – | – |
| 56 | 25.684 | 85.815 | OAP | Goda Vajidpur | Dal Singh Sarai | SP | 21 | 490 | -6.3 | -51.7 | -1.5 | – | – | – | – |
| 57 | 25.678 | 85.79 | OAP | Babupr | Sarai Ranjan | SP | 85 | 555 | -6.3 | -53.6 | -3.4 | – | – | – | – |
| 58 | 25.677 | 85.853 | YAP | Jalalpur | Dal Singh Sarai | SP | 18 | 441 | -4.7 | -42.5 | -4.8 | – | – | – | – |
| **59** | **25.672** | **85.814** | **Pond** | **Rampur** | **Dal Singh Sarai** | **SP** | **–** | **–** | **3.7** | **4.8** | **-24.5** | **–** | **–** | **–** | **–** |
| 60 | 25.672 | 85.814 | OAP | Ballo Chak | Dal Singh Sarai | SP | 17 | 533 | -5.4 | -46.4 | -3.2 | – | – | – | – |
| 61 | 25.671 | 85.234 | YAP | Jaghuwa, Hajipur | Vaishali | VS | 67 | 412 | -7.2 | -49.1 | 8.2 | – | – | – | – |
| 62 | 25.666 | 85.842 | OAP | Lok Nath Pur | Dal Singh Sarai | SP | 21 | 608 | -5.6 | -47.2 | -2.4 | – | – | – | – |
| 63 | 25.665 | 85.841 | OAP | Dal Singh Sarai | Dal Singh Sarai | SP | 30 | 600 | -6.1 | -47.7 | 1.0 | – | – | – | – |
| **64** | **25.665** | **85.829** | **R. Balan** | **Dal Singh Sarai** | **Dal Singh Sarai** | **SP** | **–** | **255** | **5.3** | **23.6** | **-18.9** | **–** | **–** | **–** | **–** |
| **65** | **25.665** | **85.828** | **R. Balan** | **Dal Singh Sarai** | **Dal Singh Sarai** | **SP** | **–** | **–** | **2.3** | **-1.0** | **-19.1** | **–** | **–** | **–** | **–** |
| 66 | 25.661 | 85.834 | OAP | Dal Singh Sarai | Dal Singh Sarai | SP | 24 | 533 | -4.9 | -43.6 | -4.3 | – | – | – | – |
| 67 | 25.659 | 85.833 | OAP | Dal Singh Sarai | Dal Singh Sarai | SP | 18 | 526 | -5.6 | -48.5 | -3.7 | – | – | – | – |
| 68 | 25.643 | 85.333 | YAP | Bidhupur | Vaishali | VS | 61 | 397 | -7.8 | -54.4 | 7.6 | – | – | – | – |
| 69 | 25.623 | 85.407 | YAP | Chainpur | Vaishali | VS | 61 | 362 | -6.3 | -43.3 | 7.0 | – | – | – | – |
| 70 | 25.617 | 85.763 | OAP | Sita Tola, Simri | Vidhyapati Nagar | SP | 12 | 489 | -5.3 | -46.4 | -4.0 | – | – | – | – |
| 71 | 25.612 | 85.806 | OAP | Mirzapur | Vidhyapati Nagar | SP | 39 | 429 | -7.8 | -49.3 | 12.7 | 37.4 | -5.9 | 80.7 | 2.88 |

**Table 4.2.** continued

| S.No. | Lat | Log | Feature | Village | Block | District | Depth (m) | $HCO_3^-$ | $\delta^{18}O$(‰) | $\delta^{2}H$(‰) | d-excess | TC | $\delta^{13}$ C(‰) | Ca | DOC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **72** | **25.612** | **85.808** | **Pond** | **Mirzapur** | **Vidhyapati Nagar** | **SP** | **–** | **220** | **-6.6** | **-44.7** | **7.9** | **–** | **–** | **31.6** | **–** |
| 73 | 25.612 | 85.475 | YAP | Muruvatpur | Vaishali | VS | 61 | 430 | 6.3 | 25.0 | -25.6 | – | – | – | – |
| 74 | 25.602 | 85.167 | YAP | Bahadurpur | Patan | PT | 76 | 463 | -7.6 | -50.7 | 9.8 | – | – | – | – |
| 75 | 25.601 | 85.167 | YAP | Bahadurpur | Patan | PT | 55 | 344 | -7.5 | -50.8 | 8.9 | – | – | – | – |
| **76** | **25.599** | **85.727** | **R. Bya** | **Mohanpur Ghat** | **Vidhyapati Nagar** | **SP** | **–** | **252** | **-3.3** | **-36.7** | **-10.0** | **–** | **–** | **–** | **–** |
| 77 | 25.588 | 85.788 | OAP | Vajidpur | Vidhyapati Nagar | SP | 61 | 394 | -7.0 | -45.4 | 10.4 | 36.4 | -3.1 | 86.9 | 2.23 |
| 78 | 25.584 | 85.534 | YAP | Hasanpur | Mohanpur | SP | 11 | 620 | -8.3 | -53.8 | 12.9 | 36.8 | -13.2 | 60.6 | 1.19 |
| 79 | 25.573 | 85.666 | YAP | Mohiuddin Nagar | Mohiuddin Nagar | SP | 33 | 438 | -7.1 | -58.5 | -2.0 | – | – | – | – |
| 80 | 25.572 | 85.668 | YAP | Mohiuddin Nagar | Mohiuddin Nagar | SP | 20 | 390 | -4.8 | -47.6 | -9.1 | – | – | – | – |
| 81 | 25.565 | 85.578 | YAP | Patthar Ghat | Mohanpur | SP | 20 | 470 | -6.8 | -56.9 | -2.7 | – | – | – | – |
| 82 | 25.563 | 85.721 | YAP | Mahmudipur | Mohiuudin Nagar | SP | 55 | 365 | -8.2 | -54.9 | 11.1 | 34.1 | -7.8 | 90.5 | 1.77 |
| 83 | 25.562 | 85.611 | YAP | Dumri | Mohanpur | SP | 30 | 396 | -5.7 | -50.5 | -5.0 | – | – | – | – |
| 84 | 25.561 | 85.269 | YAP | Sabalpur | Patan | PT | 48 | 421 | -7.1 | -45.9 | 10.6 | 35.2 | -12.4 | 148.9 | 1.06 |
| 85 | 25.56 | 85.575 | YAP | Rasalpur | Mohanpur | SP | 21 | 316 | -8.0 | -52.9 | 10.7 | 30.7 | -10.5 | 86.9 | 1.30 |
| 86 | 25.559 | 85.626 | YAP | Jalalpur | Mohanpur | SP | 30 | 386 | -8.5 | -55.4 | 12.9 | – | – | – | – |
| 87 | 25.557 | 85.779 | YAP | Chamta Number | Bachwara | SP | 27 | 351 | -9.4 | -59.7 | 15.7 | 42.6 | -11.9 | 81.2 | 1.29 |
| **88** | **25.557** | **85.572** | **R. Ganges** | **Rasalpur Ghat** | **Mohanpur** | **SP** | **–** | **150** | **-8.4** | **-64.6** | **2.9** | **–** | **–** | **–** | **–** |
| **89** | **25.557** | **85.572** | **R. Ganges** | **Mohanpur** | **Mohanpur** | **SP** | **–** | **135** | **-11.6** | **-76.2** | **16.4** | **–** | **–** | **–** | **–** |
| 90 | 25.55 | 85.658 | YAP | Chapar | Mohiuddin Nagar | SP | 24 | 455 | -7.1 | -57.5 | -1.0 | – | – | – | – |
| 91 | 25.549 | 85.665 | YAP | Usri Chapar | Mohiuudin Nagar | SP | 21 | 423 | -8.5 | -56.0 | 12.3 | 35.3 | -11.3 | 82.4 | 1.44 |
| 92 | 25.539 | 85.642 | YAP | Beri Bisanpur | Mohiuddin Nagar | SP | 36 | 382 | -7.6 | -61.8 | -1.4 | – | – | – | – |
| 93 | 25.535 | 85.624 | YAP | Jaunapur | Mohiuddin Nagar | SP | 20 | 368 | -7.3 | -58.2 | -0.1 | – | – | – | – |
| 94 | 25.516 | 85.296 | YAP | Gadhochak | Fathuha | PT | 56 | 244 | -7.1 | -48.7 | 7.8 | – | – | – | – |
| **95** | **25.515** | **85.296** | **R. Punpun** | **Gadhochak** | **Fathuha** | **PT** | **–** | **310** | **-4.3** | **-33.5** | **1.1** | **–** | **–** | **–** | **–** |
| 96 | 25.493 | 85.778 | YAP | Lamuabad | Pandarak | PT | 36 | 247 | -7.4 | -49.4 | 9.5 | – | – | – | – |
| 97 | 25.491 | 85.284 | OAP | Sundar Supanchak | Fathuha | PT | 21 | 303 | -6.6 | -47.3 | 5.3 | – | – | – | – |
| 98 | 25.489 | 85.393 | YAP | Safipur | Khusrarpur | PT | 58 | 347 | -7.1 | -48.2 | 8.3 | 32.1 | -9.7 | 65 | 0.99 |
| 99 | 25.486 | 85.452 | OAP | Gyaspur | Bhaktiyarpur | PT | 36 | 431 | -7.3 | -48.8 | 9.3 | – | – | – | – |
| 100 | 25.472 | 85.383 | OAP | Hemjapur | Khusrarpur | PT | 30 | 297 | -7.3 | -53.4 | 4.7 | 32.9 | -7.8 | 54.1 | 1.08 |
| 101 | 25.465 | 85.696 | OAP | Barh | Barh | PT | 30 | 383 | -5.9 | -41.2 | 5.9 | – | – | – | – |
| 102 | 25.462 | 85.736 | OAP | Rana Vimaha | Barh | PT | 61 | 402 | -5.8 | -40.4 | 5.9 | – | – | – | – |
| 103 | 25.461 | 85.538 | OAP | Bhaktiyarpur | Bhaktiyarpur | PT | 36 | 425 | -7.1 | -46.3 | 10.2 | – | – | – | – |
| 104 | 25.459 | 85.612 | OAP | Athmal Gola | Athmal Gola | PT | 30 | 419 | -7.0 | -46.8 | 9.0 | 27.8 | -9.6 | 72.7 | 1.06 |
| 105 | 25.445 | 85.618 | OAP | Karjaan | Kalayanpur | PT | 30 | 334 | -6.4 | -42.9 | 8.1 | – | – | – | – |

PD=Piedmont; OAP=Older Alluvial Plain; YAP=Younger Alluvial Plain; MD=Madhubani; DB=Darbhanga; SP=Samastipur, VS=Vaishali; PT=Patna.Units; $HCO_3^-$=mg/L; DOC = dissolved organic carbon; TC=mmole; Ca=mg/L; DOC=mg/L; Depth (m) = Tubewell depth in meters

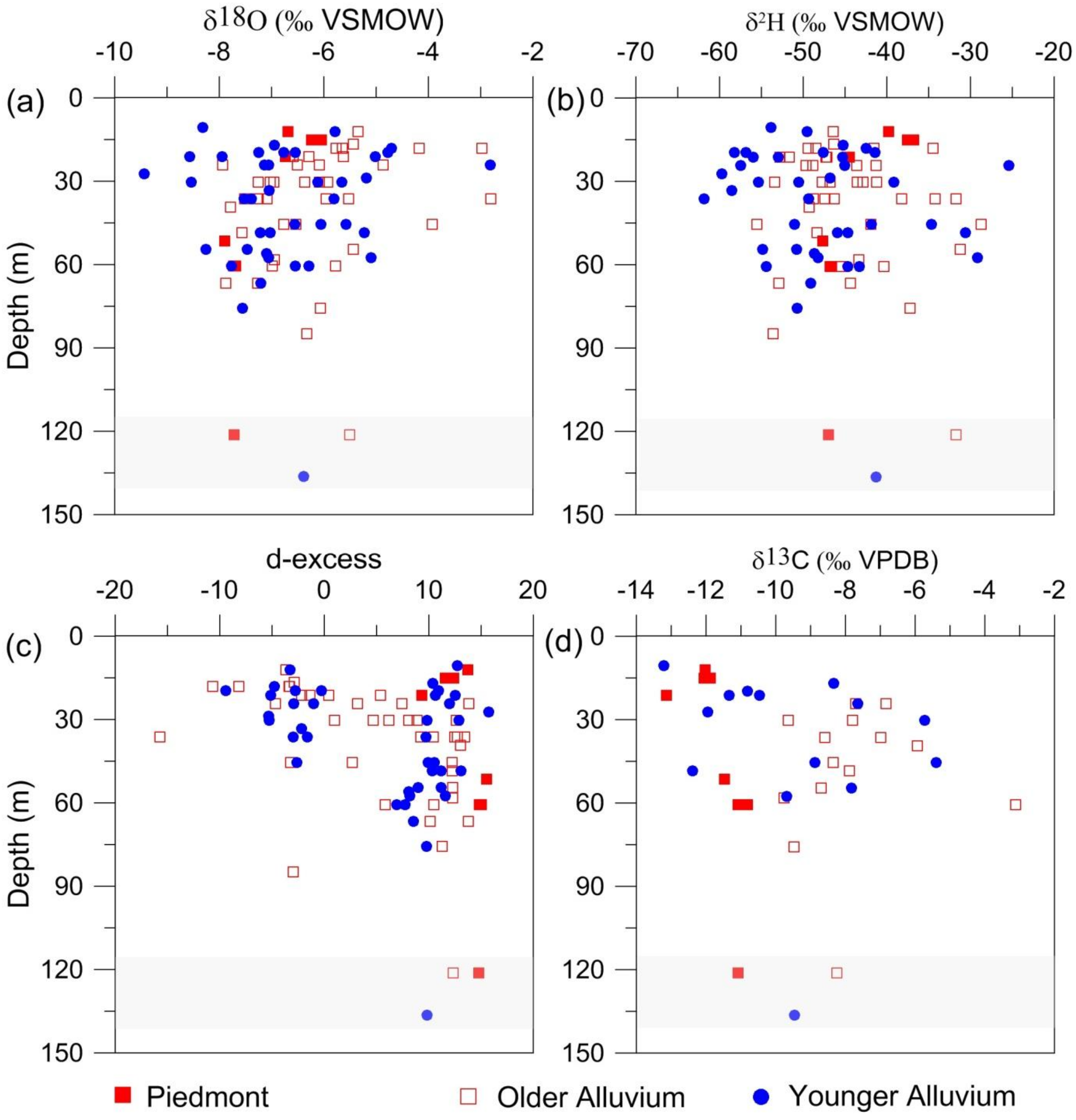

**Fig. 4.5.** Plots of depth versus (**a**) $\delta^{18}O$ (**b**) $\delta^{2}H$ (**c**) d-excess and (**d**) $\delta^{13}C$

### *4.3.3. Relationship among isotopic composition and other parameters*

Bivariate plots of the all isotopic composition with other parameters like DOC, $HCO_3^-$, Ca and TC (**Fig. 4.6 a–f**) were constructed to understand the importance of various processes controlling the origin and source identification of DOC. Some environments such as peaty lake and peat layer deposition like in the Younger Alluvium of Holocene age deposition (Saha and Sahu, 2015) of the Gangetic basin may contain DOC higher than the typical concentration in groundwater (1–2 mmole/L). In the environment $\delta^{13}C$ is present as 1 percent of the natural carbon. Variation in the abundance of the $\delta^{13}C$ reflects its physical history and helps in tracing the source and sink of the DOC

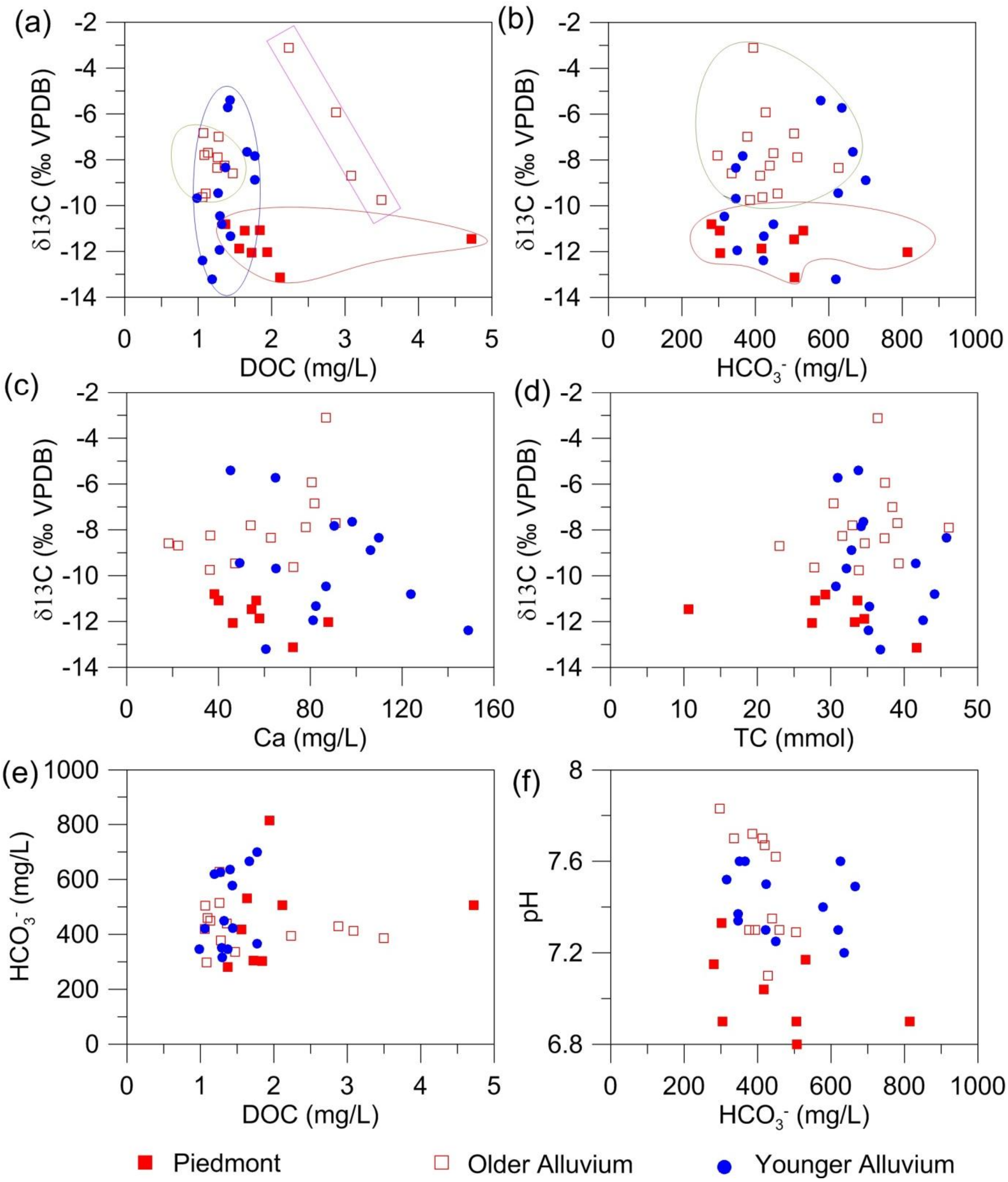

**Fig. 4.6.** Bivariate plots of (**a**) $\delta^{13}C$ vs. DOC (**b**) $\delta^{13}C$ vs. $HCO_3^-$ (**c**) $\delta^{13}C$ vs. Ca (**d**) $\delta^{13}C$ vs. TC (**e**) $HCO_3^-$ vs. DOC and (**f**) pH vs. $HCO_3^-$

(Vogel, 1959). In order to investigate the biogeochemical nature and origin of DOC, a bivariate plot of $\delta^{13}C$ and DOC was plotted (**Fig. 4.6a**).

Four distinct groups were formed with respect to the origin of DOC of the study area. Piedmont region showed the depleted $\delta^{13}C$ with moderate DOC except one location (sample #6) where the concentration was 4.72 mg/L, attributed to limited microbial activity or the presence of immobile refractory organic matter (OM) (Chapelle, 2001). Lighter $\delta^{13}C$ could have formed from oxidation of OM (Zheng et al., 2003) or might have come from dissolution of isotopically depleted Himalayan calcite in the sediments of this area (McArthur et al., 2004). It is assumed that soil zone $CO_2$ contains $\delta^{13}C$ in a range-23 to -25‰, respectively (Fontes and Garnier, 1979). While carbonate minerals in aquifers have values close to 0‰, indicating that the evolution of groundwater by carbonate dissolution should drive the $\delta^{13}C$ isotopic compositions towards more enriched compositions (Smedley et al., 2002). Samples from Older Alluvium formed two subsequent groups; one group shows moderate enrichment of $\delta^{13}C$ with lower DOC but another group shows the opposite trend between $\delta^{13}C$ and DOC (Samples #16, #22, #71 and #77), indicating active oxidation of OM in these places while in the remaining locations microbial activity is limited. In Younger Alluvium a wide spectrum of $\delta^{13}C$ was observed and is consistent with moderate DOC. In a few locations, which fall in the active floodplain of River Ganges (**Fig. 4.4d**), highly depleted $\delta^{13}C$ coupled with lower DOC is found indicating extensive microbial activity; it may promote the excess mobilization of As in this zone.

Two distinct groups were identified for the samples of Piedmont and Older Alluvium, while the Younger Alluvium showed discrete distribution (**Fig. 4.6 b**). $HCO_3^-$ shows positive trend with $\delta^{13}C$ for Younger Alluvium while negative trend for Older Alluvium indicating the involvement of the biogenic carbon dioxide in Younger Alluvium attributed to depleted C isotopes with increasing $HCO_3^{-.}$ The same reason is also given for the depletion of $\delta^{13}C$ in Piedmont. The probable factors for the enrichment of the $\delta^{13}C$ in Older Alluvium may include limited microbial activity lessened dissolution of depleted carbonates, and incomplete $CO_2$ reduction to form highly $\delta^{13}C$ depleted $CH_4^+$.

The aforesaid discussion was supported by the trend of the $\delta^{13}C$ with Ca which shows a positive trend in Older Alluvium and a negative trend in Younger Alluvium and Piedmont. The concentration of Ca increases with the enrichment of $\delta^{13}C$ and vice-versa supporting the fact that carbonate dissolution is the main source of the DOC rather than the anthropogenic influence. In Younger Alluvium $HCO_3^-$ showed a decreasing trend with DOC while in Piedmont and Older Alluvium, it does not exhibit any trend. This reflects the significant contribution of DOC is by $HCO_3^-$ dissolution in Younger Alluvium. It was postulated that pH decreases with increasing $HCO_3^-$ in older Alluvium ($r^2 = 0.31$) reflecting the reaction of incomplete $CO_2$ reduction to form highly 13C-depleted $CH_4$, thereby progressively enriching the residual $CO_2$ (Harvey et al., 2002; Mukherjee et al., 2008).

The isotopic record of $\delta^{18}O$ does not correlate with ORP in Older and Younger Alluvium while there is a positive correlation in Piedmont ($r^2$=0.52) (**Fig. 4.7a**) indicating that fresh and oxidised water is recharging the aquifers from monsoonal rainfall. Whereas, Older and Younger aquifers are recharging with mixed water to form a regional flow path along with monsoonal recharge. Reduced aquifers are enriched with $\delta^{13}$C in Piedmont ($r^2$=0.51) and Younger Alluvium ($r^2$=0.40) (**Fig. 4.7b**)

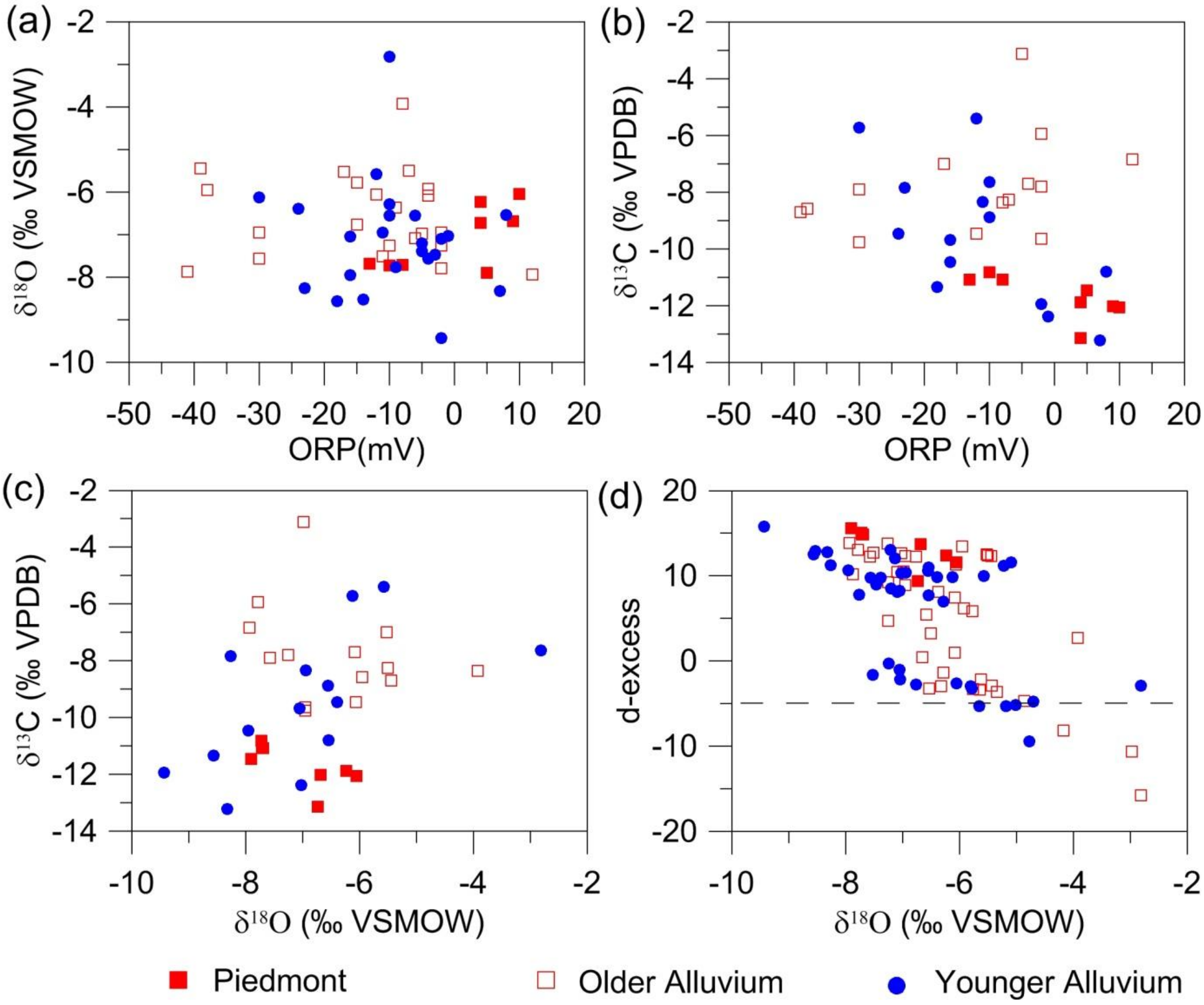

**Fig. 4.7.** Bivariate plots of (**a**) $\delta^{18}$O vs. ORP (**b**) $\delta^{13}$C vs. ORP (**c**) $\delta^{13}$C vs. δ18O (**d**) d-excess vs. $\delta^{18}$O. Samples falling below dashed line shows evaporation effect dashed line shows the high evaporation effect in (**d**)

indicating microbial degradation at a mesophilic temperature in these areas (Hornibrook et al., 2000). Younger Alluvium formed a cluster with depleted isotopic composition of both $\delta^{18}$O and $\delta^{13}$C (**Fig. 4.7c**) indicating two processes (1) aquifer recharge from the rainfall prior to evaporation and (2) water sediment (kankar) interaction in the soil which is forming relatively lighter $\delta^{13}$C. This relationship was discrete for Younger and Older Alluvium. The d-excess of all pond water samples and two small tributaries (Balan and Bya) (samples #64, #65 and #76) of river Ganges showed d-excess values <5 indicating isotopic enrichment due to higher evaporation (**Fig. 4.7d**).

## 4.4. Conclusions

This study revealed the circumneutral pH in Piedmont region along with higher $HCO_3^-$, while slightly alkaline pH with lower $HCO_3^-$ was observed in Older and Younger Alluvium. $HCO_3^-$ and $Ca^{2+}$concentration observed in groundwater of CGB were almost double to the river water indicates that groundwater has undergone through high geochemical evolution. Stable isotopes ($\delta^2H$ and $\delta^{18}O$) compositions revealed that groundwater of Piedmont had been recharged by meteoric origin water before it has undergone evaporation. Aquifers of Older and Younger Alluvium had been recharged from meteoric origin water which has undergone some evaporation. River water also had a limited contribution to recharging the adjacent aquifers while ponds are not recharging aquifers in this area. Deeper aquifer of Piedmont has much less connectivity with the upper shallow aquifers. The hydraulic connectivity of the shallow aquifers of aquitard formation (25–60 m bgl) with the main upper aquifer (~120 m bgl) was higher in Older and Younger Alluvium. Depleted $\delta^{13}C$ and low DOC indicated that active floodplains of the river Ganges are accelerating the higher microbial activity. The deeper aquifers (~ 120 m bgl) of Younger Alluvium and aquifers of Older Alluvium zones were enriched with lighter isotope and DOC due to limited microbial activity.

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# Chapter 5

# Abundance and distribution of As inorganic species in groundwater, aquifer sediment and agricultural soils

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*After*

Concentrations of inorganic arsenic in groundwater, agricultural soils and subsurface sediments from the middle Gangetic plain of Bihar, India

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**Research highlights**

- As(III) observed as major species in groundwater while As(V) in soils and sediments

- Higher As concentrations in fine and dark grey clay in subsurface sediments

- Alteration of oxyhydroxide and transformation in goethite in aquifers

- Presence of As(III) and As(V) associated with siderite in aquifer sediment

## Abstract

Concentrations of inorganic forms, arsenite, As(III) and arsenate, As(V) of arsenic (As) present in groundwater, agricultural soils and subsurface sediment located in the CGB of Bihar, India were determined. Approximately 73% of the groundwater samples (n=19) shows As(III) as the dominant species, while 27% reveals As(V) is the dominant species. The concentration of As(III) in agricultural soil samples varies from not detectable to 40 µg/kg and As(V) was observed as the major species (ranging from 1050 to 6835 µg/kg), while the total As concentration varied from 3528 to 14690 µg/kg. The subsurface sediment of Older Alluvium contains a low range As(III) from (nd–264.2 µg/kg) whilst in Younger Alluvium it was a bit higher (nd–368.5 µg/kg) indicating comparatively more reducing conditions of the aquifer. Total extracted concentration of As was higher in the subsurface soil (range 9119–20056 µg/kg in Methrapur and 4788–19681 µg/kg in Harail Chapar) than the agricultural soil, indicating the subsurface sediment as a source of As. Results of XRD and ESEM revealed the presence of hematite and goethite throughout the vertical section below while magnetite was observed only in the upper oxidized layer at Methrapur and Harail Chapar. Alteration of Fe-oxides and presence of fibrous goethite indicating the presence of diagenetic sediment. Siderite playing a role as sinks to the As in subsurface sediments. The study also concluded that microbially mediated decomposition of organic matter present in dark and grey sections promote the redox conditions and trigger mobilization of As into groundwater.

## Keywords

Inorganic arsenic, Agricultural soil, Subsurface sediments, Extractable arsenic, Central Gangetic Basin

## 5.1. Introduction

For the past few decades, arsenic (As) contamination of groundwater and soil has become an important environmental problem globally. Many As compounds exist in the environment and biological systems as well. Naturally occurring As contamination of groundwater has been reported in groundwater, in more than 105 countries of all continents except Greenland and Antarctica (Barringer and Reilly, 2013; Naujokas et al., 2013). The major natural source of As entering the soil is weathering of rocks containing As, while the anthropogenic sources include, combustion of coal, activities like smelting of base metal ores, application of As-based pesticides, chromated copper arsenate (CCA) for wood preservation and mining activities (Smedley and Kinniburgh, 2002). Since these activities, and very low depletion are mainly characterized by plant uptake, methylation, leaching or erosion, As may accumulate rapidly in the soil environment and also act as a sink in As-contaminated belts of alluvial plains (Sanyal and Nasar, 2002). Another reason may be the tendency of As to mobilize in the environment strongly, a phenomenon influenced by its association with the solid phase in sediments and soils (Pandey et al., 2004). Association of an elevated As in agricultural soils and the tubewell water used for irrigation for a long time have been confirmed by various studies from Bangladesh (Meharg and Rahman, 2003; Ahsan et al., 2009; Karim et al., 2008; Brammer and Ravenscroft, 2009), Nepal (Dahal et al., 2008), West Bengal (Roychowdhury et al., 2005) and central Gangetic Basin (CGB) (Srivastava and Sharma, 2013).

Higher As concentration (46,000 µg/kg dry wt.) was reported in agricultural soil in most affected zone compared to a low level of As (<10,000 µg/kg) in As safe groundwater zone (Meharg and Rahman, 2003). The level of As uptake and accumulation in crops is strongly influenced by the concentrations of As in soils and irrigated water (Smith et al., 2006). Few studies reported the input of As from irrigation to agricultural fields in Bengal delta. A study reported that 6.4 tonnes of As were falling on the soil as a result of using water from 3200 contaminated tube-wells for agricultural irrigation in 201 km$^2$ area of Deganga block, North 24 Parganas, West Bengal (Chowdhury et al., 1999). Another study reported that total As withdrawn by the four shallow tubewells, used for agricultural irrigation in As-affected areas of Murshidabad district was 6.8 kg per year (Roychowdhury et al., 2005). Continuous irrigation with As-contaminated groundwater may lead to a build-up of this toxic element in soils, which in turn may trigger its entry into the food chain in harmful concentrations. This process further depends on soil type and plant species.

Arsenic added by irrigation water is adsorbed to ferric oxyhydroxides in the topsoil (Roberts et al., 2007), where it gradually accumulates over time (Meharg and Rahman, 2003; Roychowdhury et al., 2005). This accumulation is more prevalent in soils used for paddy cultivation where the top soil is puddle to hold water on the surface (Brammer and Ravenscroft, 2009). Winkel et al. (2008) observed that medium-textured soils rich in organic matter presumably evolved from rapid accumulation of

Holocene sediments are key indicator of As risk areas. The soil properties particularly in seasonally flooded and irrigated area get influenced throughout the year which alternates between anaerobic and aerated conditions, hence controls the As adsorption and desorption (Brammer and Ravenscroft, 2009). Studies show that virtually As added by irrigation remain in upper 10–15 cm of the soils. Some potential sources of the loss of As from the agricultural field include volatilization of reduced As in the form of arsines (Meharg and Rahman, 2003), leaching to deeper layers and uptake by plants (Brammer and Ravenscroft, 2009). The availability of As in soils within the paddy field may also affect by diurnal and seasonal variation in microbiological activities (Brammer and Ravenscroft, 2009). More studies are needed to understand the factors which influence the gain and loss of As in soils under different environmental conditions.

In India, As contamination in groundwater was reported as early as 1976 in the states of Haryana, Punjab, Himachal Pradesh, Uttar Pradesh and some parts of northern India (Datta and Kaul, 1976; Srivastava and Sharma, 2013). The first case of groundwater As contamination in the lower Gangetic Basin of West Bengal was reported in 1984 (Garai et al., 1984) and in 1992 a high level of As contamination in groundwater was documented in Bangladesh (Ahamed et al., 2006a). Arsenic contamination of groundwater in the CGB was reported in 2002 (Chakraborti et al., 2003). Since then, several studies confirmed a very high level of As and have been evaluated the situation of groundwater in the CGB (Chakraborti et al., 2003; Chauhan et al., 2009; Kumar et al., 2016). Arsenic from geological origin could be the explanation for the elevated concentrations (Acharyya and Shah, 2007; Sanz et al., 2007). Although few earlier studies postulated the oxidation of As-enrich pyrite for As liberation in south Asia (Das et al., 1996; Mallick and Rajagopal, 1996), recent studies from the area have hypothesized the reductive dissolution is by far the most important chemical association for As mobilization. It takes place where As adsorbed to iron oxyhydroxides in sediment is get free to dissolved into groundwater when microbial degradation of organic matter (e.g. in buried peat beds) reduces Fe(III) to Fe(II) (Bhattacharya et al., 1997; Nickson et al., 2000; McArthur et al., 2001). Arsenic contaminated aquifers are mainly present in younger alluvial deposition (Holocene) aquifers, contrary to the aquifers of older deposition (Pliocene-Pleistocene) to a large extent, free of As (Smedley and Kinniburgh, 2002; Winkel et al., 2008). A study postulated that a series of redox processes, particularly reduction of Fe-oxyhydroxide and subsequent oxidation, could be key controls of As concentration in some groundwater of Ganga-Brahmaputra delta regions of Bangladesh and described that As can be enriched in reducing groundwater with elevated Fe concentrations, as well as in groundwater with only small amounts of Fe (Zheng et al., 2004).

Arsenic-rich groundwater has been used for irrigation in the CGB for more than two decades, so the agricultural soils in this plain may be at high risk of As contamination. A link between As levels in soils and groundwater has been observed in the Punjab of northwestern India (Singh et al., 2010).

Arsenic concentrations in soils ranging from 9000–390,000 µg/kg, and in sediment in the 19,000–489,000 µg/kg range, in Chhattisgarh of central India and 1090–2480 µg/kg in soils in Punjab of northwestern India have been reported (Singh et al., 2010). Elevated concentrations of As in agricultural soils were found in Ballia and Ghazipur, Uttar Pradesh of India, ranging from 5400 to 15430 µg/kg (Srivastava and Sharma, 2013).

It is noteworthy that mobility, (phyto)toxicity, potential risk, retention and bioavailability of As in the environment depend on the form in which As enters and the final form in which it is present (Sanz et al., 2007). In well drained and oxygenated soils, As(V) is present as a dominant species. The areas where reducing conditions are observed, include regularly flooded soils or organic matter rich areas. Under these conditions As(+III), elemental As and arsine(-III) are also present (Van Herreweghe et al., 2003). In the case of As, the inorganic forms are more toxic. Arsenite, As(III), however, is 10 times more soluble and mobile (weakly adsorbed) and are more toxic than As(V) (Mandal and Suzuki, 2002; van-Herreweghe et al., 2003; Charlet et al., 2007). Hence, determining the total As concentration alone is insufficient for many environmental exposure scenarios. Nonetheless, As speciation analysis is a powerful tool that can generate accurate assessments of environmental impact and risk to human health (Vassileva et al., 2001; Sanz et al., 2007; Rahman et al., 2009; Abdulrahman et al., 2012), since: firstly, the toxicity and bio-availability of As compounds depend on the chemical form present (Gong et al., 2002); and secondly, recycling of As occurs in different environmental scenarios such as lakes (Zheng et al., 2003). The forms of As present in soils depend on the type and amounts of sorbing components also in the soil, the level of pH and redox potential (Mandal and Suzuki, 2002).

Mineralogy plays an important role in the mobilization of As in different environmental conditions. Arsenic is more to be co-precipitated with or scavenged by Fe(III) and Mn(IV) in the sedimentary environment (Acharyya et al., 1999). Oxidizing conditions of the aquifers favour to immobile particularly the As which is bound to Fe and Mn oxides (Smedley and Kinniburgh, 2002). Studies show that As(III) can be strongly adsorbed on surfaces of Fe-oxyhydroxide (minerals like goethite and ferrihydrite) or Mn (birmesite) (Lin and Puls, 2000). The adsorption of As(V) magnetite, goethite, hematite reduced when pH was raised (Giménez et al., 2007). Dixit and Hering (2003) observed that the intrinsic surface compensation constants for As(V) and As(III) are higher for goethite than for amorphous iron oxide (HFO). It indicated that transformation of HFO to goethite or magnetite would not decrease the affinity of the solid phase for As(V) and As(III). The transformation of amorphous iron oxide to more crystalline phases was suggested to increase the As mobility. The presence of the framboidal pyrite in the Ganges must be diagenetic which explains the lack of sulphate in groundwater (Chowdhury et al., 1999; Nickson et al., 2000). Studies have proven siderite as a sink for As in sediments (Anawar et al., 2006; Mumford et al., 2012) and its higher As(V) adsorbing and weakly As(III) adsorbing character at a pH value below 7 (Mumford et al., 2012). Some studies also revealed that sorption of As(III) onto oxyhydroxides and goethite will be higher in pH range 7-8 (Kneebone et al., 2002; Dixit and Hering, 2003).

In lower Gangetic Basin, few recent studies have been attempted to correlate aquifer sediment colour with the occurrence of As in groundwater (Biswas et al., 2012; Bundschuh et al., 2010; von Brömssen et al., 2007; von Brömssen et al., 2008). These studies reported that grey sand aquifers are contaminated with dissolved As (>10 µg/L) whereas brown sediment aquifers may be safe (Biswas et al., 2012). Based on colour perception of the local drillers, the four colour (black, white, off-white and red) hypothesis was proposed by (Von Brömssen et al., 2007). According to this colour code, the highest risk lies with black colour sediment and gradually reduces towards red (Hossain et al., 2014).

The presence of As in the CGB is now well documented by various studies that have examined water, agricultural soil and subsurface sediments (Kumar et al., 2012; Saha and Shukla, 2013; Srivastava and Sharma, 2013; Kumar et al., 2016). All such studies focused on total As estimation except for a few that mainly focused on speciation of As in groundwater only (Chandrasekharam et al., 2007; Chauhan et al., 2009). Chandrasekharam et al. (2007) observed a median As concentration (44 µg/L) in groundwater of Ballia, Uttar Pradesh, in which the median concentration of As(III) and As(V) were observed as 10 and 32 µg/L respectively. Another study from Ballia, observed median As 27 µg/L in which As(III) and As(V) were 16 and 19 µg/L, respectively (Chauhan et al., 2009). In both studies, the concentration of As(III) was found to be equal/ higher than the As(V) in most of the samples. The co-existence of As(V) with As(III) under prevailing reducing conditions may be due to slow reduction kinetics of As(V) which was released during reductive dissolution of iron oxyhydroxides (Stollenwerk et al., 2007; Chauhan et al., 2009). These studies indicated under Eh-pH conditions of this area As(V) exist as negatively charged oxyanions $H_2AsO_4^-$ or $HAsO_4^{2-}$ and As(III) present as $As(OH)_3$. Very little attention has been directed to speciation studies on As in the environmental samples in the CGB, so it is crucial to fill this gap in our knowledge. The objective of this study was to investigate the level of As and characterize the inorganic As species present in water, agricultural soils and subsurface sediments using ion chromatography (IC) coupled to an inductively coupled plasma mass spectrometer (ICP-MS). An attempt also has been made to understand the role of mineralogy in As mobilization in aquifers, and finally to check the applicability of the four colour code for sand in the CGB of India.

## 5.2. Material and methods

### *5.2.1. Study area*

The study area covers three blocks/ precincts (Dal Singh Sarai, Mohiuddin Nagar and Mohanpur) of Samastipur district which is located in Northern Bihar, India (**Fig. 5.1**). The area is known for unevenly distributed high concentrations of As in the state's groundwater supplies (Saha and Shukla, 2013). The geography and geomorphology of the study area have been documented previously (Ahamed et al., 2006; Acharyya and Shah, 2007; Saha and Shukla, 2013). The geographic surfaces identified in the regional mapping of the Quaternary deposits of the Ganges Basin consist of an active flood plain ($T_0$), river valley terrace surface ($T_1$) and upland interfluves surface ($T_2$). A significant feature of these surfaces is that all of them are depositional surfaces, having a succession of overlying sediments of Holocene over Pleistocene. The Ganges plain foreland Basin is a repository of sediments originating from the Himalayas and Peninsular Craton (Ahamed et al., 2006; Acharyya and Shah, 2007). Aquifers of Holocene sandy sediments are unconfined or semi-confined in the CGB which are mainly used for water extraction. Most of the tubewells extend to shallow aquifers <50 meters below ground level (mbgl). A two-tier aquifer system (shallow aquifers at a depth of 120–140mbgl and deeper aquifers at 225–240 mbgl) made up of Quaternary sand layers has been identified within 300 m below ground using the drill cut method (Saha and Shukla, 2013).

### *5.2.2. Sample collection and processing*

#### *5.2.2.1. Groundwater*

Groundwater samples ($n$=19) were collected from two blocks (Mohiuddin Nagar and Mohanpur) in Samastipur district, Bihar, during June 2015 in order to determine the ratio of arsenite, As(III) and arsenate, As(V) in the CGB of Bihar. Each sample's location was recorded using a portable global positioning system (GPS) (Garmin etrex30) device. Redox sensitive parameters like pH and ORP were analyzed *in situ* by the HANNA (HI 9828) multi-parameter. Water samples were passed through a disposable cartridge (Metal Soft Center, PA, USA) which absorbs As(V) and allows As(III) to pass through. Filtered samples were then stored below 4 $^0$C in a portable ice-box to minimize chemical alteration. Another sample of water (50 ml) was also collected for total As estimation, and this, in turn, was followed by adding 2–3 drops of 7M nitric acid ($HNO_3$).

#### *5.2.2.2. Agricultural soils*

Agricultural soil samples (0–15 cm depth) were collected from 11 different locations in the same area. In this area 2–3 crops are grown in different seasons annually such as rice, wheat and corn, etc. Shallow pumps are usually employed to withdraw water for irrigation in this area, which has become contaminated with geogenic As. We were unable to collect irrigation water due to the unavailability of functioning pumps that helped to operate the tubewell. Agricultural soil samples were collected in

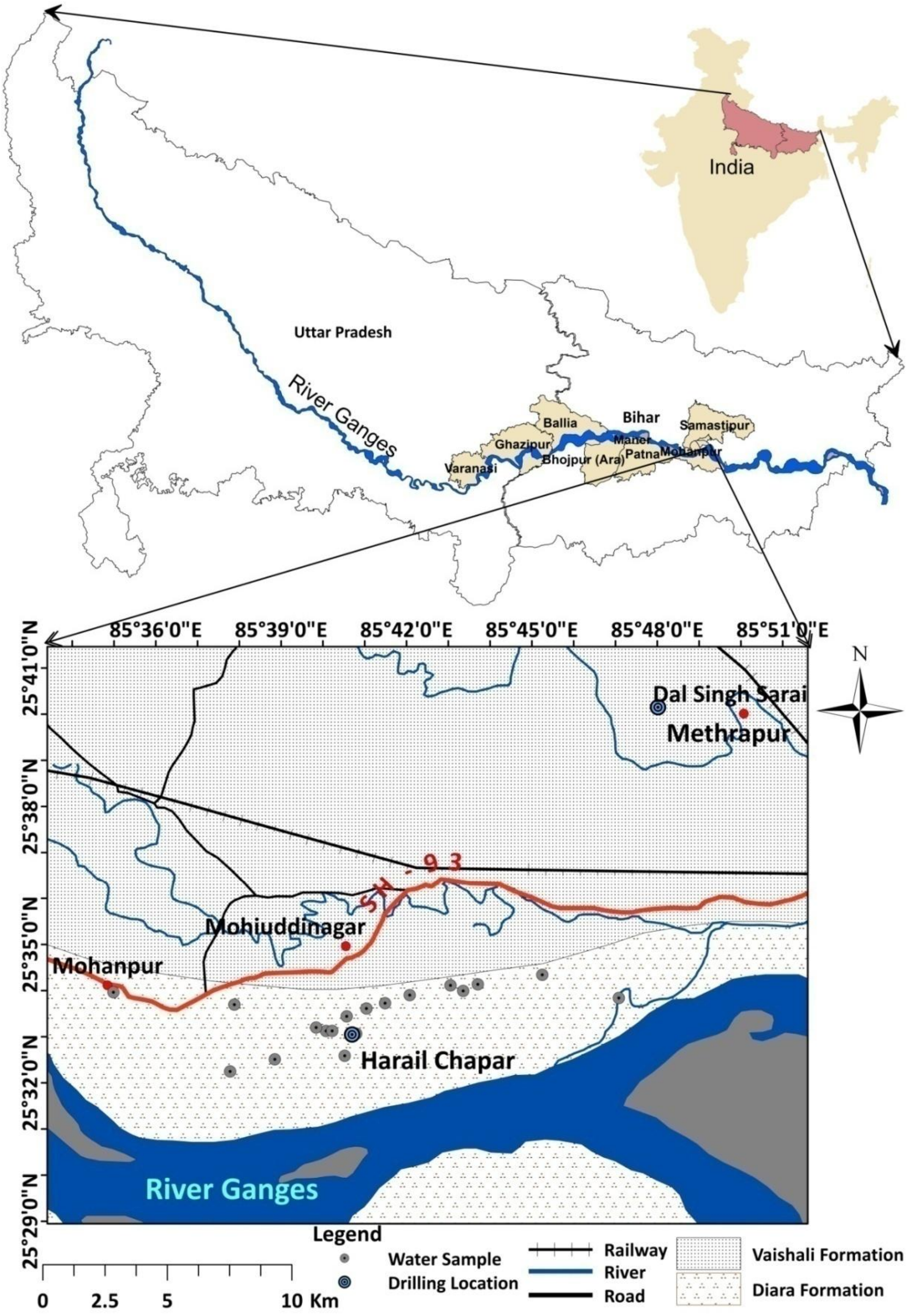


**Fig. 5.1.** Study area map (a) India, (b) Uttar Pradesh and Bihar (c) water sample and drilling locations

double zip lock plastic bags and stored in an ice box. Samples were then completely dried at 50 ºC in an oven, ground and passed through <2 mm stainless steel sieves to remove the plant litter.

### *5.2.2.3. Subsurface sediment (core) collection*

Two sites, specifically a new alluvium region (also known as the Diara formation) and older alluvium deposition (also known as the Vaishali formation) (Saha and Shukla, 2013) were selected to collect the subsurface sediments. The water table in this area varies from 3.0 to 7.0 m bgl, with mid and pre-monsoon season fluctuation in 2.0–4.5 m (Saha and Sahu, 2016). The hydrograph of this area revealed shallowest water table in August and deepest in May (Saha and Shukla, 2013). Since the samples were collected during pre-monsoon hence the water table assumed to be as 6.5 m bgl for this study. Core samples were collected utilizing the hand-flapper drilling method up to a depth of 46.2 and 33.5 m at Methrapur and Haral Chapar, respectively. Samples were collected at depths of 1.5, 4.5, 9.1, 21.3, 36.6 and 42.6 mbgl at Methrapur of Dal Singh Sarai block, while depths of 1.5, 9.1, 18.3, 24.4 and 33.5 m bgl were employed at Harail Chapar of Mohiuddin Nagar block. Samples were chosen on the basis of the sediment having different colours and grain size. Samples were stored in black plastic bags and kept in the ice box and transported to the laboratory. After transportation from the study area to the laboratory, the sediment was freeze dried. Finally, it was ground into a powdered form with an agate, and mortar and stored for further processing.

### *5.2.3. Chemicals and reagents*

All chemicals were of analytical grade and used without any further purification. Any solution and reagents were prepared with Milli-Q water (ELGA Lab Pure) having a resistivity of 18.2 MΩ/cm. To calibrate the instrument, stock solutions were prepared as follows: arsenite ($NaAsO_2$, Sigma-Aldrich), arsenate ($Na_2HAsO_4.7H_2O$, Sigma-Aldrich), monomethylearsonate (MMA; $CH_3AsNa_2O_3$, Sigma) and dimethylearsenite (DMA); $(CH_3)_2AsO(OH)$, Sigma) were dissolved in Milli-Q water. All the standards were kept in a state of darkness at 4 °C until required for use. Standards were prepared freshly from their respective stock solution on the same day of the analysis. Ortho-phosphoric acid (APS Chemicals, 85% purity) was used for microwave extraction of soils and sediment samples. There is no commercially available standard reference material for individual As species in soil and sediment. Consequently, we used NIST SRM 2711 (Montana soil) for total As concentration to validate our analytical data. The analytical result of As in SRM soil showed that experimental value (105 ± 8 µg/g) was similar to the certified value (105±10 µg/g).

### *5.2.4. Digestion procedure for the total elemental extraction*

A microwave digester (CEM, MARS 6) consisting of 42 digester vessels was employed to digest all soil and sediment samples. Ground soil and sediment sample (approximately 0.5 g of each) was weighed directly into a Teflon vessel, and 5mL aqua regia was added to it. Samples were allowed to predigest by standing open for 30 min before sealing the vessels. Each vessel was sealed and placed into the rotor. The microwave conditions were followed as given in (Kumar et al., 2016). After digestion and cooling, each digestion solution was transferred to a 50-mL plastic centrifuge tube and diluted to 20 mL using Milli-Q water. Samples were filtered through syringe filters (PTFE 0.45 µm). The samples were analyzed on the same day of preparation or otherwise stored in a fridge at 4 °C.

### 5.2.5. *Extraction procedure of soil and sediment samples*

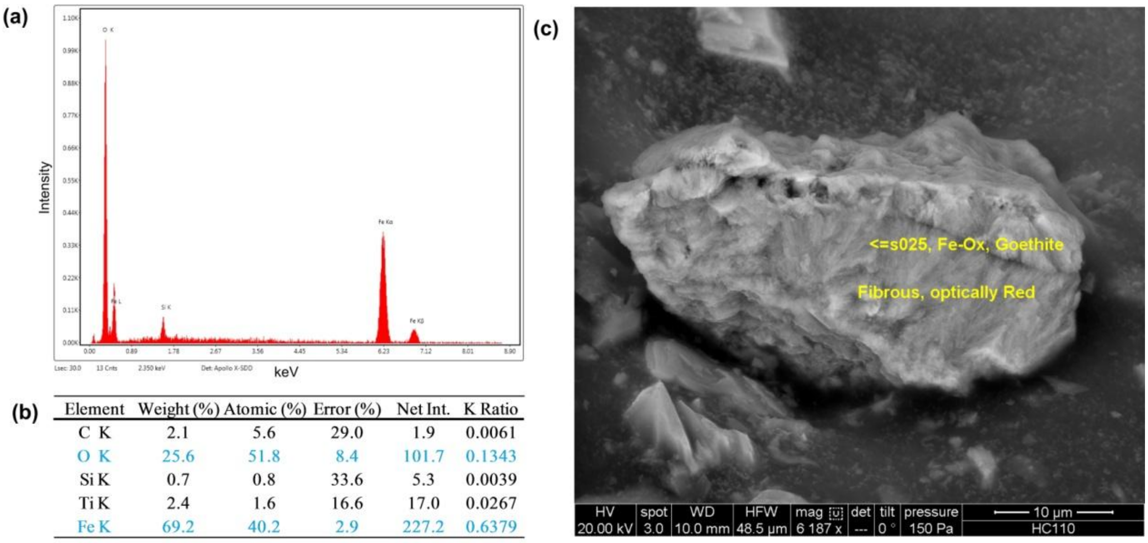
Microwave-assisted extraction technique along with 1M Ortho-phosphoric acid was used to extract the As species from agricultural soil and subsurface sediment samples as per the procedure noted in (Rahman et al., 2009).

### *5.2.6. Analysis*

All samples were examined utilizing the inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies, Japan 7500ce) for As. For As speciation, ion chromatography (IC) coupled with ICP-MS was used. The details concerning the ICP-MS and IC instruments and operating conditions of analysis have been described previously (Rahman et al., 2009). The concentration of As in water was calculated on the solute basis, and for soil it was calculated on dry weight basis. Grain size distribution was done with the help of Laser Diffraction Particle Size Analyzer (Microtrac, S3500 coupled with Microtrac SDC unit).

### *5.2.7. Scanning electron microscopy (SEM) and X-Ray diffraction (XRD analysis)*

Mineralogical investigations were done with the help of XRD-6000, Shimadzu diffractometer (Shimadzu Corporation, Japan) analysis and environmental scanning electron microscopes (ESEM) (FEI Quanta 450 FEG) fitted with an EDAX Apollo X SDD EDX detector depicted in **Fig. 5.2**



| Element | Weight (%) | Atomic (%) | Error (%) | Net Int. | K Ratio |
|---|---|---|---|---|---|
| C K | 2.1 | 5.6 | 29.0 | 1.9 | 0.0061 |
| O K | 25.6 | 51.8 | 8.4 | 101.7 | 0.1343 |
| Si K | 0.7 | 0.8 | 33.6 | 5.3 | 0.0039 |
| Ti K | 2.4 | 1.6 | 16.6 | 17.0 | 0.0267 |
| Fe K | 69.2 | 40.2 | 2.9 | 227.2 | 0.6379 |

**Fig. 5.2.** Tool used for identification of SEM images (a) intensity vs. keV plot (b) table of elements indentified (c) SEM image of FeOx.

## 5.3. Result and discussion

### *5.3.1. Total and inorganic As in groundwater*

Results of As speciation along with their respective pH and pe values in groundwater are shown in **Table 5.1**. The pH of the groundwater varies from 7.1–7.8 (mean value 7.5) and pe values indicated anoxic/ reducing conditions (mean pe values -2.1) in this area. The concentration of As in this study ranged from 1.3 to 104.7 µg/L (**Table 5.1**). Average As concentrations (20 µg/L) are twice of the limit (10 µg/L) of As set by WHO for drinking water**.** In this study, the concentration of As was lower than those in other studies of groundwater in the CGB. The mean As concentration in Ballia has been reported as 137 µg/L (Chandra et al., 2011) and 331 µg/L (Srivastava and Sharma, 2013). A higher level of As concentration in Bhojpur, Bihar has been reported with mean values of 84 and 123 µg/L respectively by Saha et al. (2009) and Saha et al. (2011), respectively.

However, the values were larger than the Varanasi, Uttar Pradesh where the mean concentration of As was 11 µg/L. Approximately 73% (14 out of 19) of the samples shows As(III) as the dominant species, while 27% (5 out of 19) reveals As(V) was the dominant species (**Table 5.1**). These results have been supported by the pe-pH diagram plotted for As species existing in this area (**Fig. 5.3**). It clearly demonstrates that more than 73% of the samples fall under the $As(OH)_3$ section while the remaining percentage falls under $HAsO_4^{--}$. This outcome is expected for groundwaters where reducing conditions occur in the aquifers. Spatial distribution of the As in groundwater of Mohiuddin Nagar and Mohanpur has been discussed earlier (Kumar et al., 2016). Arsenic concentrations in groundwater usually vary from region to region based on regional geology (Rahman et al., 2015). Other studies have also found As(III) is the primary As species present in groundwater in the CGB (Kumar et al., 2010a; Kumar et al., 2010b), West Bengal and Bangladesh (Kim et al., 2003). The As in groundwater generally found to be present in the inorganic form (Chen et al., 2006; Elci et al., 2008; Hughes et al., 2011). Arsenite was observed in higher concentration (39 µg/L) in groundwater from Ghazipur, Uttar Pradesh (Kumar et al., 2010a), and Bhagalpur (34 µg/L), Bihar (Kumar et al., 2010b), which is similar to this study, whilst As(V) was detected in larger quantities (33 µg/L) in groundwater from Ballia, Uttar Pradesh (Chandrasekharam et al., 2007; Chauhan et al., 2009) (**Fig. 5.4**). The reason may be the difference in regional geology (including mineralogy) and unevenness of the covered thick sediments with varying content of organic matter and organic carbon (Chandrasekharam et al., 2007).

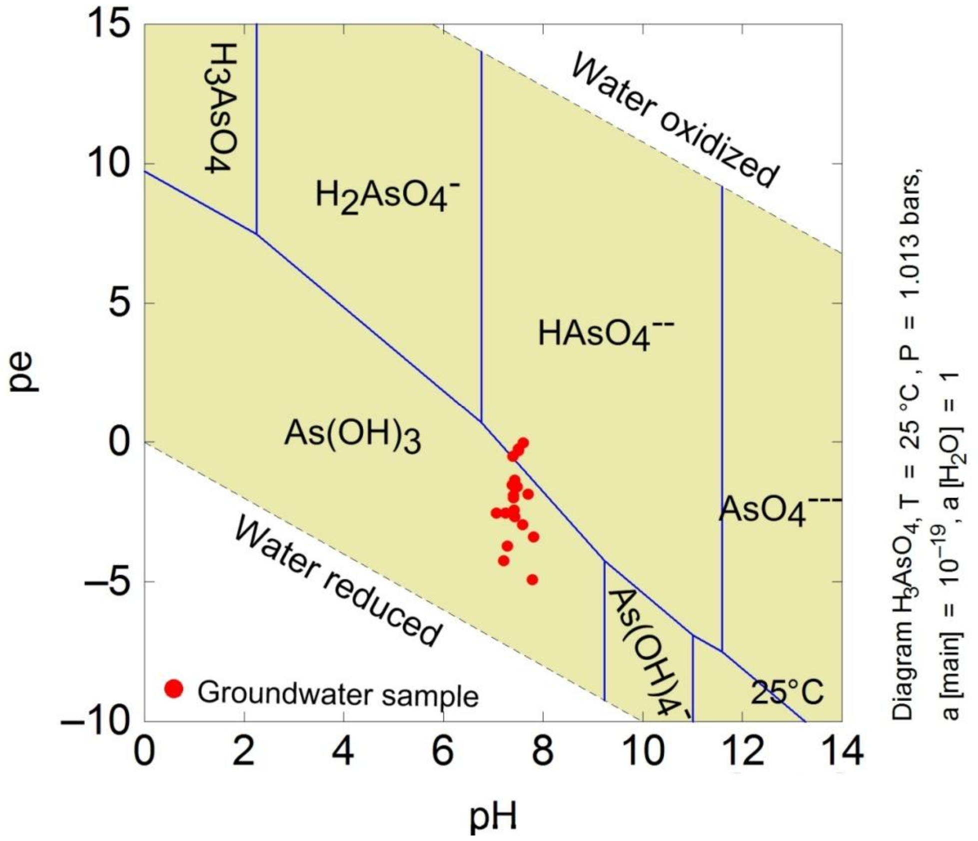


**Fig. 5.3.** pe-pH diagram for As species existing in the study area

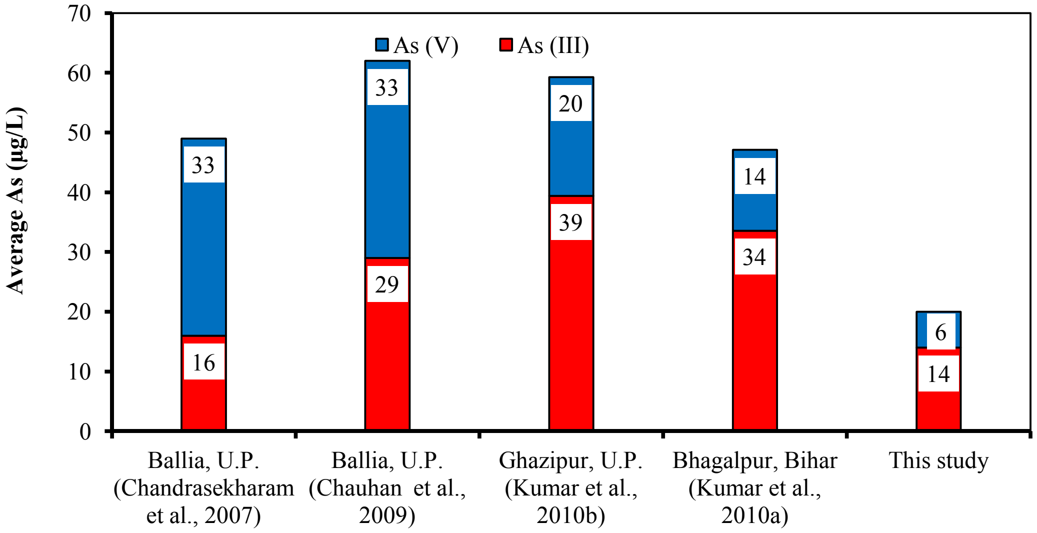


**Fig. 5.4.** Comparison of mean concentration of inorganic As species (values in μg/L inserted **a**t the top of the bars) in groundwater from the CGB of Uttar Pradesh and Bihar of India

**Table 5.1**
Groundwater sample location with pe, pH and inorganic arsenic (results expressed in µg/L and are based on peak area calculation)

| S. No. | Latitude | Longitude | Depth (m) | pH | pe | As(III) (µg/L) | As(III) (%) | As(V) (µg/L) | As(V) (%) | As(t) (µg/L) | As(III)/As(V) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 25.547 | 85.673 | 30.5 | 7.4 | -2.4 | 17 | 57.8 | 12.4 | 42.2 | 29.4 | 1.4 |
| 2 | 25.549 | 85.662 | 24.4 | 7.8 | -4.9 | 78 | 95.8 | 3.4 | 4.2 | 81.4 | 23 |
| 3 | 25.539 | 85.669 | 15.2 | 7.2 | -2.5 | 15.8 | 44.9 | 19.4 | 55.1 | 35.1 | 0.8 |
| 4 | 25.554 | 85.671 | 21.3 | 7.6 | -3 | 5.1 | 84.6 | 0.9 | 15.4 | 60 | 5.5 |
| 5 | 25.556 | 85.679 | 18.3 | 7.7 | -1.9 | 11.6 | 91.8 | 1 | 8.2 | 12.6 | 11.2 |
| 6 | 25.558 | 85.686 | 30.5 | 7.5 | -1.6 | 1.1 | 76.7 | 0.3 | 23.3 | 1.5 | 3.3 |
| 7 | 25.56 | 85.696 | 27.4 | 7.4 | -1.4 | 2.3 | 88.1 | 0.3 | 11.9 | 2.6 | 7.4 |
| 8 | 25.561 | 85.718 | 54.9 | 7.4 | -1.5 | 0.5 | 8.1 | 5.1 | 91.9 | 5.6 | 0.1 |
| 9 | 25.563 | 85.723 | 36.6 | 7.4 | -2.7 | 10 | 67.6 | 4.8 | 32.4 | 14.8 | 2.1 |
| 10 | 25.566 | 85.749 | 18.3 | 7.4 | -2 | 13.6 | 70.9 | 5.6 | 29.1 | 19.2 | 2.4 |
| 11 | 25.563 | 85.713 | 19.8 | 7.4 | -1.9 | 0.8 | 57.7 | 0.6 | 42.3 | 1.4 | 1.4 |
| 12 | 25.535 | 85.624 | 36.6 | 7.4 | -0.5 | 2.5 | 87.5 | 0.4 | 12.5 | 2.8 | 7 |
| 13 | 25.55 | 85.658 | 24.4 | 7.1 | -2.5 | 7.2 | 42.9 | 9.5 | 57.1 | 16.7 | 0.8 |
| 14 | 25.539 | 85.642 | 36.6 | 7.2 | -4.2 | 4.1 | 58.9 | 2.9 | 41.1 | 7 | 1.4 |
| 15 | 25.547 | 85.674 | 21.3 | 7.8 | -3.4 | 1.3 | 94.6 | 0.1 | 5.4 | 1.3 | 17.4 |
| 16 | 25.565 | 85.578 | 19.8 | 7.3 | -3.7 | 0.4 | 14.8 | 2.3 | 85.2 | 2.7 | 0.2 |
| 17 | 25.557 | 85.779 | 27.4 | 7.6 | 0 | 2.7 | 11.6 | 20.8 | 88.4 | 23.5 | 0.1 |
| 18 | 25.549 | 85.665 | 21.3 | 7.5 | -0.3 | 83.4 | 79.6 | 21.3 | 20.4 | 104.7 | 3.9 |
| 19 | 25.559 | 85.626 | 30.5 | 7.5 | -0.2 | 10.9 | 77.8 | 3.1 | 22.2 | 14 | 3.5 |
| Mean | | | 27.1 | 7.5 | -2.1 | 14.1 | 63.8 | 6 | 36.2 | 20.1 | 1.8 |

### *5.3.2. Total and inorganic As in agricultural soil and comparison with previous studies*

The total concentration of As observed in agricultural soils ranged from 3527–14690 µg/kg (**Table 5.2**), and this finding is approximately 2 to 7 times higher than the world typical average value of 2000 µg/kg for igneous and sedimentary rocks (Mandal and Suzuki, 2002) (**Fig. 5.5**). A high variability was observed in the concentration of As in agricultural soils in the study area. The concentration of As in groundwater (range 6–389.4) (Saha and Shukla, 2013) and 6.25–135 (Kumar et al., 2016) µg/L, respectively, has been reported earlier in this area. It is known that presence of higher concentration of As in soils may be attributed to geogenic contribution (Meharg and Rahman, 2003; Kumar et al., 2016), although few studies indicate higher As concentration in soils than sediments (Chowdhury et al., 1999). This suggests that other sources must contribute to the anomalous high concentration of As in soils. The situation of an elevated As in agricultural soils has been documented in previous studies conducted from As prone areas of Bangladesh, a country in which it has been confirmed that As levels were elevated in zones where As in groundwater used for irrigation was high (Meharg and Rahman, 2003). Mean As concentration in agricultural soils has been reported as 101,000 µg/kg in West Bengal, India (Norra et al., 2005).

**Table 5.2**
Concentration of inorganic As species with their respective extractable amount (%) in agricultural soil (*n* = 11) (results expressed in µg/kg and are based on peak area calculation)

| S.ID. | Latitude | Longitude | As(III) | As(V) | As (ext) | As (tot) | (%) extractable |
|---|---|---|---|---|---|---|---|
| 1 | 25.572 | 85.668 | Nd | 1050 | 1050 | 3528 | 29.8 |
| 2 | 25.570 | 85.638 | Nd | 2413 | 2413 | 10600 | 22.8 |
| 3 | 25.554 | 85.669 | 39 | 6835 | 6874 | 12940 | 53.1 |
| 4 | 25.561 | 85.718 | 20 | 5913 | 5933 | 10830 | 54.8 |
| 5 | 25.563 | 85.723 | Nd | 3420 | 3420 | 9527 | 35.9 |
| 6 | 25.563 | 85.713 | 31 | 4257 | 4289 | 9525 | 45.0 |
| 7 | 25.539 | 85.642 | 40 | 5404 | 5444 | 9742 | 55.9 |
| 8 | 25.579 | 85.677 | Nd | 4403 | 4403 | 12410 | 35.5 |
| 9 | 25.545 | 85.662 | 0.1 | 4513 | 4513 | 11630 | 38.8 |
| 10 | 25.608 | 85.666 | 12 | 3766 | 3779 | 13490 | 28.0 |
| 11 | 25.549 | 85.670 | Nd | 6152 | 6152 | 14690 | 41.9 |

Another study conducted in West Bengal in an As contaminated area revealed a range of 10,000–35,000 µg/kg (Sanz et al., 2007) in agricultural soils. Arsenic concentration of surface soils having a range of 1090 to 2480 µg/kg and any specific trend was not observed in a concentration with the depth of 2 m bgl (Singh et al., 2010). The As concentration in agricultural soils varied from 880 to 4960 µg/kg in Feni district of Bangladesh while it ranged from 3110–8900 for Dhamri, Bangladesh and 1,7600–65,000 µg/kg for Faridpur, Bangladesh (Ahsan et al., 2009). The arsenic concentration in this study area was higher than the 8500–10300 µg/kg in Japanese paddy soils, 2000–4600 µg/kg in

South Korean soils and 6700–9100 µg/kg in soils from Thailand (Mandal and Suzuki, 2002). It was, however, almost comparable to As concentration in agricultural soils in Ballia and Ghazipur which are situated in eastern Uttar Pradesh.

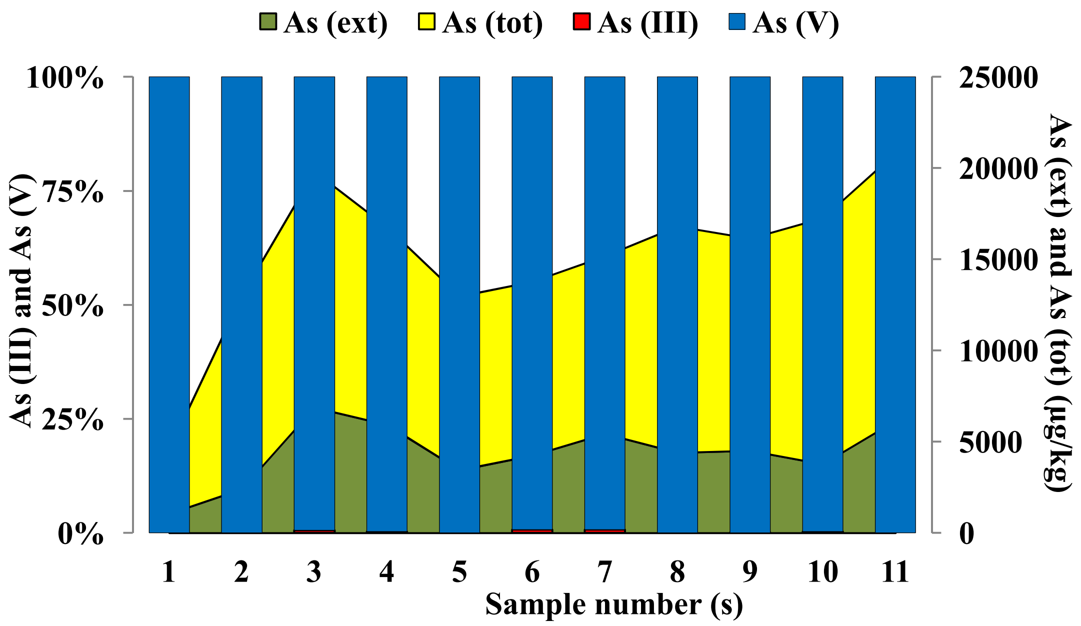


**Fig. 5.5.** Inorganic As species in agricultural soil samples. As(ext)= extractable As, As(tot) = total As

The percentage of extractable concentration of inorganic As with 1M Ortho-phosphoric acid ranged from 22.9 to 56. The concentration of As(III) and As(V) varied from not detectable to 40.1 and 1050 to 6835 µg/kg, respectively. Arsenate was detected in almost all agricultural soil samples while As(III) was detected only in 6 samples in a low-spanning range, i.e. 0.1–40.1 µg/kg (**Table 5.2**) (**Fig. 5.5**). Arsenate species dominated in oxygen-rich environments and well-drained soils, whereas As(III) is the stable oxidation state in the reducing conditions, such as regularly flooded soils (Vicky-Singh et al., 2010). This study also observed the same trend. For paddy field soils samples of West Bengal, inorganic As made up as much as 95% of the total As content. Being the major species As(V), this meant there was a very low concentration of As(III) being detected and in a few samples only (Sanz et al., 2007).

### *5.3.3. Arsenic in subsurface sediments*

#### *5.3.3.1. Total and inorganic As in subsurface sediment: an association with sediment colour tool*

**Table 5.3** summarizes the depth-wise As concentration As(t), As(III) and As(V) and grain size distribution. On the basis of texture and lithology, the sediment was categorized into five distinct lithofacies for both cores. A modified Munsell Color Chart, which was reduced into a four colour tool (**Fig. 5.6**) on the basis of comparative analysis of 2240 sediment samples was served to categorize the samples into four colours (Hossain et al., 2014). The purpose was to make a direct and consistent comparison of sediment colour in the CGB (**Fig. 5.7** and **Fig. 5.8**). A photographic view of fresh sediment has also been shown along the lithofacies. Larger amounts of As(t) along with As(V) and As(III) in Methrapur, Dal Sing Sarai were reported at a depth of 21.3 m bgl with concentrations of 20057 and 6289 and 264 µg/kg, respectively (see **Table 5.3** and **Fig. 5.7**). This section contains dark grey micaceous sand with organic matter and was below to the water table (i.e. 6.5 m bgl). Clay can absorb As because of the oxide-like characters of their edge (Smedley and Kinniburgh, 2002). The sum of the total extracted As i.e. As(III) and As(V) was less than the total digestion in both the core sediments due to binding of As with crystal lattice. pH plays an important role in adsorption and desorption of As particularly As(V) from hydrous oxide (Charlet et al., 2007).

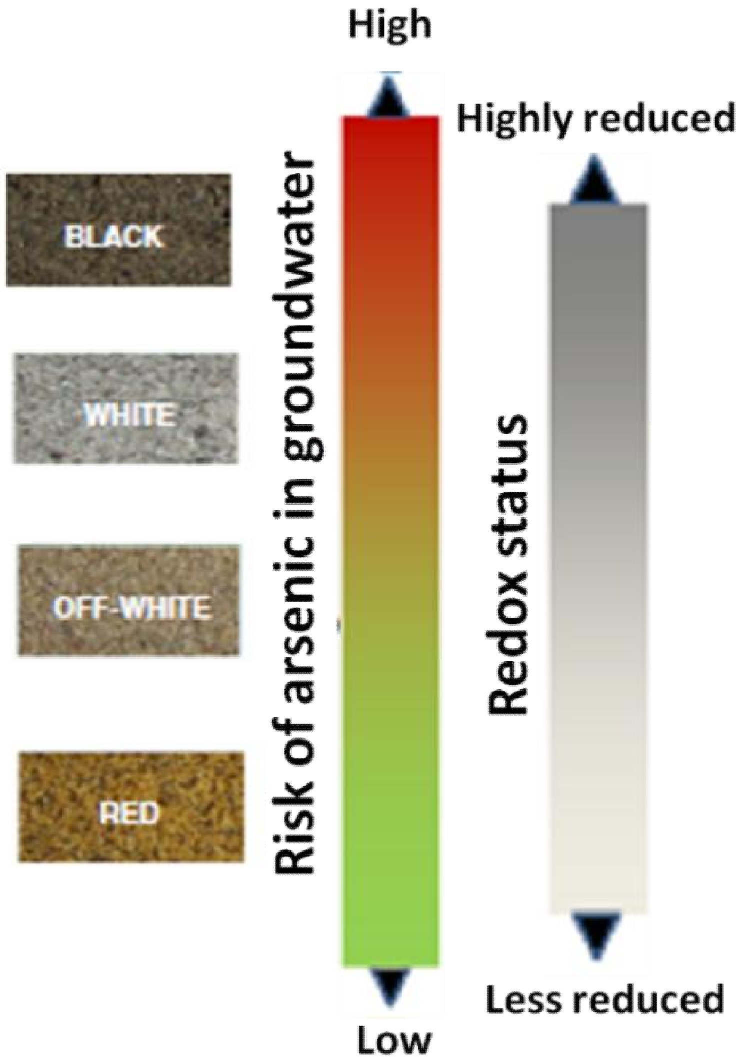


**Fig. 5.6.** Four colour sands with corresponding risks of As concentration in groundwater under varying redox status adopted from (Hossain et al., 2014)

**Table 5.3.**
Concentration of inorganic As species with their respective extractable amount (%) in subsurface sediments of (**a**) Methrapur, Dalsingh Sarai and (**b**) Harail Chapar, Samastipur (*n* = 11) (results of inorganic As are expressed in µg/kg and are based on peak area calculation)

| Depth (m) | pH | As(III) | As(V) | As (ext) | As (tot) | % (ext) | Sand (%) | Silt (%) | Clay (%) | EOC (%) | OM (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *(a)* | | | | | | | | | | | |
| 1.5 | 8.3 | Nd | 4328.0 | 4328.0 | 16007.1 | 27.0 | 27.7 | 63.8 | 8.6 | 0.8 | 2.2 |
| 4.5 | 8.2 | Nd | 3480.0 | 3480.0 | 16450.1 | 21.2 | 29.7 | 66.8 | 3.6 | 0.6 | 1.8 |
| 9.1 | 8.3 | Nd | 3203.7 | 3203.7 | 9876 | 32.4 | 26.5 | 63.9 | 9.6 | 0.5 | 1.6 |
| 21.3 | 8.4 | 264.2 | 6288.6 | 6552.8 | 20056.7 | 32.7 | 89.8 | 9.4 | 0.7 | 0.5 | 1.3 |
| 36.5 | 8.3 | 117.8 | 2328 | 2445.8 | 11291 | 21.7 | 39.0 | 57.4 | 3.7 | 0.5 | 1.6 |
| 42.6 | 8.2 | Nd | 3332.5 | 3332.5 | 9119 | 36.5 | 56.2 | 41.1 | 2.7 | 0.6 | 1.8 |
| Mean | 8.3 | 191.0 | 3826.8 | 3890.5 | 13800.0 | 28.6 | 44.8 | 50.4 | 4.8 | 0.6 | 1.7 |
| Min | 8.2 | Nd | 2328.0 | 2445.8 | 9119.0 | 21.2 | 26.5 | 9.4 | 0.7 | 0.5 | 1.3 |
| Max | 84 | 264.2 | 6288.6 | 6552.8 | 20056.7 | 36.5 | 89.8 | 66.8 | 9.6 | 0.8 | 2.2 |
| *(b)* | | | | | | | | | | | |
| 1.5 | 8.3 | Nd | 8820.6 | 8820.6 | 15663.4 | 56.3 | 31.4 | 59.2 | 9.4 | 0.5 | 1.3 |
| 9.1 | 7.8 | 368.5 | 6921.8 | 7290.2 | 19681.1 | 37.0 | 21.7 | 66.3 | 12 | 0.9 | 2.7 |
| 18.3 | 8.2 | 22.8 | 7224.8 | 7247.6 | 13654.7 | 53.1 | 35.1 | 56.5 | 8.5 | 0.5 | 1.3 |
| 24.4 | 8.3 | Nd | 2211.3 | 2211.3 | 4788.9 | 46.2 | 47.7 | 51.8 | 8.1 | 0.8 | 2.2 |
| 33.5 | 8.0 | Nd | 1134.9 | 1157.7 | 5515.6 | 21.0 | 82.5 | 15.3 | 2.1 | 0.5 | 1.6 |
| Mean | 8.1 | 195.7 | 5267.2 | 5345.5 | 11860.7 | 42.7 | 43.7 | 49.8 | 8.0 | 0.6 | 1.8 |
| Min | 7.8 | Nd | 1134..9 | 1157.7 | 4788.9 | 21.0 | 21.7 | 15.3 | 2.1 | 0.5 | 1.3 |
| Max | 8.3 | 368.5 | 8820.6 | 8820.6 | 19681.1 | 56.3 | 82.5 | 66.3 | 12.0 | 0.9 | 2.7 |

*M = Methrapur; HC = Harail Chapar;  EOC=Easily Oxidizable organic carbon; OM = Organic matter; Nd = not detected. As(ext)= extractable As, As(tot) = total As

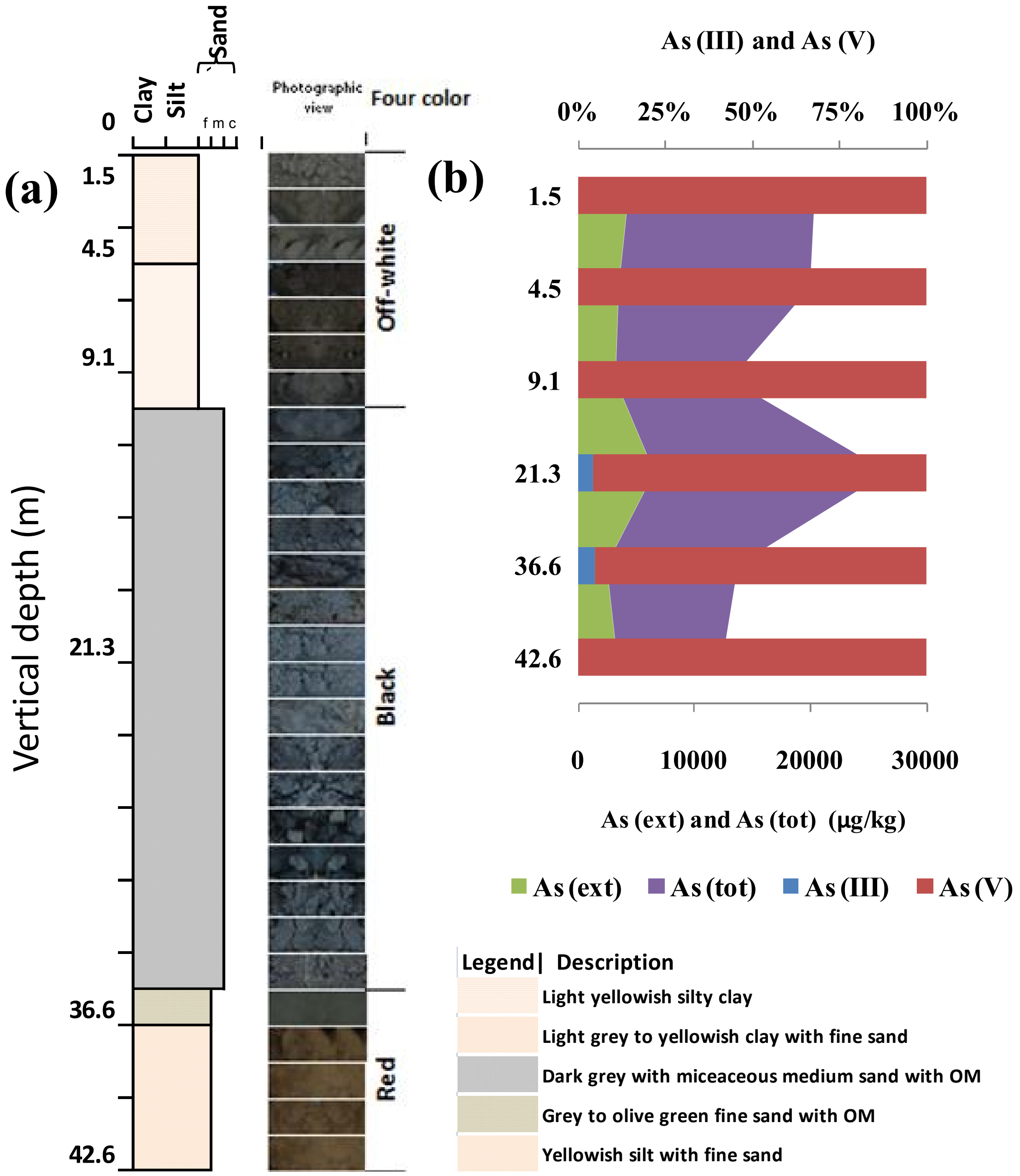


**Fig. 5.7.** Litholog prepared from core samples along with their corresponding photographic view of sediment (**a**), Graphs shows inorganic As species in subsurface sediment samples of Methrapur, Dal Singh Sarai (**b**). As(ext)= extractable As, As(tot) = total As

Total extracted concentration of As was higher in the subsurface soil than the agricultural soil and shows a significant difference indicating the source of As as the subsurface sediment. The upper layer (above water table of 6.5 m bgl) did not exhibit As(III) due to the presence of an oxidizing environment made possible by the exchange of oxygen. In Harail Chapar, larger amounts of As(t) and As(III) were observed at a depth of 9.1 m bgl having a range of 19681 and 368 µg/kg, respectively. Meanwhile, the highest As(V) concentration was observed at a depth of 1.5 m bgl and having a value of 8821 µg/kg (**Fig. 5.8**). There was a decline in As concentration after 9.1 m bgl and this supports the assumption of low As concentration in deeper aquifers. It has been reported that the concentration of As varies according to the colour and grain size of the sediment in the Gangetic Basin. Brown to a yellowish colour with coarser sediment contains small amounts of As while having a grey to black colour with fine grain size contains comparatively larger concentrations (Hasan et al., 2009). A very good correlation ($r^2$=0.96) was observed between soil and sediment samples in Chhattisgarh, situated in central India (Patel et al., 2005).

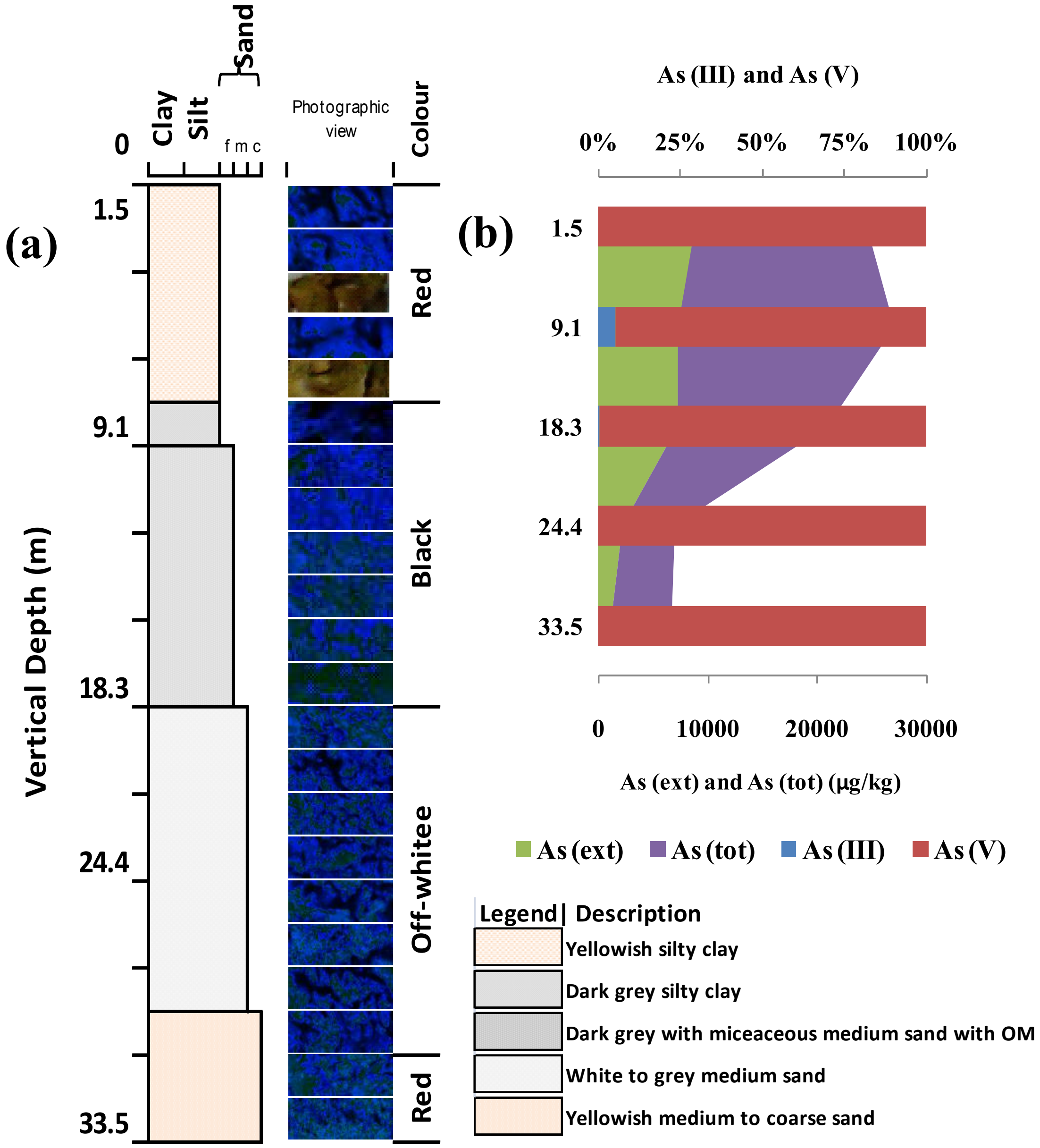


**Fig. 5.8.** Litholog prepared from core samples along with their corresponding photographic view of sediment (**a**). Graph shows inorganic As species in subsurface sediment samples of Harail Chapar, Mohiuddin Nagar (**b**). As(ext)= extractable As, As(tot) = total As

### *5.3.3.2.* Statistical analysis for subsurface sediments

Statistical amalgamations do not necessarily manifest cause-effect relationships; however they allow to simultaneously evaluating the variability of different variables within a suit of samples. Principal component analysis was applied to the data to understand the geochemical processes taking place in this area which is shown in **Fig. 5.9**. The factors having Eigen value <1 were considered for the explanation of dataset. Three factors were observed in both the subsurface sediments to explain a large percentage of variance expressed by data matrix (Methrapur, 91.62%; Harail Chapar 98.79%). The principal component 1 (PC1) of Methrapur was responsible for 41.42% of the cumulative variance, expressed by very high loading on As(V), As (ext), As (tot) and a high loading on pH and As(III). This factor explains that adsorption of As(III) and A(V) fluctuating with pH in subsurface sediment. A study shows that the pH range 6–9, typical of natural environment As(III) is sorbed to a similar or greater extent than As(V) on oxyhydroxides and goethite (Dixit and Hering, 2003). The PC2 was responsible for 67.09% of the cumulative variance with positive loading on silt and clay and negative loading on core depth and sand attributed to fining upward of the sediment deposition. PC3 have positive loading on EOC and OM with a cumulative variance of 91.62 attributed to their close association in sediments of the study area.

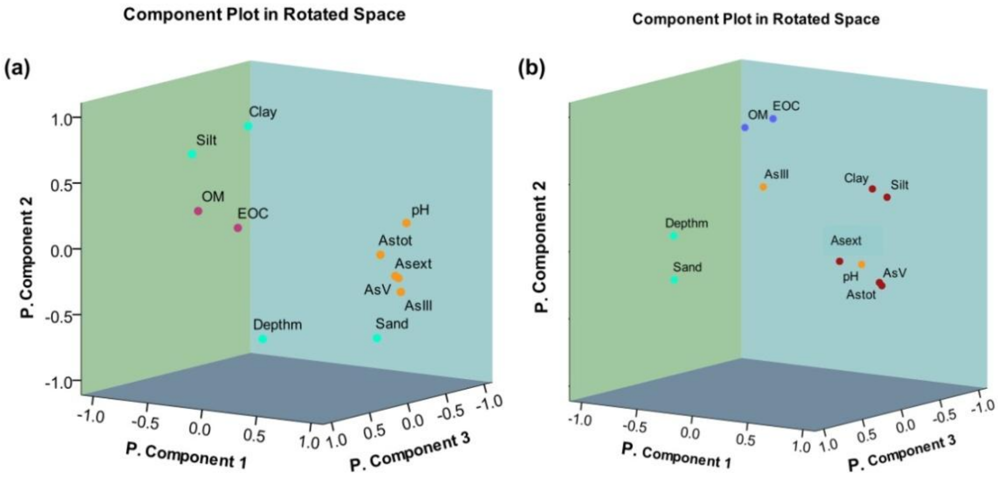


**Fig. 5.9.** Multivariate analysis, principal component in rotated space (**a**) Methrapur, (**b**) Harail Chapar

In case of Harail Chapar, PC1 was responsible for 55.92% of the cumulative variance and expressed by positive loading on As(V), As(ext), As(tot), silt and clay and negative loading on depth and sand resulting from the presence of very high As contamination in fining section of upper layers, while very less in lower section. It is depicting also from **Fig. 5.8**. PC2 has positive loading on EOC and OM with cumulative variance (81.80) further indicating that EOC is derived from OM in the sediment. The PC3 indicates 98.79% of the cumulative variance with positive loading on As(III) and negative loading on pH. The negative association of both shows lack relationship. A study from

Bhojpur district, Bihar has been reported only a very little fraction of As bound to organic matter, while the significant fraction was bound to reducible phase (Kumar et al., 2012).

Results of correlation of As and other parameters; As (ext), As (tot), Sand (%), Silt (%), Clay (%), EOC (%) and OM (%) are shown in (**Table 5.4**). pH shows positive but not very significant correlation with As(III), As(V), As (ext) As (tot) and sand but negative correlation with silt and OM (**Table 5.4a**). As(V) has a very positive and significant correlation with As (ext) and As (tot) indicating that more in As zone the presence of As(V) and As (ext) was also higher. As(III) exhibited positive correlation with sand while the negative correlation with silt. Sand shows a negative correlation in As (tot) in Harail Chapar while no significant correlation in Methrapur indicating less association of As with this fraction of sediment. For Harail Chapar pH is negatively correlated with As(III) and OM (**Table 5.4b**). As (ext) and As (tot) show a negative correlation with sand while the positive correlation with silt and clay. In both the cores sand exhibits a negative correlation with silt and clay.

### *5.3.3.3. Mineralogical evidence for As mobilization in subsurface sediments*

XRD results revealed that aquifer sediment at Methrapur composed primarily of quartz, calcite ($CaCO_3$), muscovite and chlorite with minor amounts of smectite, feldspar, hematite, siderite, goethite and magnetite (**Fig. 5.6**) The significant presence of altered feldspar, chert and chlorite indicated the sedimentary and meta-sedimentary origin of sands (Ahmed et al., 2004). The presence of calcite and muscovite in the upper oxidized sediments suggested a close relationship with chelation of the metals in the zone of oxidation (Hasan et al., 2009). A larger concentration of As was observed in the upper section in both places **Fig. 5.6(b)** and **Fig. 5.7(b)**. Peaks of hematite ($Fe_2O_3$) and goethite ($FeO(OH)$) were observed throughout the profile but magnetite ($Fe_3O_4$) was reported only in the upper yellowish oxidized silty clay. A small amount of kyanite (in detrital form) was also reported. The mineralogical result revealed the absence of pyrite but the XRD traces indicate the presence of siderite and magnetite in the core sediments (at a depth of 1.5) and the presence of siderite at 21.3 mbgl. The presence of this secondary mineral was noted in early studies of As in Southeast Asia by Islam et al. (2004) and Anawar et al. (2006). Jönsson and Sherman (2008) investigated on sorption of As to siderite and find As(V) sorbs strongly, but As(III) sorbs weakly. Due to its weakly bounding towards siderite and high mobility characters As(III) was reported only in deeper (21.3 and 36.6 m bgl) sediments, and (Mumford et al., 2012) show 184 mg/kg (184,000 µg/kg) of As in a siderite separate which included quartz, so the actual concentration in the siderite is probably higher. Hence, siderite is decidedly a sink for As. But the sudden drop in the concentration of As in deeper section of the core (**Fig. 5.6**) can be explained by the absence of siderite and magnetite minerals (**Fig. 5.8**).

**Table 5.4**

Correlation matrix of As with other parameters (a) Methrapur, Dalsingh Sarai and (b) HarailChapar

| Variables | Depth (m) | pH | As(III) | As(V) | As (ext) | As (tot) | Sand (%) | Silt (%) | Clay (%) | EOC (%) | OM (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *(a)* | | | | | | | | | | | |
| Depth (m) | 1.00 | | | | | | | | | | |
| pH | -0.10 | 1.00 | | | | | | | | | |
| As(III) | 0.27 | 0.80 | 1.00 | | | | | | | | |
| As(V) | -0.25 | 0.64 | 0.64 | 1.00 | | | | | | | |
| As (ext) | -0.22 | 0.67 | 0.68 | 0.99** | 1.00 | | | | | | |
| As (tot) | -0.48 | 0.51 | 0.57 | 0.81* | 0.82* | 1.00 | | | | | |
| Sand (%) | 0.46 | 0.51 | 0.83* | 0.72 | 0.75 | 0.44 | 1.00 | | | | |
| Silt (%) | -0.42 | -0.58 | -0.83* | -0.76 | -0.78 | -0.44 | -0.99** | 1.00 | | | |
| Clay (%) | -0.58 | -0.06 | -0.64 | -0.34 | -0.37 | -0.35 | -0.78 | 0.71 | 1.00 | | |
| EOC (%) | -0.44 | -0.27 | -0.50 | 0.08 | 0.04 | 0.18 | -0.38 | 0.37 | 0.39 | 1.00 | |
| OM (%) | -0.37 | -0.52 | -0.76 | -0.30 | -0.34 | -0.15 | -0.66 | 0.66 | 0.54 | 0.92** | 1.00 |
| *(b)* | | | | | | | | | | | |
| Depth | 1.00 | | | | | | | | | | |
| pH | -0.07 | 1.00 | | | | | | | | | |
| As(III) | -0.37 | -0.82 | 1.00 | | | | | | | | |
| As(V) | -0.92* | 0.07 | 0.30 | 1.00 | | | | | | | |
| As (ext) | -0.93* | 0.03 | 0.34 | 0.99** | 1.00 | | | | | | |
| As (tot) | -0.84 | -0.39 | 0.69 | 0.89* | 0.91* | 1.00 | | | | | |
| Sand (%) | 0.86 | 0.01 | -0.54 | -0.85 | -0.85 | -0.82 | 1.00 | | | | |
| Silt (%) | -0.82 | 0.08 | 0.48 | 0.78 | 0.78 | 0.73 | -0.99** | 1.00 | | | |
| Clay (%) | -0.82 | -0.08 | 0.62 | 0.75 | 0.76 | 0.78 | -0.93** | 0.98** | 1.00 | | |
| EOC (%) | -0.12 | -0.44 | 0.73 | -0.10 | -0.06 | 0.20 | -0.41 | 0.46 | 0.57 | 1.00 | |
| OM (%) | -0.01 | -0.61 | 0.78 | -0.20 | -0.16 | 0.17 | -0.27 | 0.30 | 0.43 | 0.97** | 1.00 |

*. Correlation is significant at the 0.05 level (2-tailed); **. Correlation is significant at the 0.01 level (2-tailed).

EOC=Easily Oxidizable organic carbon; OM = Organic matter; As(ext)= extractable As, As(tot) = total As.

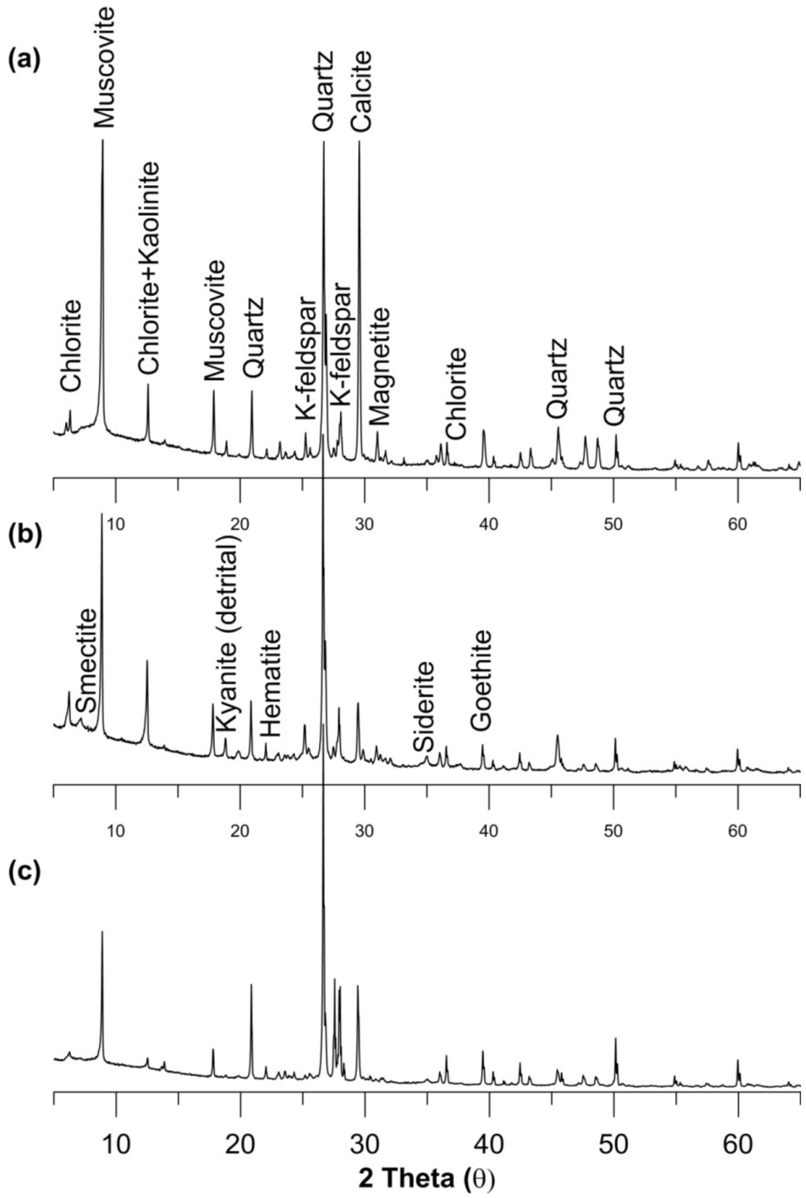


**Fig. 5.10.** Comparative XRD pattern of three different depths (**a**) upper light yellowish silty clay (off-white) at 1.5m vertical depth (**b**) dark grey with micaceous medium sand with OM (black) at 21.3 m vertical depth and (**c**) lower yellow silt with fine sand (red) sediments at 42.6 m vertical depth of Methrapur, Dalsingh Sarai

The presence of chlorite, muscovite and Fe-OH coated quartz in core sediments (fine grains with black colour) could be another probable cause for elevated As in upper section at Methrapur. The mineralogy of Harail Chapar was similar to Methrapur, but an interesting association of As with siderite mineral was observed. The higher level of As was observed in an upper section of the core where siderite was present but there was a sudden drop in As concentration in deeper sediments in the absence of this mineral (**Fig. 5.9**). In deeper sediment, the formation was made up of mainly medium to coarse sand (**Fig. 5.7**). The presence of As(III) was reported at 9.1 m bgl at Harail Chapar. The

XRD traces indicate the presence of goethite and magnetite in this section. Dixit and Hering (2003) reported that at typical pH range 6–9

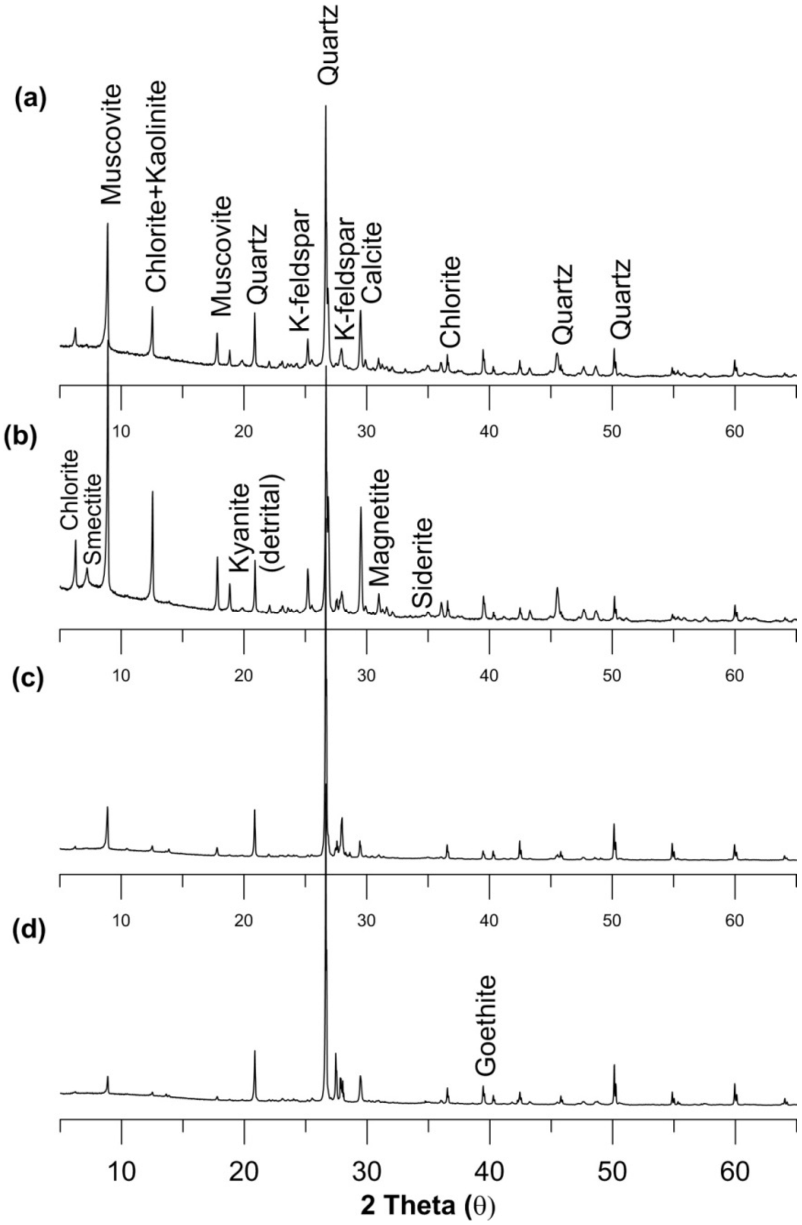


**Fig. 5.11.** Comparative XRD pattern of four different depth (**a**) upper light yellowish silty clay (red) at 1.5m vertical depth (**b**) middle dark grey silty clay (black) at 9.1m vertical depth (**c**) middle white to grey sand (off-white) at 24.4 m vertical depth and (**d**) lower yellowish sand (red) sediments at 33.5m vertical depth of Harail Chapar

As(III) is sorbed to a similar or greater extent than As(V) on oxyhydroxide and goethite minerals. Further, this section contains dark grey silty clay with higher OM produces favourable conditions for adsorption of As(III) and As(V).

### *5.3.3.4. Scanning electron microscopy of subsurface sediment*

Scanning electron microscopic images of the minerals support the XRD results in Methrapur as shown in **Fig. 5.12**. It shows common rock-forming minerals present in CGB like (a) layered mica (b) calcite (c) Fe-oxide on Al-silicate (e) Ferric oxide and (h) muscovite. A mechanically weathered biotite was also observed in the upper yellowish silty clay (d). **Fig. 5.12** (**f**) highlights the presence of intense chemical weathering in this area. The Fe-oxide precipitate was observed in the yellowish silt with fine sand (red). All rock forming minerals like mica, muscovite, calcite and feldspar (image not given) were observed in throughout the section in Harail Chapar except the some rare minerals like Na-Mg-Fe-Al silicates, which were also observed in the sediment of dark grey micaceous sand (see **Fig. 5.13** (**a**). Weathered pyrite framboid was noted in the lower dark grey micaceous sand at a depth of 9.1m, indicating active sulphate reduction (lack of sulphate) (Chowdhury et al., 1999) and prevalence of the highly reducing condition

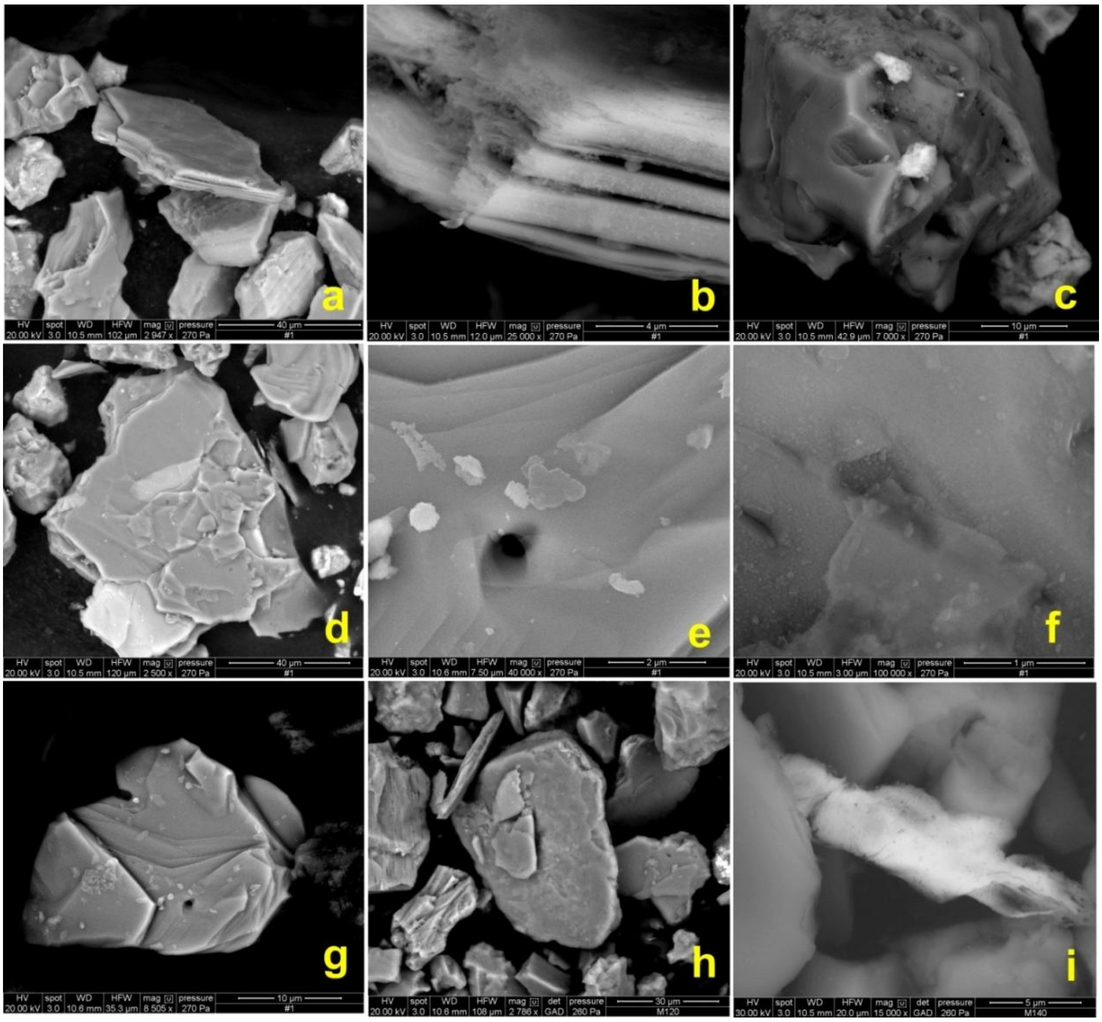


**Fig. 5.12.** Backscattered close view obtained by Environmental SEM of sediment of different depths: (**a**) layered mica (**b**) calcite (**c**) Fe-oxide on Al-silicate (**d**) weathered pyrite (**e**) Ferric-oxide (**f**) show intense chemical weathering (**g**) hematite (**h**) muscovite on biotite (large piece) (**i**) Fe-oxide in precipitated form (bright object)

in the aquifer. Fe-Oxide in altered form in white to the grey sand of 24.4 m depth and presence of fibrous goethite in the yellowish medium to coarse sand also are the evidence to support the partial solubilization in the presence of highly reducing conditions in the aquifer sediments. Dixit and Hering (2003) reported that the transformation of oxyhydroxides to goethite by a microbial action would not decrease the affinity of the solid phase for As(III). However, a decrease in the specific surface area resulting site density that accompanies transformation of amorphous Fe-oxides to more crystalline phase could increase the mobility of As (Dixit and Hering, 2003).

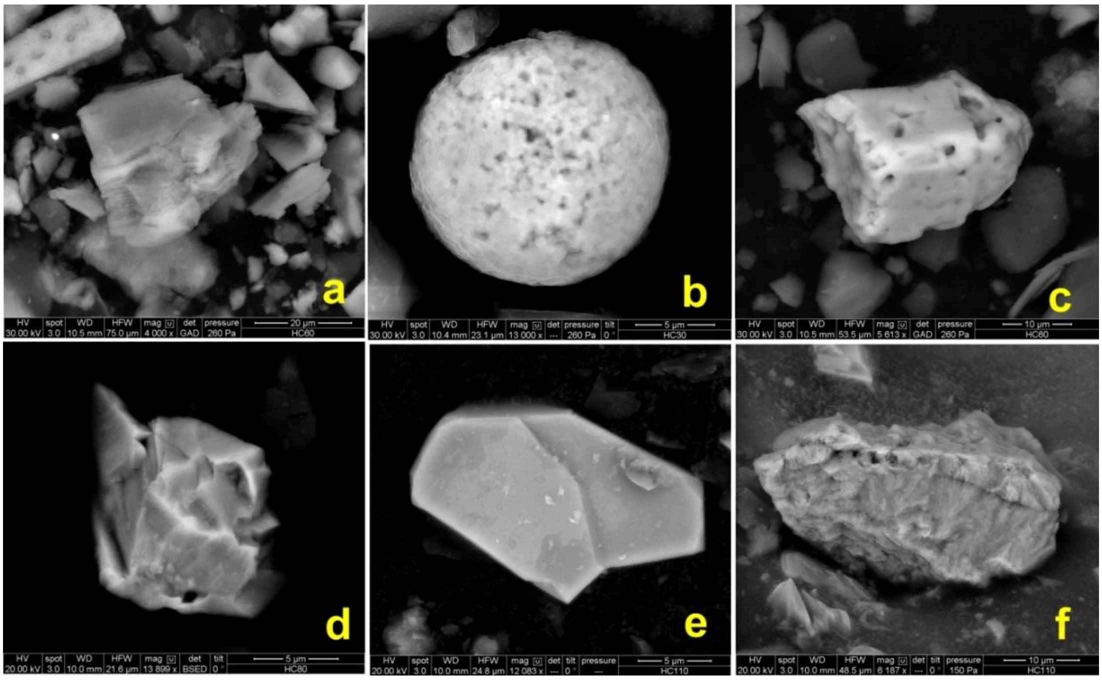


**Fig. 5.13.** Backscattered Environmental SEM images of sediment of different depths: (**a**) Na-Mg-Fe-Al silicate (**b**) weathered pyrite framboid (**c**) highly weathered zircon (d) Fe-oxide (**e**) Fe-oxide (surface alteration) (**f**) fibrous goethite

## 5.4. Conclusions

The present study finds that As(III) is dominant in groundwater, while As(V) is dominant in agricultural field soil and subsurface sediment. Concentrations of As(III) were larger in subsurface sediment than the agricultural field soil. The As in extracted or in totally digested samples indicates that subsurface sediments are necessarily the source to soils. Variations in inorganic As forms were associated with: firstly, the redox conditions of the aquifer depicted in sediment's colour; and secondly, with grain size, dark sediment with fine grain size contains more As(III) as well as As(V). Siderite appears in the reduced portion of the sediments, and it is a known sink for As. The alteration of Fe-oxides and presence of a fibrous form of goethite indicating partial solubilization of oxyhydroxides in this area.

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# Chapter 6

# Source identification and heath risk assessment of As and other trace elements in groundwater and selected dietary components

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*After*

Arsenic and other elements in drinking water and dietary components from the middle Gangetic plain of Bihar, India: Health risk index

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**Research highlights**

- Concentrations of As and other elements in water and dietary components

- Comparative analysis of concentration of As in uncooked and cooked rice

- Daily intake of As and other elements via water and dietary components

- Estimation of potential health hazards by comparing JECFA values of metals

- Estimation of chronic daily intake and health risk index

## Abstract

This study investigates the level of contamination, source identification and health risk assessment for arsenic (As) and other elements in drinking water, vegetables and other food components in two blocks (Mohiuddinagar and Mohanpur) from the Samastipur district, Bihar, India. Groundwater (80%) samples exceeded the World Health Organization (WHO) guideline value (10 µg/L) of As while Mn exceeded the previous WHO limit of 400 µg/L in 28% samples. The estimated daily intake of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn from drinking water and food components were 169, 19, 26, 882, 4645, 14582, 474, 1449 and 12,955 µg, respectively (estimated exposure 3.70, 0.41, 0.57, 19.61, 103.22, 324.05, 10.53, 32.21 and 287.90 µg per kg bw, respectively). Twelve of 15 cooked rice contained high As concentration compared to uncooked rice. Water contributes (67%) considerable As to daily exposure followed by rice and vegetables. Whereas food is the major contributor of other elements to the dietary exposure. Correlation and principal component analysis (PCA) indicated the natural source for As, but for other elements, the presence of diffused anthropogenic activities was responsible. The chronic daily intake (CDI) and health risk index (HRI) were also estimated from the generated data. The HRI were >1 for As in drinking water, vegetables and rice, for Mn in drinking water, vegetables, rice and wheat, for Pb in rice and wheat indicated the potential health risk to the local population. An assessment of As and other elements of other food components should be conducted to understand the actual health hazards caused by ingestion of food in people residing in the central Gangetic Basin.

## Keywords

Arsenic, Central Gangetic Basin, Dietary components, Groundwater, Total daily intake, Health risk index.

## 6.1. Introduction

Contamination of groundwater through naturally occurring arsenic (As) has been reported in many countries around the world, particularly in Southeast Asia causing a serious threat to humans (Mandal and Suzuki, 2002; Mukherjee et al., 2006; Naidu et al., 2006). This has received significant attention in the last three decades due to its serious health effects on millions of people and has been termed "the biggest As calamity in the world" (Smith et al., 2000). Arsenic contamination of tubewells in the central Gangetic Basin (CGB) was first reported in 2002 in Semria Ojha Patti village (area 4 km$^2$), Sahapur block in the Bhojpur district of Bihar, India (Chakraborti et al., 2003). About 89% geographical area of Bihar (~ 94,000 km$^2$), India is located in the CGB and is known for surplus food production and intensive ground-water extraction for drinking and irrigation (Saha, 2009). It was reported that 57 blocks in 15 districts of Bihar are As-affected (Saha, 2009). Arsenic in low concentration can stimulate plant growth but in higher concentration, it can be accumulated above the WHO threshold concentrations for safe ingestion of food crops (Rahman and Naidu, 2009). As a consequence, food crops accumulate elevated As which pose serious risks to the health of the local residing population (Dudka and Miller, 1999). Therefore, it is crucial to assess As exposure via commonly used food grains such as wheat, rice, maize and green gram. High concentrations of As in tubewell water and sediments of the CGB have been documented (Chauhan et al., 2009; Kumar et al., 2010a, 2010b; Saha, 2009; Saha et al., 2010a, 2010b; Shah, 2013). The As concentration N50 μg/L has been reported in Samastipur district, Bihar (Saha and Shukla, 2013). Significant As concentration was reported in hair, average values 5500 μg/kg (range: 4000–8800 μg/kg) and 14,200 μg/kg (range: 6100–24,000 μg/kg) in nails of people living in Maner district of Bihar, India (Sanz et al., 2007). In another study from Maner, Bihar, As concentrations have been reported in wheat, maize, rice-grain, and lentil to be 24, 11, 19 and 15 μg/kg, respectively (Singh and Ghosh, 2011).

Arsenic is a toxic element, known as a class (I) human carcinogen and widely distributed in the environment as both inorganic and organic forms (Hughes et al., 2011). In general, the inorganic forms (arsenite and arsenate) of As are much more toxic than the organic forms (monomethylarsonic acid, dimethylarsinic acid, arsenobetaine, etc.) of As. Arsenite is more toxic than arsenate and humans are exposed to both forms of inorganic As from water and food. There are many pathways by which As can enter the human body via food chain (ingestion by water and food sources), and occupational exposure is the most common (Rahman et al., 2009). Various inorganic species (arsenite and arsenate) and organic species (methylated anionic species, volatile As hydride and organo-As) in food materials have been reported as the main pathways to human exposure (Momplaisir et al., 2001). From a health perspective, it is equally important to study the trace elements other than As present in water and dietary food components. The concentration of other toxins in drinking water and dietary food materials may cause synergistic effects. For instance, deficiency of beneficial elements such as selenium (Se) and zinc (Zn) may increase As toxicity (Frisbie et al., 2002). A study has concluded that groundwater of Bangladesh is unsafe because tubewell waters exceeded the WHO guidelines for As, lead (Pb), manganese (Mn) nickel (Ni), chromium (Cr), molybdenum (Mo), uranium (U), boron (B), and barium (Ba) (Frisbie et al., 2002). The same conditions have also been suspected in the densely populated areas of the CGB due to the geological similarities in alluvial and deltaic plains (Frisbie et al., 2002).

Several attempts have been made to investigate the concentration of As in groundwater, health effect due to As toxicity and the mechanism of mobilization process of As in the CGB of Bihar (Chakraborti et al., 2003; Chauhan et al., 2009; Saha, 2009; Kumar et al., 2010b; Kumar et al., 2015). Arsenic above 50 µg/L was detected in 47% of tubewells in Bhagalpur, Bihar (Kumar et al., 2010b), while it was 58.6% in Semaria Ojha Patti, Bihar, India (Chakraborti et al., 2003). A range of 6–389.4 µg/L of As was also observed in Samastipur, India (Saha and Shukla, 2013). Very limited efforts have been directed to determine the degree of As contamination in food components and the associated risk to human through consumption of food. No study has reported elemental concentrations in commonly consumed food components from the CGB of Bihar. It is, therefore, timely to determine the level of As and other toxic elements present in water, vegetables and other food components grown in this particular area. The total exposure to As and other elements in water, vegetables and other dietary components in the Samastipur district of Bihar, India was the main focus of this study. An attempt was also made to under-stand the potential health risk due to consumption of contaminated water and food components and the role of other elements because they may have a synergetic effect on people living in the study area.

## 6.2. Material and methods

### *6.2.1. Study area description, sample collection and preparation*

Samastipur district, Bihar, which is situated in the eastern part of the Gangetic Basin, is characterized by a monotonous flat alluvial landform known as the North Ganges plain (Saha et al., 2010b). **Fig. 6.1** shows the location of the study area in CGB, Bihar, India, and the corresponding sampling points. Hand-pumps and tubewells are mainly logged in shallow aquifers (20–60 m) only. Irrigation undertaken in this area relies on the shallow aquifers (Saha and Shukla, 2013). Tubewell water samples (n = 23), wheat (n = 35), uncooked rice (n = 15), cooked rice (n = 15), maize (n = 31) and vegetables (n = 34), commonly consumed by residents of this area, were collected from two blocks (Mohiuddinagar and Mohanpur) of Samastipur district, Bihar, India in May 2013. According to Census of India 2011, the total area of Mohiuddinagar block is 129.54 km$^2$ (population 184,521); while the area of Mohanpur is 81.02 km$^2$ (population 115,032). Rice (both uncooked and cooked rice), wheat, maize and green gram samples were collected from households. All surveyed families revealed that collected samples were grown locally in their respective agricultural fields. In the study area, rice was cooked using excess water (ratio is 1:2); excess water was removed after cooking. Tubewell water was used for rice cooking by surveyed families. Vegetables were collected from the nearby gardens of each surveyed household.

The local, English and botanical names of the vegetables and other dietary components collected are provided in **Table 6.1**. Water samples were collected in pre-cleaned (washed with concentrated nitric acid followed by Milli-Q water) polypropylene bottles followed by acidification. After collection, the food samples were stored in a cool box and then store at 4 °C upon return to the laboratory. Before processing, all food samples were kept at room temperature for several hours. Food samples process method was reported elsewhere (Rahman et al., 2013). Briefly, all food samples except cooked rice were washed three times with tap water followed by de-ionized water (twice). All food samples were dried in an oven at 65 °C and homogenized by grinding with a stainless steel grinder. Each sample was then stored in a separate plastic zip-lock bag. All samples were then transported to Adelaide, South Australia by air under strict quarantine rules and regulations.

### *6.2.2. Daily serving of vegetable, rice, wheat, maize and green gram for adults*

During the field sampling, families were surveyed regarding the intake quantities of water and food. Interviews were undertaken based on 46 adults from 23 families (23 males and 23 females, 12–60 years of age) to determine the daily intake rates of water, vegetables, rice, wheat, maize and green gram by each. People in the area eat rice for breakfast and lunch while generally consuming chapatti (handmade bread) made up of wheat and maize during dinner along with vegetables and green gram in each meal. To know the correct volume of water intake, two calibrated glasses (250 and 500 mL volumes) were used. The amount and frequency of consumption by an individual were confirmed

**Table 6.1**

Vegetables and other dietary components with their Local, English and Botanical names

| S.No. | Local name (Hindi) | English name | Botanical name |
|---|---|---|---|
| 1. | Bhindi | Ladyfinger (okra) | *Abelmoschus esculentus* |
| 2. | Ghiya | Gourd | *Lagenaria siceraria* |
| 3. | Torai | Luffa | *Luffa aegyptiaca* |
| 4. | Kheera | Cucumber | *Cucumis sativus* |
| 5. | Bengan | Brinjal | *Solanum melongena* |
| 6. | Chawal | Rice | *Oryza sativa* |
| 7. | Gehun | Wheat | *Triticum aestivum* |
| 8. | Makka | Maize | *Zea mays* |
| 9. | Mung | Green gram | *Vigna radiata* |

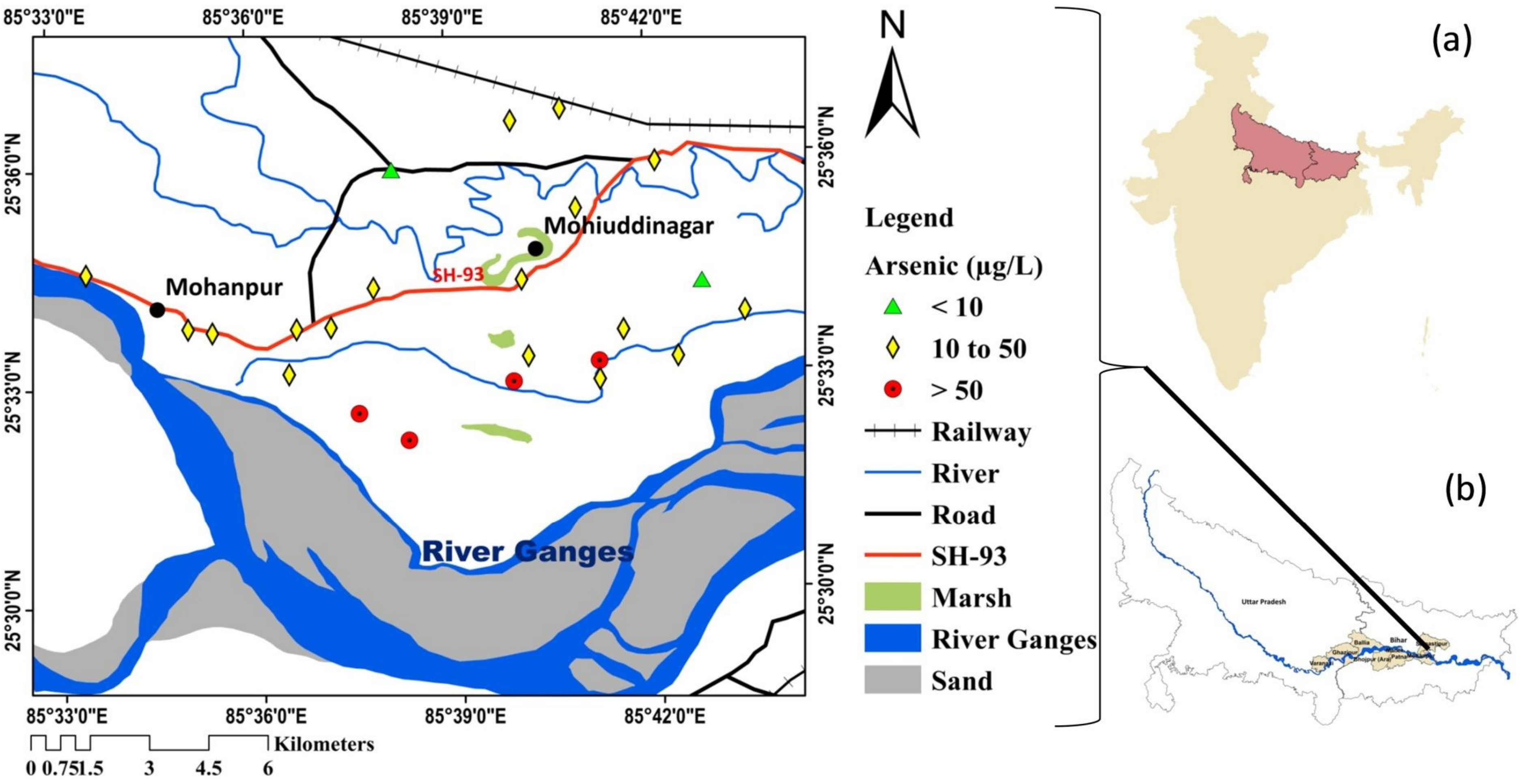

**Fig. 6.1.** The location of the study area in CGB (Samastipur district of Bihar), India and the distribution of As concentration in groundwater

with our calibrated glasses. To calculate the average consumption of individual for vegetables, wheat, rice, maize and green gram; the total amount was divided by a number of members of respective surveyed family (minors below 11 years were excluded). The self-reported mean daily serving of water consumed ranged from 2.5 to 5 L/day with a mean of 3.5 L/day, while the mean daily serving of uncooked rice ranged from 250 to 500 g rice/day with a mean of 378 g/day for each adult. The mean daily intake of wheat, maize and green gram were 259 g (range: 100–400 g), 79 g (range: 30–300 g), and 48 g (range: 30–70 g), respectively. The self-reported fresh vegetable intake for an adult in this study was 353 g per day in composites of all three diets (viz. breakfast, lunch and dinner), which is better than the recommended amount of 200 g/person/day from the nutritional point of view (Hasan and Ahmad, 2000). Vegetable intake is somewhat higher in Bihar compared to West Bengal, India and Bangladesh, probably because the CGB is a very fertile belt that makes agricultural activities possible. Also, vegetables are a regular staple of people who are relatively poor.

The mean daily intake of vegetables as dry wt. was 53 g (30–75 g), if we consider 85% of the water content in fresh vegetables. The mean value of per capita water consumption of 5.0 L in Rampur Diara, Bihar and 5.2 L in Haldichapra, Bihar was reported, and per capita consumption by adults for uncooked rice, pulses and vegetables was 159.2 g, 36.5 g and 32.7 g in Rampur Diara while 169.5 g, 38.2 g and 138.2 g in Haldichapra, respectively (Singh and Ghosh, 2012). The intake of uncooked rice, green gram and vegetables were higher in this study compared to (Singh and Ghosh, 2012) study although lower than per capita water intake in Rampur Diara and Haldichapra. It was reported that an average serving size of cooked rice and vegetables was 405 g (wet weight) and 72 g (wet weight), respectively, for Bangladeshi females (n = 47) of Pabna district (Kile et al., 2007). In the another study, it was reported that the average cooked rice consumption rates per day were 776 g (wet wt.) for adult males (n = 12) and 553 g (wet wt.) for adult females (n = 6) from Chapai Nawabganj of Bangladesh (Ohno et al., 2007). The average consumption rates of water, rice and vegetables for adults were 3.0 L, 425 g and 205 g, respectively, from Noakhali district of Bangladesh (Rahman et al., 2013). The estimated mean daily water intake was 2.8 L per day for an adult from West Bengal, India (Mondal et al., 2010). It was also reported that the average daily intake of water, rice and vegetables by an adult (both male and female) were 5 L (4 L as drinking water and 1 L during food preparation), 712 g (dry wt., wet wt.: 750 g) and 100 g (dry wt., wet wt.: 500 g), respectively, from West Bengal, India (Roychowdhury, 2008).

### *6.2.3. Chemical and reagents*

Milli-Q water (ELGA LabPure System) was used throughout the dilution and other analysis. All reagents used in the digestion and extraction processes were of analytical grade. Concentrated nitric acid ($HNO_3$) and 30% hydrogen peroxide ($H_2O_2$) were obtained from Fisher Chemicals.

### 6.2.4. Digestion process of food components

A microwave digester (CEM, MARS 6) along with 42 digester vessels was used to digest all food samples. Ground food sample (approximately 0.5 g of each) was weighed directly into a Teflon vessel, then adding 5 mL concentrated $HNO_3$ and 2 mL $H_2O_2$. Samples were allowed to predigest by standing open for 30 min before sealing vessels. Each vessel was sealed, placed into the rotor. The microwave conditions were; microwave power: 1020–1800 W, ramp time: 20–25 min, hold time: 15 min at 210 °C. After cooling for 30 min, the vessels were opened carefully. Each digestion solution was transferred to a 50-mL plastic centrifuge tube and diluted to 20 mL using milli-Q water. Samples were filtered through syringe filters (PTFE 0.45 µm). The samples were analyzed on the same day of preparation otherwise stored in the fridge at 4 °C.

### 6.2.5. Instrumentation

An Agilent 7500ce (Agilent Technologies, Tokyo, Japan) inductively coupled plasma mass spectroscopy (ICP-MS) determined the concentration of As and other elements in water, vegetables and other dietary components. The instrumental detection limits (DLs) for As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se and Zn were 0.01, 0.03, 0.05, 0.03, 0.02, 0.01, 0.10, 0.05, 0.2 and 0.01 µg/L in solution matrix, respectively. Selenium was analyzed in water samples only.

### 6.2.6. Standard Reference Materials (SRMs) analysis

Standard reference materials (SRMs), trace elements in natural water (SRM 1640) and tomato leaves SRM (1573a) from the National Institute of Standards and Technology (NIST) were used to verify the results for As and other elements in water and food samples. Tomato leaves were digested using the same procedure as the food samples. The certified values of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in trace elements in natural water (SRM 1640) are 26.67 ± 0.41, 22.79 ± 0.96, 20.28 ± 0.31, 38.6 ± 1.6, 85.2 ± 1.2, 121.5 ± 1.1, 27.4 ± 0.8, 27.89 ± 0.14 and 53.2 ± 1.1 µg/L, respectively and the observed values detected in this study were 25.36 ± 1.82, 21.26 ± 1.49, 20.03 ± 0.75, 36.2 ± 1.4, 88.2 ± 3.6, 117.1 ± 4.4, 26.5 ± 0.9, 27.63 ± 1.15 and 51.3 ± 4.3, respectively. The certified values of As, Cd, Co, Cr, Cu, Mn, Ni and Zn in tomato leaves SRM (1573a) are 112 ± 0.004, 1520 ± 40, 570 ± 20, 1990 ± 60, 4700 ± 140, 246,000 ± 8000, 1590 ± 70 and 30,000 ± 700 µg/kg, respectively, and the observed values detected in this study were 119 ± 3, 1460 ± 60, 610 ± 40, 1850 ± 80, 5010 ± 190, 235,000 ± 6000, 1680 ± 80 and, 32,200 ± 900, respectively. There is no certified value for Pb in SRM Tomato leaves. The analytical results of As and other elements in natural water and tomato leaves indicate that the observed values are very close to certified values (**Tables 6.2–6.3**).

### 6.2.7. Statistical analysis

The Pearson correlation coefficient was used to determine the strength of the relationships between As and other elements. A p value of <0.01 was considered to indicate statistical significance. SPSS 21 was used for principle component analysis (PCA). Multivariate factor analysis was also used to determine a common source of metals. The linear correlation between metal concentration in groundwater and food components enabled interpretation of correlation of elements in the study area. Principal component analysis was used to determine the association between individual elements in groundwater and food components. In this study, factors with eigenvalues greater than 1 were taken into account. Microsoft Excel 2007 was used to plot all pie charts. Origin 6.0 was used to plot bar charts. ArcMap 10.1 was used to prepare the map of the study area.

### 6.2.8. Calculation of chronic daily intake (CDI) and health risk index (HRI)

The total daily intake (TDI) of As and other elements from drinking water and various food components by an adult in this study were calculated by multiplying the mean daily serving with mean concentrations of corresponding elements obtained from water and other food components. The chronic daily intake (CDI) was determined by using the following equation

$$\mathrm{CDI} = \frac{\mathrm{TDI}}{\mathrm{B_{average\ weight}}}$$ (Singh and Ghosh, 2012).

TDI: daily intake of an element from water and food components. $B_{\text{average weight}}$: average body weight of an adult.

Assessment of health risk index (HRI) for locals through consumption of contaminated water, vegetables and other dietary components was estimated by using following equation

$$\mathrm{HRI} = \frac{\mathrm{CDI}}{\mathrm{RFDo}}$$

(US-EPA, 2002) Where; RfDo = reference oral dose. The RfDo for As Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn are 3.0E-7, 5.0E-7, 2.0E-5, 1.5E-3, 4.0E-5, 2.4E-5, 2.0E-5, 5.0E-6 and3.0E-4 µg/kg/day (US-EPA, IRIS). The HRI < 1 means that the exposed population assumed to be safe. HRI > 1 may cause a potential health risk.

## 6.3. Result and discussion

### 6.3.1. Concentration of As and other elements in tubewell water

The concentrations of As and other toxic elements in groundwater are shown in **Table 6.2**. The location of the study area in the Samastipur district of Bihar, India and the distribution of As concentration in groundwater is presented in **Fig. 6.1**. Arsenic concentration ranged from 6.25–135

**Table 6.2**

Concentrations of As and other elements in groundwater samples of Samastipur district. SD = standard deviation, unit; (µg/L)

| Elements | Detection Limits of ICP-MS | Drinking water (n = 23) | | | | | | NIST SRM water 1640 (n=3) | |
|---|---|---|---|---|---|---|---|---|---|
| | | Mean ± SD | Median | Range | WHO guideline Values | BIS standards | No. of samples exceeding WHO guideline values | Certified values | Observed Values |
| As | 0.01 | 32.14 ± 32.85 | 17.19 | 6.25 – 135 | 10 | 10 | 22 (88%) | 26.67 ± 0.41 | 25.36 ± 1.82 |
| Cd | 0.03 | 0.08± 0.04 | 0.07 | 0.03 – 0.12 | 3 | 3 | – | 22.79 ± 0.96 | 21.26 ± 1.49 |
| Co | 0.05 | 0.26 ± 0.10 | 0.24 | 0.12 – 0.49 | – | – | – | 20.28 ± 0.31 | 20.03 ± 0.75 |
| Cr | 0.03 | 0.47± 0.33 | 0.40 | 0.09 – 1.34 | 50 | 50 | – | 38.6 ± 1.6 | 36.2 ± 1.4 |
| Cu | 0.02 | 3.51 ± 2.76 | 3.09 | 0.59 – 13.7 | 2000 | 50 | – | 85.2 ± 1.2 | 88.2 ± 3.6 |
| Mn | 0.01 | 451.70 ± 338.31 | 317 | 139.9 – 1232 | – | 100 | – | 121.5 ± 1.1 | 117.1 ± 4.4 |
| Ni | 0.1 | 1.36 ± 0.70 | 1.09 | 0.50 – 3.53 | 70 | 20 | – | 27.4 ± 0.8 | 26.5 ± 0.9 |
| Pb | 0.05 | 3.19 ± 2.26 | 2.5 | 0.59 – 8.4 | 10 | 10 | – | 27.89 ± 0.14 | 27.63 ± 1.15 |
| Se | 0.2 | 0.58 ± 0.30 | 0.61 | 0.21 – 0.90 | 40 | 10 | – | 21.96 ± 0.51 | 22.10 ± 3.54 |
| Zn | 0.01 | 30.82 ± 27.60 | 21.36 | 2.8 – 108.20 | 3000 | 5000 | – | 53.2 ± 1.1 | 51.3 ± 4.3 |

µg/L, with around 88% of the water samples exceeding the WHO and the Bureau of Indian Statistics (BIS) guideline value (10 µg/L) for As (**Table 6.2**). This study revealed that mean and median As concentrations were 30.2 µg/L and 17 µg/L. The mean As the level in this study was comparatively lower than the previous study where the mean As concentration in groundwater samples was 62.2 µg/L (range: 0.01 to 389.4 µg/L) in Samastipur district (Saha and Shukla, 2013). Mean As concentration was reported 52 µg/L in Rampur Diara and Haldichapra areas of the Maner block in the Patna district, Bihar, India (Singh and Ghosh, 2012). Average As the concentration of 331 µg/L has been reported in Ballia and Ghazipur of Uttar Pradesh, India (Srivastava and Sharma, 2013), which is higher than this study. This may be attributed to variations in regional geology and unevenness of the sediments, the content of organic matter and organic carbon varies (Chandrasekharam et al., 2007). However, this is a complex process and most probably other confounding factors are also responsible for the variation of As concentrations in groundwater The Mn concentrations ranged from 140 µg/L to 1232 µg/L, with 28% of the water samples exceeding the previous WHO limit of 400 µg/L (**Table 2**). Currently, there is no limit value for Mn set by WHO (WHO, 2011) and BIS for drinking water. As per USEPA, the concentration of Mn in drinking water not to exceed 500 µg/L and 26% of the water samples were found to exceed this. Besides As and Mn, the levels of other elements such as Cd, Co, Cr, Cu, Ni, Pb, Se and Zn in drinking water were below the selected reference drinking water standards of WHO and BIS (**Table 6.2**). In a study from Noakhali district of Bangladesh, it was reported that most of the examined elements such as. Cd, Co, Cr, Cu, Ni, Pb and Zn in drinking water were below the WHO guideline values except As (Rahman et al., 2013).

### *6.3.2. Concentration of As and other elements in different types of vegetables, food components and comparisons with relevant studies*

**Table 6.3** summarizes the level of As and other elements in different types of food samples. In this study, the vegetables with the highest mean As concentration were luffa > brinjal > cucumber > ladyfinger > gourd > green gram with mean values of 800, 492, 399, 375, 268 and 174 µg/kg, respectively (**Fig. 6.2a**). In other dietary components, the highest mean As concentrations were rice N wheat N maize (**Fig. 6.2b**). Variation in As and other elements' accumulation in plants depends on many factors: viz. availability of As in water, soils, accumulation capacity by the plant, the life span of plants grown, etc. (Roychowdhury et al., 2003). Among all food categories such as vegetables, rice, wheat, maize and green gram; vegetables contained elevated concentrations of As (**Table 6.3**). In a previous study, it was reported that As concentrations (dry wt.) in wheat and maize were 24 µg/kg and 11 µg/kg, respectively from Maner district of Bihar, India (Singh and Ghosh, 2011). These are consistent with this study.

Vegetables contained a highest mean concentration of Cd (102 µg/kg) compared to other food categories such as rice, wheat and green gram where no variation in mean Cd levels was observed (**Table 6.3**). The mean concentrations of Cd in rice, wheat in this study were comparable to Bombay, India where mean values in rice and wheat were 18.9 µg/kg and 21.8 µg/kg, respectively (Tripathi et al., 1997). The highest level of Co was observed in vegetables (173 µg/kg) followed by the green gram (65 µg/kg). The mean Co concentration in vegetables in this study was almost half that of Noakhali, Bangladesh with mean values of 252 and 228 µg/kg for leafy and non-leafy vegetables, respectively (Rahman et al., 2013).

Vegetables with the highest levels of Cr concentration were luffa > brinjal > ladyfinger > cucumber > gourd (**Fig. 6.2c**) while other dietary components were wheat N maize N green gram N rice (**Fig. 6.2d**). The mean Cr concentrations in vegetables found in the study were considerably higher than those found in Noakhali (leafy vegetables 1120 µg/kg and non-leafy vegetables 640 µg/kg) (Rahman et al., 2013) and lower than vegetables having concentrations (13,480, 10,120 and 6210 µg/kg for Spinach leaf, Amaranth leaf and Cabbage leaf, respectively) grown in sewage sludge, Hyderabad, India (Srikanth and Reddy, 1991). The concentration of Cu in vegetables (17,253 µg/kg) found in this study was almost comparable to Varanasi, India with mean concentrations of 20,270, 16,070 and 16,630 µg/kg dry wt. for palak, lady finger (okra) and cauliflower, respectively (Sharma et al., 2009). The Cu contents in wheat and rice in Bombay, India were 3145 and 1694 µg/kg dry wt., respectively, which are lower than this study (Tripathi et al., 1997). The highest mean concentration of Mn was observed in wheat (31,821 µg/kg) followed by vegetables (24,040 µg/kg). The mean Mn concentrations in leafy vegetables and non-leafy vegetables were 160,000 µg/kg and 34,500 µg/kg, respectively, in Noakhali district, Bangladesh (Rahman et al., 2013), higher than this study. The mean Mn concentrations in vegetables (3290 and 4190 µg/kg) and cereals (9900 and 12,700 µg/kg) from Jalangi and Domkal blocks in West Bengal, India (Roychowdhury et al., 2003). The mean Mn concentrations in vegetables observed in this study are much higher than West Bengal.

Nickel concentrations are usually low in all food categories. The mean Ni concentrations for vegetables (360 µg/kg and 160 µg/kg) and cereals (870 and 720 µg/kg) were estimated from Jalangi and Domkal blocks, West Bengal, India, respectively (Roychowdhury et al., 2003). The mean Ni concentrations in leafy and non-leafy vegetables were 2470 and 1439 µg/kg dry wt., respectively, in Noakhali district, Bangladesh (Rahman et al., 2013). The mean Ni concentration in vegetables in this study area was higher than the West Bengal, India but comparable with Noakhali, Bangladesh.

The estimated Pb concentration in this study was much higher than in Bombay where Pb concentrations were 18.2, 253.3, 100.4 and 4.1 µg/kg in cereals, pulses, leafy vegetables and other vegetables, respectively (Tripathi et al., 1997). The mean Pb concentration in this study was higher

**Table 6.3**

Concentrations of As and other elements (μg/Kg) in vegetables, rice, wheat, green gram and maize of Samastipur district

| Parameters | As | Cd | Co | Cr | Cu | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| Vegetable (n = 34) | | | | | | | | | |
| Mean ± SD | 452 ± 712 | 102 ± 107 | 173 ± 78.68 | 5823 ± 4205 | 17,253 ± 5439 | 24,040 ± 11,546 | 2921 ± 2070 | 717 ± 374 | 35,413 ± 8579 |
| Median | 145 | 65 | 162.25 | 4416 | 17,311 | 21,569 | 2308 | 634 | 34,635 |
| Range | 37–3947 | 19.36–605 | 61.72–418 | 1568–23,359 | 9471–31,764 | 11,345–57,370 | 621–10,884 | 204–1703 | 22,191–68,059 |
| Rice (n = 15) | | | | | | | | | |
| Mean ± SD | 51 ± 41 | 19 ± 34 | 10 ± 6 | 294 ± 105 | 4255 ± 1266 | 5928 ± 3745 | 378 ± 161 | 2277 ± 1054 | 9123 ± 2714 |
| Median | 59 | 9.11 | 8.5 | 264 | 4633 | 4874 | 341 | 1932 | 9737 |
| Range | 2.51–132 | 1.82–127 | 2.60–21 | 189–592 | 2367–5725 | 2566–17,123 | 144–779 | 1107–4325 | 4122–13,264 |
| Wheat (n = 35) | | | | | | | | | |
| Mean ± SD | 27 ± 24 | 18.8 ± 8.6 | 33 ± 57 | 1354 ± 615 | 5459 ± 1922 | 31,821 ± 8674 | 449 ± 339 | 1395 ± 1005 | 20,474 ± 4823 |
| Median | 19 | 16 | 15 | 1171 | 4949 | 32,000 | 315 | 1136 | 18,489 |
| Range | 7.7–108 | 6.1–36 | 1.50–241 | 825–3799 | 3566–14,572 | 11,210–47,712 | 170–1460 | 88–5484 | 13,433–31,139 |
| Maize (n = 31) | | | | | | | | | |
| Mean ± SD | 13 ± 8.4 | 1.70 ± 1.00 | 3.71 ± 3.5 | 1087 ± 110 | 2554 ± 563 | 5664 ± 1189 | 187 ± 40 | 1636 ± 806 | 12,373 ± 2402 |
| Median | 11 | 1.38 | 3.10 | 1077 | 2437 | 5639 | 178 | 1377 | 12,702 |
| Range | 4.8–43 | 0.36–4.31 | 0.34–11.65 | 909–1437 | 1711–3982 | 2559–8708 | 138–286 | 554–3747 | 7005–18,694 |
| Green gram (n = 6) | | | | | | | | | |
| Mean ± SD | 23 ± 15 | 17 ± 14.7 | 65 ± 43 | 728 ± 252 | 10,990 ± 1782 | 16,857 ± 7350 | 894 ± 400 | 1345 ± 296 | 28,707 ± 7956 |
| Median | 23 | 11 | 47 | 608 | 10,293 | 13,820 | 661 | 1320 | 25,691 |
| Range | 7.9–49 | 6.7–46 | 33–143 | 538–1174 | 9421–13,375 | 11,155–30,491 | 615–1530 | 918–1727 | 24,087–44,859 |
| NIST SRM 1573a (Rahman et al., 2013) | | | | | | | | | |
| Certified values | 112 ± 0.004 | 1520 ± 40 | 570 ± 20 | 1.99 ± 0.06 | 4.70 ± 0.14 | 246 ± 8 | 1.59 ± 0.07 | – | 30.0 ± 0.7 |
| Observed values | 119 ± 3 | 1460 ± 60 | 610 ± 40 | 1.85 ± 0.08 | 5.01 ± 0.19 | 235 ± 6 | 1.68 ± 0.08 | 1.46 ± 0.06 | 32.2 ± 0.9 |

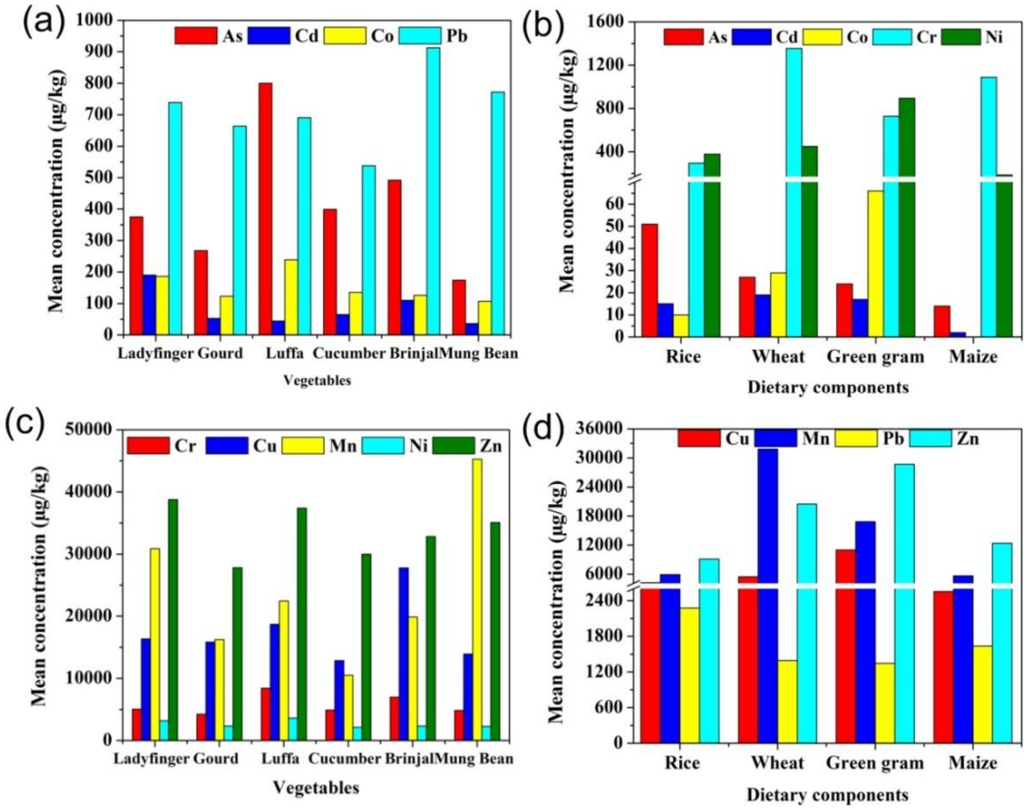

**Fig. 6.2.** (**a**) the concentration of As, Cd, Co and Pb in vegetables (**b**) concentration of As, Cd, Co, Cr and Ni in dietary components (**c**) concentration of Cr, Cu, Mn, Ni and Zn in vegetables (**d**) concentration of Cu, Mn, Pb and Zn in dietary components

for all food components than Bombay (mean values in cereals, pulses, leafy vegetables and other vegetables were 19,043.5, 19,718.2, 4811.0 and 1938.8 µg/kg dry wt., respectively) (Tripathi et al., 1997). The highest concentration of Zn was observed in vegetables with a mean and range values of 35413 (22191–8059) µg/kg, dry wt. The mean Zn concentration in this study was higher for vegetables, rice, wheat, maize and green gram were higher than Bombay, India with mean values in cereals, pulses, leafy vegetables and other vegetables being 19,043.5, 19,718.2, 4811.0 and 1938.8 µg/kg dry wt., respectively (Tripathi et al., 1997). The mean Zn concentrations in vegetables grown in Varanasi, India in palak, lady finger (okra) and cauliflower were 38.40, 34.69 and 51.56 µg/kg, respectively (Sharma et al., 2009).

### *6.3.3. Correlation analysis*

A correlation matrix of As and other elements found in groundwater and food components was measured (**Fig. 6.3** and **Fig. 6.4**). Significant correlation was found As and Co ($p < 0.01$), indicating their similar source of geogenic origin and mobility but the poor correlation between As and Mn shows the presence of the reducing conditions in the source aquifer (**Fig. 6.3**). A poor and insignificant correlation of As with Se and Zn was also observed. Selenium is an important element of the human body which prevents the cytotoxic effect of As (Ahsan et al., 2009). Since the water is assumed as the principle source of essential nutrients hence the general deficiency of Se and Zn in water can decrease the nutrient level in the human body hence increase the As toxicity which results in an increase in As related health diseases. Significant correlation was also observed between Co and Mn (0.73, $p < 0.01$), indicating their geogenic source and Pb and Cr (0.91) to their anthropogenic insertion to the system.

For food components (**Fig. 6.4**), a significant positive correlation of As was observed with almost all metals (Cd, Co, Cr, Cu, Ni and Zn) and a significant negative correlation was ob-served with Pb. This correlation indicates that in the food components all the metals has a common source excluding Pb. Except Pb, all metals also have a significant positive correlation with each other. Mn also shows the less significant correlation among all metals. It is often not recognized that toxic elements present in water are often 100% bioavailable although the toxicity of elements ingested will depend on their chemical species, for instance, As(III) (arsenite) being more toxic than As(V) (arsenate) (Mandal and Suzuki, 2002). Both bioavailability and toxicity are further impacted by the presence of other contaminants that may either enhance the severity of toxicity or reduce it depending on the nature of chemical species. A strong interaction of As and Se was reported earlier (NRC, 1999).

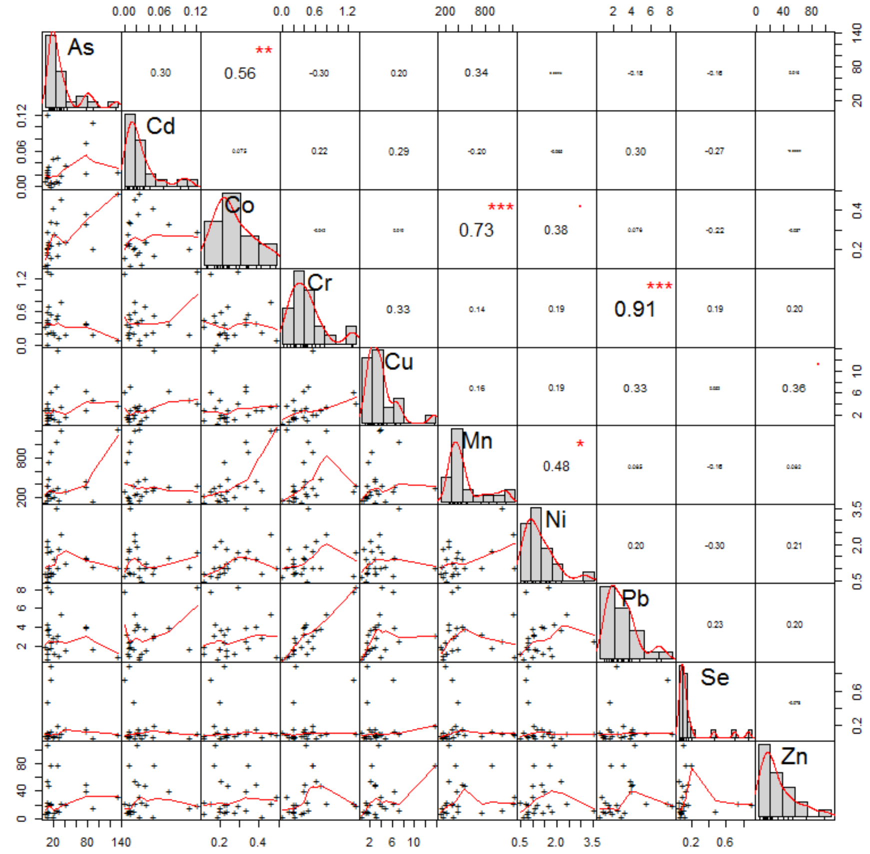

**Fig. 6.3.** Correlation coefficients of elements in groundwater samples

Research on humans shows that Se may reduce the accumulation of As in the organism and protect against As related skin lesions (Zwolak and Zaporowska, 2012). It was reported that the lack of Se and Zn in food and drinking water of Bengal delta regions of Bangladesh and India might magnify As toxicity (Frisbie et al., 2002). A study from Bangladesh shows that spirulina extract plus Zn removed 47% of As from scalp hair and may be useful for the treatment of arsenical skin lesion such as melanosis and keratosis (Misbahuddin et al., 2006).

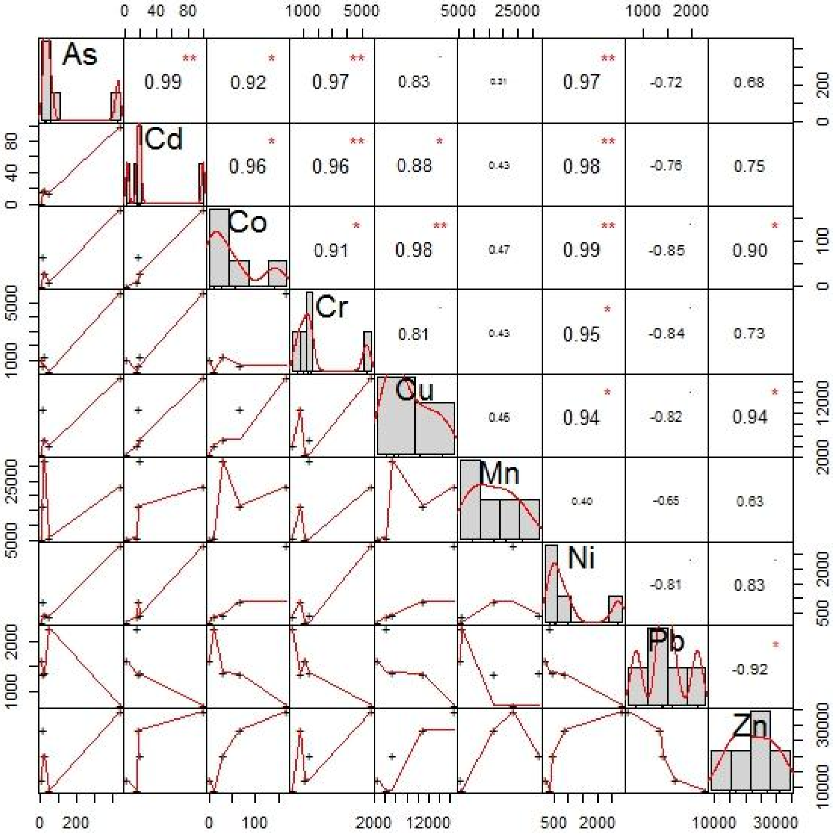

**Fig. 6.4** Correlation coefficients of elements in dietary components

### *6.3.4. Factor analysis*

For groundwater, five independent factors were considered, which described 85.81% of the cumulative variance. The principal component plot of groundwater in rotated space represented in (**Fig. 6.5a**). Factor 1 was responsible for 22.32% of the cumulative variance with positive loading on As, Co and Mn. This factor indicated strong association and shows the common source of As, Co and Mn in groundwater, attributed to the geogenic processes representing background concentration of As, Co and Mn in groundwater. Cobalt usually occurs in the environment in association with other metals such as Cu, Ni, Mn, and As. Factor 2 shows 44.42% of the cumulative variance with positive loading on Cr and Pb, explains the anthropogenic influence of these trace metals in groundwater. The

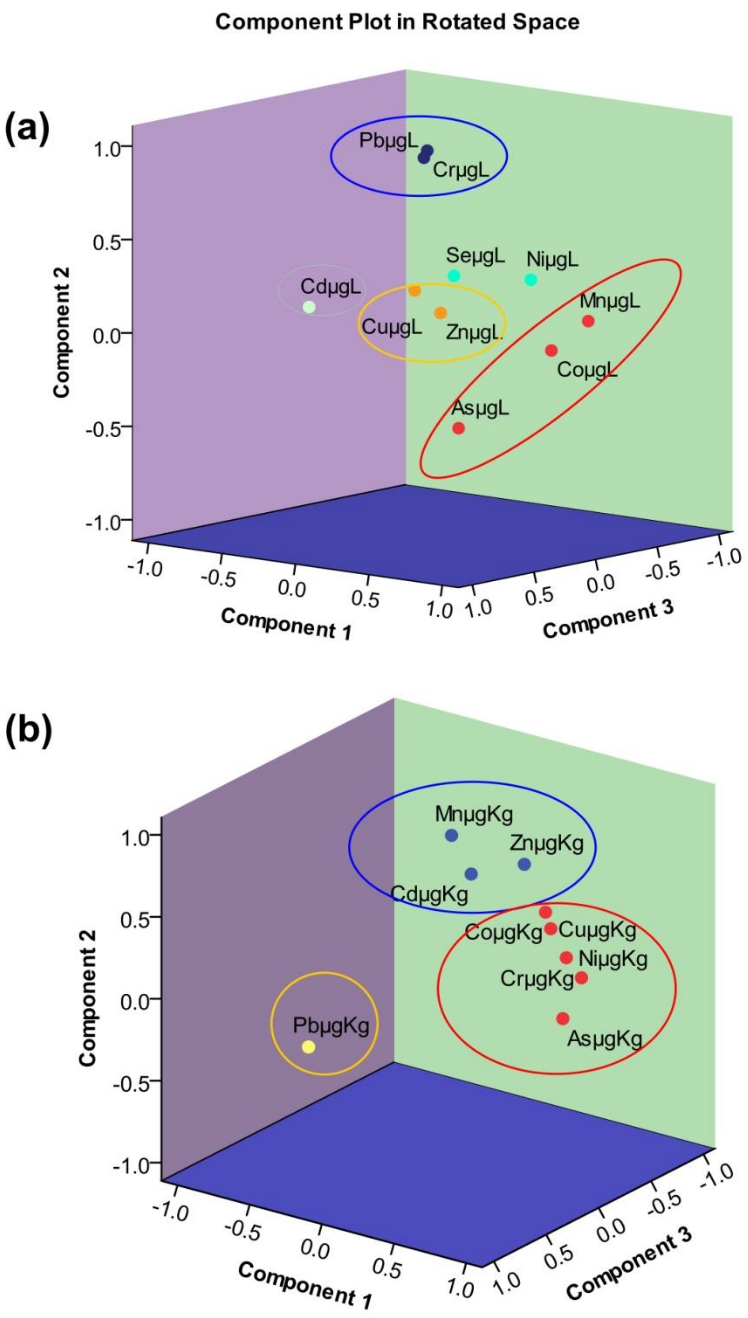

**Fig. 6.5.** Multivariate factor analysis; principal component analysis (PCA) plots in rotated space **(a)** groundwater **(b)** dietary components

major contributor of Cr to the environment is the vehicular exhaust, coal combustion while for Pb the sources may be vehicle exhaust, incinerator and metals industry (Wu et al., 2007). Factor 3 shows 59.03% of the cumulative variance with positive loading on As and Cd. This factor may be attributed to the anthropogenic source via agrochemicals and fossil fuel combustions. Factor 4 indicates 73.14% of the cumulative variance with positive loading on Cu and Zn. This factor attributed the presence of diffused anthropogenic activities (viz. municipal discharge, city runoff and vehicular emission) (Kumar et al., 2015) while Factor 5 indicates 85.81% of the cumulative variance with the negative loading on Ni and positive loading on Se. A negative correlation was also observed between Ni and Se. The concentration of Ni was observed 0.5–3.53 µg/L might have some influence from industrial effluents. Thus, factor analysis indicates the multiple sources and processes controlling the overall concentrations of metals in groundwater.

For food components, three independent factors were considered, which described 78.26% of the cumulative variance. The principal component plot of groundwater in rotated space represented in (**Fig. 6.5b**). Factor 1 was responsible for 38.40% of the cumulative variance with positive loading on As, Co, Cr, Cu and Ni. This factor indicated strong associations on As, Co, Cr, Cu and Ni (0.71–0.90) in food components which explains the combination of geogenic and anthropogenic sources for their origin. The well-known source of As in the study area is geogenic. The source of metals like Cr and Cu knew as the vehicular exhaust, for Ni as industrial oil combustion (Wu et al., 2007), and some amount of As might contribute from agrochemicals used in the agricultural practices. Factor 2 shows 66.86% of the cumulative variance with positive loading on Cd,

Co, Mn and Zn, may be attributed to anthropogenic sources like industrial emission and vehicular exhaust (Kumar et al., 2015). Factor 3 shows 78.26% of the cumulative variance with positive loading on Pb only, a significant negative correlation of Pb also observed among all metals (**Fig. 6.4**), the correlation and PCA results indicate the anthropogenic source of Pb to the study area, probable source may be effluents from an incinerator and metal industry from local or somewhere else.

### *6.3.5. Arsenic concentration in uncooked and cooked rice*

The mean, median and range of 15 uncooked rice samples were 51, 58 and 2.51–132.2 µg/kg dry wt., respectively; while for cooked samples, it was 119, 77 and 10.5–727.7 µg/kg dry wt., respectively. The results indicated twelve (80%) out of 15 cooked rice samples had higher As concentration than uncooked rice (**Fig. 6.6**). The reason may be the presence of higher As concentration in household water used for cooking (average concentration of As in rice cooking water was 36 µg/L; range: 6–135 µg/L). In a study, As concentration in raw rice samples for Bhawangola-I, Chakdha, and Khejuri blocks in West Bengal were 120, 160 and 120 µg/kg, respectively (Mondal et al., 2010). A much higher concentration of As (496 µg/kg) in rice was observed in Bangladesh (Meharg and Rahman, 2003). Low As concentration was also observed in another Bangladeshi study when compared cooked and uncooked rice as rice was cooking with low As the concentration of pond water (Rahman et al., 2011). It was reported that average As the concentration of 340 and 460 µg/kg in uncooked and cooked rice samples, respectively (Ohno et al., 2007). In two previous studies (Ohno et al., 2007, 2009) conducted in the highly As-contaminated Chapai Nawabganj district of Bangladesh, results revealed the presence of larger concentrations of As in cooked rice samples compared to uncooked rice samples, which suggested that As in cooking water affected the concentration after cooking.

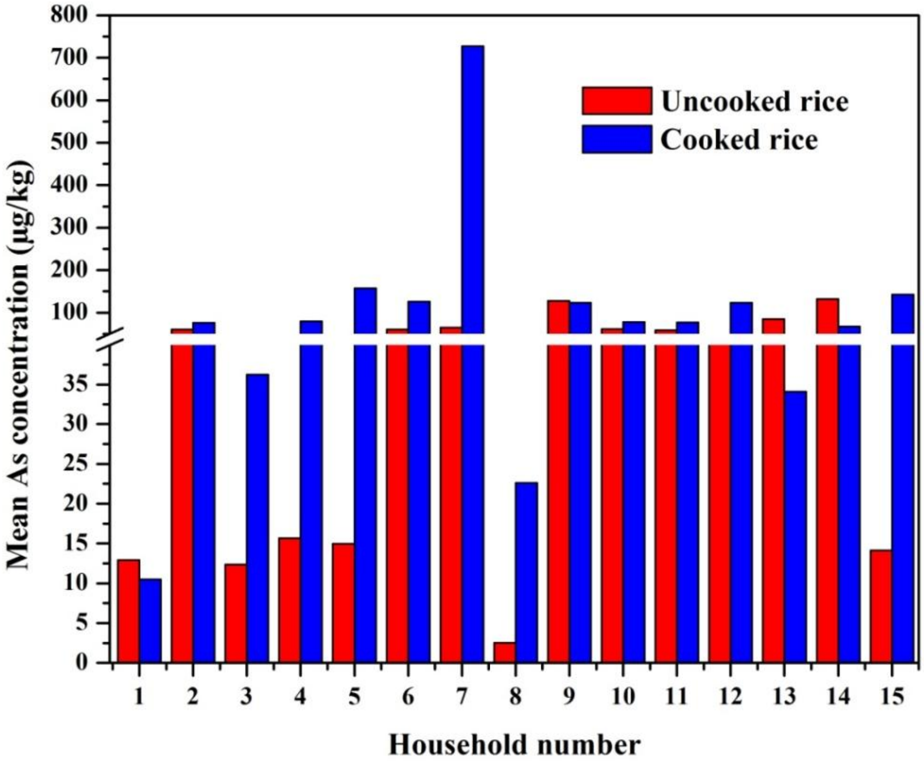

**Fig. 6.6.** Comparisons of As concentration in uncooked and cooked rice

There was a significant difference in As concentration for uncooked and cooked rice samples. In this study, a few uncooked rice samples also showed less concentration than cooked rice samples (sample #1, #9, #13 and #14).

### *6.3.6. Estimated daily intake and risk assessment of As and other elements through consumption of water, vegetables and other food components*

The total daily intake of As and other elements from drinking water, vegetables and other dietary components including the mean daily serving of water and food components and their corresponding concentrations of elements are presented in **Table 6.4**. The calculated daily As intakes from drinking water, vegetables, rice, wheat, maize and green gram were 116.67, 23.96, 19.59, 7.09, 0.96 and 1.11 µg, respectively. In this study, an adult consumes 169 µg of As from drinking water and other dietary components. Access to drinking water facilitates daily exposure to As. Vegetable, rice and wheat also made a significant contribution to daily As intake. The average consumption of As through drinking water was 120 µg/day and 320 µg/day for 5–10-year old children and subjects older than 41 years from Rampur Daira, Bihar, India respectively, and for Haldichapra, Bihar, these values were 580 µg/day and 1470 µg/day, respectively (Singh and Ghosh, 2012), which is higher than this study.

**Table 6.4**
Daily intake of As, Mn and other elements from water, vegetables, rice, wheat, maize and green gram

| Elements | Water[1] | | | Vegetables[2] | | | Rice[3] | | | – |
|---|---|---|---|---|---|---|---|---|---|---|
| | Mean daily serving (L) for adults | Mean concentration (µg) | Daily total Intake (µg) | Mean daily serving (kg) for adults (dry wt.) | Mean concentration (µg /kg) | Daily total Intake (µg) | Mean daily serving (g) for adults | Mean concentration (µg/kg) | Daily total Intake (µg) | – |
| As | 3.63 | 32.14 | 116.67 | 0.053 | 452 | 23.96 | 0.378 | 51 | 19.59 | – |
| Cd | | 0.08 | 0.29 | | 102 | 5.41 | | 19 | 7.18 | – |
| Co | | 0.26 | 0.94 | | 173 | 9.17 | | 10 | 3.78 | – |
| Cr | | 0.47 | 1.71 | | 5823 | 308 | | 294 | 111 | – |
| Cu | | 3.51 | 12.74 | | 17253 | 914 | | 4255 | 1608 | – |
| Mn | | 451 | 1637 | | 24040 | 1274 | | 5928 | 2240 | – |
| Ni | | 1.36 | 4.94 | | 2921 | 154.8 | | 378 | 143 | – |
| Pb | | 3.19 | 11.58 | | 717 | 38 | | 2277 | 861 | – |
| Zn | | 30.82 | 112 | | 35413 | 1876 | | 9123 | 3448 | – |
| Elements | Wheat[4] | | | Maize[5] | | | Green gram[6] | | | Combined 1+2+3+4+5+6 |
| | Mean daily serving (kg) for adults | Mean concentration (µg/kg) | Daily total Intake (µg) | Mean daily serving (kg) for adults | Mean concentration (µg /kg) | Daily total Intake (µg) | Mean daily serving (kg) for adults | Mean concentration (µg/kg) | Daily total Intake (µg) | Daily intake from water, vegetable, rice, wheat, maize and green gram (µg) |
| As | 0.259 | 27.36 | 7.09 | 0.0792 | 13.74 | 0.96 | 0.0470 | 23.67 | 1.11 | 169 |
| Cd | | 18.77 | 4.86 | | 1.7 | 0.12 | | 16.71 | 0.79 | 19 |
| Co | | 33 | 8.55 | | 3.71 | 0.26 | | 65.68 | 3.09 | 26 |
| Cr | | 1354 | 351 | | 1087 | 76 | | 728 | 34.22 | 882 |
| Cu | | 5459 | 1413 | | 2554 | 179 | | 10990 | 516 | 4645 |
| Mn | | 31821 | 8241 | | 5664 | 396 | | 16857 | 792 | 14582 |
| Ni | | 449 | 116 | | 187 | 13.09 | | 894 | 42 | 474 |
| Pb | | 1395 | 361 | | 1636 | 115 | | 1345 | 62 | 1449 |
| Zn | | 20474 | 5303 | | 12373 | 866 | | 28707 | 1349 | 12955 |

The total estimated average intake of As from leafy and non-leafy vegetables in Samta, Bangladesh was 27.78 µg/day (Alam et al., 2003) while in Noakhali, Bangladesh the average daily intake of As from leafy and non-leafy vegetables was 2.3 µg/day for adults (Rahman et al., 2013). In this study, the average daily intake of As from vegetables was lower than Samta but much higher than Noakhali. The contribution of each category to the total daily As intake was drinking water (67%), vegetables (15%), rice (12%), wheat (4%), maize (1%) and green gram (1%) (**Fig. 6.7a**). In this study, speciation of As in water and food components were not included. Groundwater usually contains 100% inorganic As in the Ganges plain, whereas the total As in food components analyzed is usually a combination of inorganic and less toxic methylated As species (Williams et al., 2005, 2006).

It was reported that inorganic As is predominant in rice and only a small percentage of DMA is also found in rice (Williams et al., 2005). Only inorganic forms of As were found in vegetables (Williams et al., 2006). Therefore, we can assume that the food components included in this study contained a substantial percentage of inorganic As.

As per JECFA, the provisional tolerable daily intake (PTDI) value of As was 2.1 µg per kg bw, which was withdrawn in 2011. Based on the average bw (45 kg) of an adult from Bangladesh, which was used in the previous study (Rahman et al., 2013) a plot of estimated exposure of elements (µg per kg bw) from drinking water and food components in Samastipur, Bihar was plotted (**Fig. 6.8**). It can be observed from the plot that drinking water and food components contribute 3.76 µg of As per kg bw daily. Drinking water, vegetables and rice contribute 2.52 µg, 0.52 µg and 0.44 µg, respectively, of As per kg bw daily. Calculated daily Cd intake from drinking water, vegetables, rice, wheat, maize and green gram were 0.29, 5.41, 7.18, 4.86, 0.12 and 0.79 µg, respectively (**Table 6.4**). Daily total Cd concentration from all dietary components was 19 µg. The daily intake of Cd from vegetables reported in this study was half that of Samta (9.5 µg), Bangladesh (Alam et al., 2003) but much higher than Noakhali (2.9 µg), Bangladesh (Rahman et al., 2013). So, an adult consumes 0.41 µg of Cd per kg bw daily from water and food. The provisional daily weekly intake (PTWI) of Cd is 7 µg per kg bw. Rice, vegetables and wheat contribute major daily exposure to Cd at 34%, 31% and 29%, respectively (**Fig. 6.7b**).

The daily intakes of Co from drinking water, vegetables, rice, wheat, maize and green gram were 0.94, 9.17, 3.78, 8.55, 0.26 and 3.09 µg, respectively, and the total intake was 26 µg from all dietary components. Thus, an adult consumes 0.57 µg of Co per kg bw daily from water and food (**Fig. 6.8**). The total estimated intakes of Co from vegetables and water were 4.4 and 0.36 µg, respectively in Noakhali, Bangladesh (Rahman et al., 2013) which is lower than that this study. Major contributors of Co in the diet are vegetables (36%) and wheat with 31% (**Fig. 6.7c**). Drinking water made a much lower contribution (1.66 µg) to the daily dietary intake of Cr in Samastipur. The daily Cr intakes from vegetables, rice, wheat, maize and green gram were 308, 111, 351, 76, and 34.22 µg, respectively. The total Cr intake from all dietary components was 882 µg. Wheat and vegetables made up the bulk of the diet with 40% and 34%, respectively (**Fig. 6.7d**). Daily dietary intake of Cu from water, vegetables, rice, wheat, maize and green gram were 12.74, 914, 1608, 1413, 179 and 516 µg, respectively. The estimated daily dietary intake of Cu from all composite food was 4645 µg (**Table 6.4**). Thus, water and food components contribute 103.22 µg of Cu per kg bw daily. The estimated daily Cu intake in this study was comparable with that of a study conducted from Samta, Bangladesh (Alam et al., 2003) and double that of another study conducted in Noakhali, Bangladesh (Rahman et al., 2013). Rice and wheat constitute the major proportion of Cu in people's daily diets (**Fig. 6.7e**). Wheat was the major contributor of Mn with 57% of the total intake from all composite food (**Fig. 6.7f**). The daily Mn intakes from water, vegetable, rice, wheat, maize and green gram were 1637, 1274, 2240, 8241, 396 and 792 µg, respectively (total Mn intake was 14,582 µg from water and food). Therefore, water and food components contribute 324.05 µg of Mn per kg bw daily. The

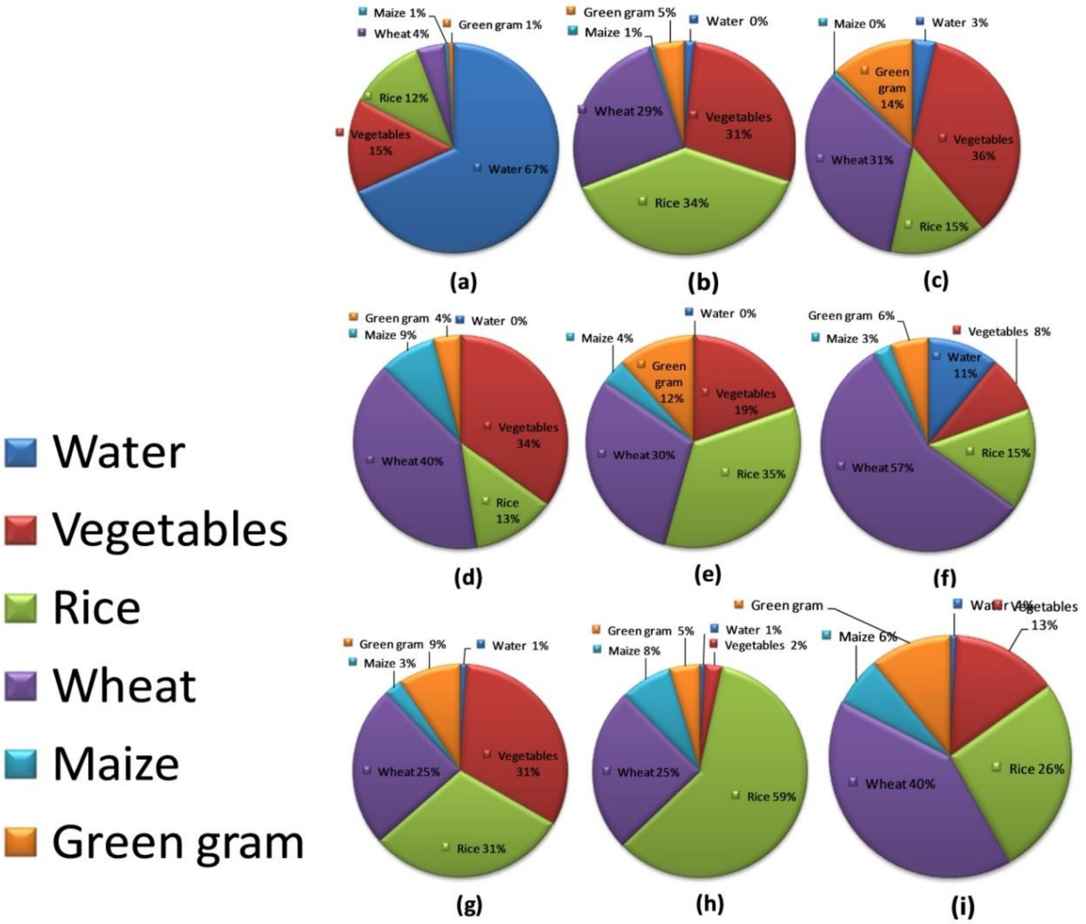

**Fig. 6.7**. The contribution of each category of the total daily intake of elements (**a**) As (**b**) Cd and (**c**) Co (**d**) Cr (**e**) Cu, (**f**) Mn, (**g**) Ni (**h**) Pb and (**i**) Zn

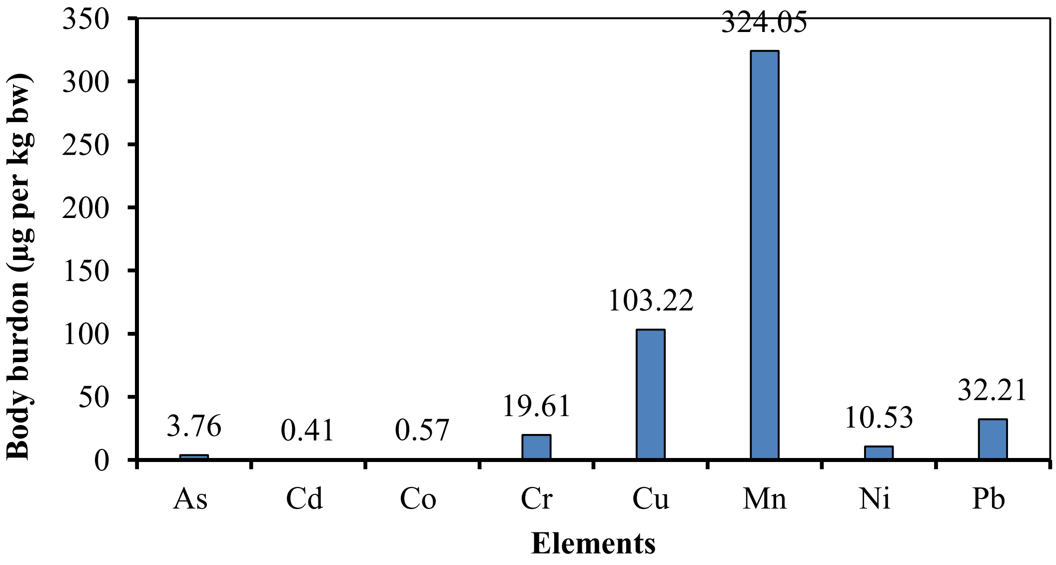

**Fig. 6.8.** Estimated exposure of elements (µg per kg bw) from drinking water and food components in Samastipur, Bihar

calculated daily intakes of Mn from vegetables and water were 1.7 and 0.336 µg in Noakhali, Bangladesh (Rahman et al., 2013). The calculated daily intakes of Mn from vegetables and water were 1.7 and 0.336 µg in Noakhali, Bangladesh (Rahman et al., 2013). Water contributed only a negligible amount of Ni to daily intake to the residing population. The daily total Ni intake from all food components was 474 µg with contributions from vegetables, rice, wheat, maize and green gram were 154.8, 143, 116, 13.09 and 42 µg, respectively. Thus, water and food components contribute 10.53 µg of Ni per kg bw daily. The daily intake of Ni from vegetables and water were 0.046 and 0.049 µg, respectively in Noakhali, Bangladesh (Rahman et al., 2013), which is lower than this study. Vegetables and rice contribute the same amount of Ni to daily dietary intake (**Fig. 6.7g**).

Daily dietary intakes of Pb from water, vegetables, rice, wheat, maize and green gram were 11.58, 38, 861, 361, 115 and 62 µg, respectively (total intake was 1449 µg). Thus, water and food components contribute 32.21 µg of Pb per kg bw daily. Rice (59%) and wheat (25%) contribute the major daily dietary intake of Pb (**Fig. 6.7h**). Daily dietary intakes of Zn from water, vegetable, rice, wheat, maize and green gram were 112, 1876, 3448, 5303, 866 and 1349 µg, respectively (total intake 12,955 µg). So, water and food components contribute 287.9 µg of Zn per kg bw daily. The total intakes from vegetables and water of Noakhali, Bangladesh were 1300 and 23,100 µg, respectively (Rahman et al., 2013). Wheat (40%) and rice (26%) contribute a major source of daily dietary intake of Zn (**Fig. 6.7i**).

### *6.3.7. Health risk index*

The CDI and HRI of elements through the consumption of water and food chain by adults are presented in **Table 6.5**. It appears that HRI values exceed safe limit 1 for As in drinking water, vegetable and rice (**Fig. 6.9**) with a value of 8.6E+00, 1.8E+00 and 1.4E+00 respectively while the values were <1 for other dietary components like wheat, maize and green gram (**Table 6.5**). The

**Table 6.5**
Estimation of CDI and HRI for individual element by consumption of water and different food components by adults

| Elements | Index | As | Cd | Co | Cr | Cu | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| Drinking | CDI | 2.6E-03 | 6.5E-06 | 2.1E-05 | 3.8E-05 | 2.8E-04 | 3.6E-02 | 1.1E-04 | 2.6E-04 | 2.5E-03 |
| water | HRI | 8.6E+00 | 1.3E-02 | 1.0E-03 | 2.5E-05 | 7.1E-03 | 1.5E+00 | 5.5E-03 | 5.1E-02 | 8.3E-03 |
| Vegetables | CDI | 5.3E-04 | 1.2E-04 | 2.0E-04 | 6.9E-03 | 2.0E-02 | 2.8E-02 | 3.4E-03 | 8.4E-04 | 4.2E-02 |
|  | HRI | 1.8E+00 | 2.4E-01 | 1.0E-02 | 4.6E-03 | 5.1E-01 | 1.2E+00 | 1.7E-01 | 1.7E-01 | 1.4E-01 |
| Rice | CDI | 4.3E-04 | 1.6E-04 | 8.4E-05 | 2.5E-03 | 3.6E-02 | 5.0E-02 | 3.2E-03 | 1.9E-02 | 7.7E-02 |
|  | HRI | 1.4E+00 | 3.2E-01 | 4.2E-03 | 1.6E-03 | 8.9E-01 | 2.1E+00 | 1.6E-01 | 3.8E+00 | 2.6E-01 |
| Wheat | CDI | 1.6E-04 | 1.1E-04 | 1.9E-04 | 7.8E-03 | 3.1E-02 | 1.8E-01 | 2.6E-03 | 8.0E-03 | 1.2E-01 |
|  | HRI | 5.2E-01 | 2.2E-01 | 9.5E-03 | 5.2E-03 | 7.9E-01 | 7.6E+00 | 1.3E-01 | 1.6E+00 | 3.9E-01 |
| Maize | CDI | 2.1E-05 | 2.6E-06 | 5.8E-06 | 1.7E-03 | 4.0E-03 | 8.8E-03 | 2.9E-04 | 2.5E-03 | 1.9E-02 |
|  | HRI | 7.1E-02 | 5.3E-03 | 2.9E-04 | 1.1E-03 | 9.9E-02 | 3.7E-01 | 1.5E-02 | 5.1E-01 | 6.4E-02 |
| Greengram | CDI | 2.5E-05 | 1.7E-05 | 6.9E-05 | 7.6E-04 | 1.1E-02 | 1.8E-02 | 9.3E-04 | 1.4E-03 | 3.0E-02 |
|  | HRI | 8.2E-02 | 3.5E-02 | 3.4E-03 | 5.1E-04 | 2.9E-01 | 7.3E-01 | 4.7E-02 | 2.8E-01 | 1.0E-01 |

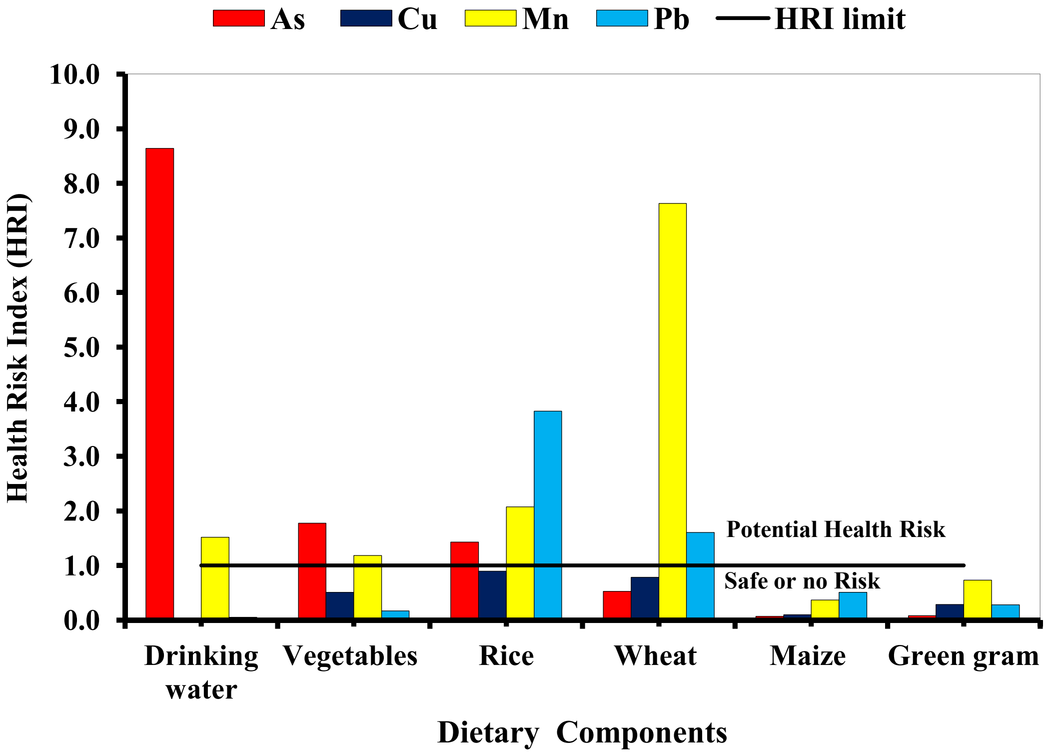

**Fig. 6.9.** Health risk index for As, Cu, Mn and Pb

concentration of As in drinking water, vegetables and rice were also higher than dietary components (viz. wheat, maize and green gram). It shows that drinking water, vegetables and rice may cause As health risk to the study population. In a previous study, the HRI values in the case of As contaminated groundwater at Rampur Diara and Haldichapra, Bihar, India were found to be between 13.6–46.4 and 65.5–219.5, respectively (Singh and Ghosh, 2012). The HRI values for Mn varies from 1.2E+00 to 7.6E+00 for drinking water, vegetable, rice and wheat while for Pb it was 3.8E+00 and 1.6E+00 for rice and wheat respectively. It can be concluded that rice is more contaminated having a higher concentration of As, Mn and Pb. The HRI values were >1 with respect to all metals for remaining food components (Fig. 6.10). Therefore, the health risk of heavy metals exposure through water and food chain was of no consequences and assumed to be safe.

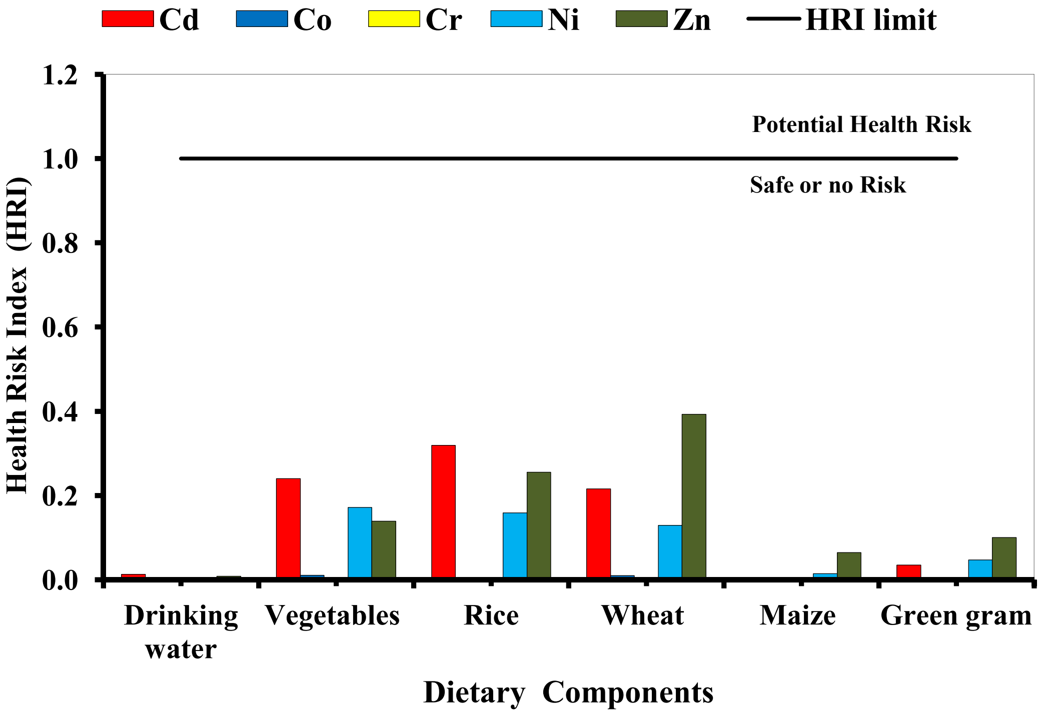

**Fig. 6.10.** Health risk index for Cd, Co, Cr, Ni and Zn

## 6.4. Conclusions

This study revealed that 88% of the tubewell water samples exceeded the recommended level of As (10 μg/L) set by the WHO and BIS. It also appears that 26% of the water samples had Mn above the US-EPA recommended value. Other examined elements in groundwater were below the WHO guideline values. The concentrations of As and other elements in vegetables and other dietary components varied extensively. Vegetables were found to be enriched in As and other elements. Cooked rice samples were found to have more As contamination than uncooked rice samples due to higher As concentration in water used for cooking purposes. Drinking water contributed the major fraction (67%) of daily dietary As intake, and the remaining intakes were from other food components. Rice emerged as a major contributor for Cd, Cu, Pb and Ni while wheat was found to be a major contributor for Mn, Cr and Zn in the population's daily dietary intake. Vegetables served as a major contributor of Co and Ni to the daily dietary intake. The PCA revealed that the source of As is natural whereas diffused anthropogenic activities were responsible for other elements. The study also found the potential health risks for As in drinking water, vegetables and rice, for Mn in drinking water, vegetables, rice and wheat, for Pb in rice and wheat. The HRI for other estimated metals were b1, indicating the relative absence of health risk associated with the consumption of contaminated food.

Although we collected various types of commonly consumed food components from the study area, they are not representative of all vegetables consumed by the populations in other areas of CGB. The daily intakes of other elements from other food sources such as cooked food need to be evaluated to determine the actual exposure to As and other elements better to evaluate the health risk of this section of the population. This study included small sample size for water and other food components; future studies should focus on appropriate sample size and more food components. Although As is the major concern for the study area, food surveys in the Ganga plain should not be restricted to As alone; other elements also need to be regularly monitored.

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# Chapter 7

# Summary and conclusions

The current study was performed on a regional scale on geocehmical triggers for groundwater and sediments on arsenic (As) and other solutes fate along regional groundwater flowpath through different geomorphic terrain in parts of the central Gangetic Basin (CGB). Geomorphology and flowpaths seem to have a substantial influence on solute chemistry and As distribution. Three major geomorphic units (Piedmont, Older Alluvium and Younger Alluvium) were identified and demarcated with the help of remote sensing, available lithologs and field observations. The groundwater of Piedmont has nearly neutral pH with Ca-$HCO_3^-$ water types while in Younger and Older Alluvium type of water ranged from Ca-$HCO_3^-$ to Na-$HCO_3^-$. Furthermore, Ca-Mg-Cl type had slightly alkaline pH. A median concentration of As 0.2 (15 µg/L) and 0.12 µM (9 µg/L) were observed in Piedmont and Younger Alluvium, respectively, while 0.02 µM (1.5 µg/L) was evident in Older Alluvium. The median concentrations of As in the core sediments of Piedmont (up to 57mbgl), Older Alluvium (up to 42.6 mbgl) and Younger Alluvium (33.5mbgl) were observed as 0.07, 0.15 and 0.15 molal concentrations, respectively. Aquifers indicated the existence of anoxic to post-oxic conditions in all three geomorphic units. Almost 70% of the groundwater samples fell in $As(OH)_3$/ As(III) field and reaming (30%) in field of $HAsO_4^{2-}$ / As(V). In pe-pH plot ~60% of the samples fell in FeOOH field and 40% fell in $Fe^{2+}$ field.

Cation exchange played an important role in Piedmont and Older Alluvium while carbonate dissolution in Younger Alluvium served to control the groundwater solute chemistry. The groundwater is in the equilibrium with kaolinite, Ca-smectite, Na-smectite and orthoclase but showed disequilibrium with anorthite and albite, which could be the major source of $Ca^{2+}$ and $K^+$ to the solute in the groundwater via silicate weathering. These results of weathering and flowpaths were also supported by inverse geochemical modelling applied to the data. The inverse grochemical modelling results indicated that water in different geomorphic units i.e. Piedmont, Older and Younger Alluvium evolved by different geochemical processes. The groundwater is governing by silicate weathering and carbonate dissolution and the evolution was also affected by local and regional flowpath followed by the groundwater along with mixing and other ion exchange reactions. Dissolution of Fe-Mn (oxyhydr)oxide and competitive exchange were suggested as the most likely mechanism for As liberation in Piedmont while multiple/ complex processes control the mobilization and of As in Younger Alluvium.

The study further investigated the groundwater in the aquifers with respect to recharge process and dissolved organic carbon (DOC) behaviour of in this area by using stable isotopes. Records of ($\delta^2$H and $\delta^{18}$O) revealed that groundwater of Piedmont had been recharged by meteoric origin before evaporation while aquifers of Older and Younger Alluvium had been recharged with water which has undergone little evaporation loss. River Ganges and its tributaries passing through this area have a little contribution in recharging while ponds are playing no role in recharging the adjoining aquifers.

This is also supported by previous studies which found no or minimal leaching of DOC to the aquifers from the ponds. Shallow aquifer of Piedmont has very less connectivity with the deeper aquifer. The connectivity of the shallow aquifers of aquitard formation (25–60m bgl) with the main upper aquifer at the depth of (> 120m bgl) was found to be higher in Older and Younger Alluvium. Depleted $\delta^{13}C$ (median -9.57‰; range -13.21 to -5.4) and low DOC (median 1.35 mg/L; range 0.99–1.77mg/L) indicated acceleration in microbial activities in the Younger Alluvium especially in the active floodplain of the river Ganges and its proximity. In deeper aquifers (> 120m bgl,) of Younger Alluvium and both shallow and deeper aquifers of Older Alluvium the groundwater was found to be enriched with $\delta^{13}C$ coupled with the significant concentration of DOC indicated limit microbial activity in these formations.

Approximately 73% of the groundwater samples (n=19) shows As(III) as the dominant species while 27% reveals As(V) is the dominant species. The concentration of As(III) in agricultural soil samples varies from not detectable (nd) to 40 µg/kg and As(V) was observed as the major species (ranging from 1050 to 6835 µg/kg) while the total As concentration varied from 3528 to 14690 µg/kg. The subsurface sediment of Older Alluvium contains a low range As(III) from (nd–264.2 µg/kg) whilst in Younger Alluvium it was a bit higher (nd–368.5 µg/kg) indicating comparatively more reducing conditions of the aquifer. Total extracted concentration of As was higher in the subsurface sediment (range 9119–20056 µg/kg in Older Alluvium and 4788–19681 µg/kg in Younger Alluvium) than the agricultural soil, indicating the subsurface sediment are in situ source to soils. Results of XRD and ESEM revealed the presence of hematite and goethite throughout the vertical depth while magnetite was observed only in the upper oxidized layer at Methrapur and Harail Chapar. Alteration of Fe-oxides and presence of fibrous goethite shows the presence of diagenetic sediment indicating partial solubilization of oxyhydroxides in this area. Siderite playing a role as sinks to the As in subsurface sediments. The study also concluded that microbially mediated decomposition of organic matter which is present in dark and grey sections of the aquifer promote the redox conditions and trigger mobilization of As into groundwater.

The PCA and correlation analysis revealed that the source of As is natural, whereas diffused anthropogenic activities were responsible for other elements. In order to calculate the risk, the concentrations of the trace elements present in groundwater were compared with the latest national and international guideline and standards set by WHO and BIS. Groundwater data shows that most of the tubewell water samples exceeded the recommended level of As (10 µg/L) set by the WHO (2011) and BIS (2012), particularly in Piedmont and Younger Alluvium. It was also observed that a considerable groundwater samples had Mn above the US-EPA recommended value (500 µg/L). Other examined elements in groundwater were below the latest WHO guideline and BIS standard values. The concentrations of As and other elements in vegetables and other dietary components varied extensively. Vegetables were found to be enriched in As and other elements. Cooked rice samples were found to have more As contamination than uncooked rice samples due to higher As concentration in water that are used for cooking purposes. Drinking water contributed the major fraction (67%) of daily dietary As intake and the remaining intakes were from other food components. Rice emerged as a major contributor for Cd, Cu, Pb and Ni while wheat was found to be a major contributor for Mn, Cr and Zn in the population's daily dietary intake. Vegetables served as a major contributor of Co and Ni to the daily dietary intake. The study also found the potential health risks for As in drinking water, vegetables and rice, for Mn in drinking water, vegetables, rice and wheat, for Pb in rice and wheat. The HRI for other estimated metals were b1, indicating the relative absence of health risk associated with the consumption of contaminated food.

Although we collected various types of commonly consumed food components from the study area but they are not representative of all vegetables consumed by the populations in other areas of CGB. The daily intakes of other elements from other food sources such as cooked food need to be evaluated to determine the actual exposure to As and other elements to better evaluate the health risk of this section of the population. This study included small sample size for water and other food components, future studies should focus on appropriate sample size and more food components. Although As is the major concern for the study area, food surveys in the Ganga plain should not be restricted to As alone; other elements also need to be monitored regularly.

For the current study, a long stretch (~150km) was surveyed and found few novel information. Further study is recommended by covering a wide range of area with systematic and a holistic approach by applying more advanced methodologies to get better outcomes.

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# List of publications

## *List of Publications*

### (I) Paper in peer review Journals (total IF 11.675)

*Already published (6)*

#Manoj Kumar, M.M. Rahman, AL. Ramanathan, Ravi Naidua, 2016. Arsenic and other elements in drinking water and dietary components from the middle Gangetic plain of Bihar, India: Health risk index. Science of the Total Environment-Journal Elsevier. 539; 125–134. DOI http://dx.doi.org/10.1016/j.scitotenv.2015.08.039, ISSN: 0048-9697. (IF 4.099)

Alok Kumar, AL. Ramanathan, M. B. K. Prasad, Dilip Datta, Manoj Kumar, Swati Mohan Sappal. 2016. Distribution, enrichment, and potential toxicity of trace metals in the surface sediments of Sundarban mangrove ecosystem, Bangladesh: a baseline study before Sundarban oil spill of December, 2014. Environmental Science and Pollution Research-Journal Springer. DOI 10.1007/s11356-016-6086-6. (IF 2.828)

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Virendra Bahadur Singh, AL. Ramanathan, Jose George Pottakkal, Manoj Kumar. 2014. Seasonal variation of the solute and suspended sediment load in Gangotri glacier meltwater, central Himalaya, India. Journal of Asian Earth Sciences-Journal Elsevier. 79, 224–234. ISSN: 1367-9120. http://dx.doi.org/10.1016/j.jseaes.2013.09.010 (IF 2.741)

Virendra Bahadur Singh, AL. Ramanathan,Jose George Pottakkal, Manoj Kumar, 2015. Hydrogeochemistry of meltwater of the Chaturangi glacier, Garhwal Himalaya, India. Springer, PNAS, India Section A: Physical Sciences. 85(1): 187–195. Online ISSN 2250-1762. (IF 0.242)

AL. Ramanathan, Manoj Kumar, Mukesh Kumar, Alok Kumar, Pankaj Kumar, Manish Kumar, Parijat Tripathi and Prosun Bhattacharya., 2012. Arsenic enrichment in the aquifers of the central Gangetic Plain, India. Journal of Applied Hydrology, Vol. XXV No. 3 & 4, pp. 77-84. ISSN 0971 – 670X. (IF awaited)

*Revised Manuscripts Submitted (2)*

Manoj Kumar, AL. Ramanatahn, Ritu Tripathi, Sandhya Farswan, Devendra Kumar, Prosun Bhattacharya. 2016. A study of trace element contamination using multivariate statistical techniques and health risk assessment in groundwaters of Chhaprola Industrial Area, Gautama Buddha Nagar, Uttar Pradesh, India. Chemosphere-Journal Elsevier, CHEM-XX, June, 2016.

#Manoj Kumar, AL. Ramanathan, Mohammad Mahmudur Rahmana, Ravi Naidu. 2016. Inorganic arsenic toxicity in groundwater, agricultural soils and subsurface sediments from the middle Gangetic plain of Bihar, India. Science of the Total Environment-Journal Elsevier. STOTEN-D-XX, May 2016

*Manuscripts Submitted (4)*

Manoj Kumar, Ritu Tripathi, Prabhat Ranjan, AL. Ramanathan, Prosun Bhattacharya. 2016. Geospatial and multivariate analysis of trace metal in groundwater: concern from rapid urbanization in upper Ganga-Yamuna Alluvial Plain, India. Environmental Earth Sciences-Springer, ENGE-D-XX; Dated: June, 2016.

Manoj Kumar, AL. Ramanatahn, Shyam Ranjan, Prosun Bhattacharya.2016. Groundwater evolution and its utility in upper Ganges-Yamuna Alluvial plain of Northern India, India: Evidence from solute chemistry and stable isotopes. Environmental Earth Sciences-Springer. ENGE-D-XX, June 2016.

#Manoj Kumar, AL. Ramanathan, Abhijit Mukherjee, Ravi Sawlani. 2016. Basin-scale stable isotopic study on groundwater recharge and dissolved organic carbon behaviour in an arsenic-contaminated province of central Gangetic basin, Bihar, India. Journal of Hydrology-Journal Elsevier, HYDROL-S-XX, July, 2016.

#Manoj Kumar, AL. Ramanathan, Abhijit Mukherjee, Mohammad Mahmudur Rahman, Ravi Naidu. Hyrdogeochemical triggers for regional scale arsenic release and fate in the central Gangetic Basin, India. Water Research-Journal Elsevier, WR-S-XX, July, 2016.

## *List of Publications*

*Manuscript under preparation*

Manoj Kumar, Alok Kumar, Naveen Pandey, AL. Ramanathan. Distribution and speciation of arsenic and other selected trace metals (Fe, Mn Zn and Cu) in the sediments of central Gangetic plain: sequential extraction and statistical approach). To be communicated in expected journal "Journal of Geochemical Exploration-Journal Elsevier".

**(II) Book chapters (3)**

#Manoj Kumar, AL. Ramanathan, Alok Kumar, Shailesh Kumar Yadav, 2016. Evolution of Arsenic Contamination Process and Mobilization in Central Gangetic Plain Aquifer System and Its Remedial Measures In Groundwater, Assessment, Modeling And Management (eds.) M.Thangarajan Vijay. P. Singh. CRC Press (A unit of Taylor & Francis Group, UK), ISBN 978-1-4020-5729-8.

#Manoj Kumar, Mukesh Kumar, Alok Kumar, VB Singh, Senthil Kumar, AL. Ramanathan, and Prosun Bhattacharya (2015). Arsenic distribution and mobilization: A case study of three districts of Uttar Pradesh and Bihar (India). In: AL. Ramanathan, Scott Johnston, Abhijit Mukherjee & Bibhash Nath (eds.) *"Safe and Sustainable Use of Arsenic-Contaminated Aquifers in the Gangetic Plain: A Multidisciplinary Approach"* Copublished by Springer, International Publishing, Cham, Switzerland with Capital Publishing Company, New Delhi, India. (ISBN 978-93-81891-08-7), pp. 121-135.

Virendra Bahadur Singh, AL. Ramanathan, P.G.Jose, Manoj Kumar, Parmanand Sharma & Anurag Linda (2011**)**. Hydro-Geochemical characteristics of Gangotri glacier. *Climate change in the Himalayas*, Editors- Vir Singh et al**.** pp. 125-141. IndusPublishing Company, New Delhi, ISBN 978-81-7387-228-0.

**(III) Conference Proceedings chapters with ISBN (3)**

#Manoj Kumar, AL. Ramanathan Prosun Bhattacharya (2014). Evaluation of arsenic and its controlling factors in aquifer sands of district Samastipur, Bihar, India. In: M.I. Litter, H.B. Nicolli, M. Meichtry, N. Quici, J. Bundschuh, P. Bhattacharya and R. Naidu (eds.) *"One Century of the Discovery of Arsenicosis in Latin America (1914–2014) As 2014"*. Interdisciplinary Book Series: *"Arsenic in the Environment—Proceedings"*. Series Editors: J. Bundschuh and P. Bhattacharya, CRC Press/Taylor and Francis Group, London, UK (ISBN 978-1-138-00141-1), pp. 108-109.

#Manoj Kumar, AL. Ramanathan, M.M. Rahman, Ravi Naidu, Prosun Bhattacharya. 2016, June. Arsenic and trace elements in groundwater, vegetables and selected food grains from middle Gangetic plain—human health perspective. In *Arsenic Research and Global Sustainability: Proceedings of the Sixth International Congress on Arsenic in the Environment (As2016), June 19-23, 2016, Stockholm, Sweden* (p. 320). CRC Press.

AL. Ramanathan, Parijat Tripathi, Manoj Kumar, Alok Kumar, Pankaj Kumar, Manish Kumar, Prosun Bhattacharya., 2012. Arsenic in groundwaters of the central Gangetic plain regions of India. In *Understanding the Geological and Medical Interface of Arsenic,* Editors Jack C. Ng et al., CRC Press/Taylor and Francis Group, London, UK (ISBN 978-0-415-63763-3**)**, pp. 63-64**.**

# From my PhD work.

For other information related to paper presentation and achievements, please see update CV append

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# Arsenic and other elements in drinking water and dietary components from the middle Gangetic plain of Bihar, India: Health risk index

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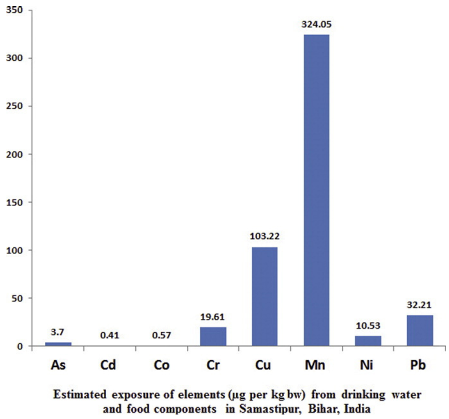
## HIGHLIGHTS

- Concentrations of As and other elements in water and dietary components
- Comparative analysis of concentration of As in uncooked and cooked rice
- Daily intake of As and other elements via water and dietary components
- Estimation of potential health hazards by comparing JECFA values of metals
- Estimation of chronic daily intake and health risk index

## GRAPHICAL ABSTRACT



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## ABSTRACT

This study investigates the level of contamination and health risk assessment for arsenic (As) and other elements in drinking water, vegetables and other food components in two blocks (Mohiuddinagar and Mohanpur) from the Samastipur district, Bihar, India. Groundwater (80%) samples exceeded the World Health Organization (WHO) guideline value (10 µg/L) of As while Mn exceeded the previous WHO limit of 400 µg/L in 28% samples. The estimated daily intake of As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn from drinking water and food components were 169, 19, 26, 882, 4645, 14582, 474, 1449 and 12,955 µg, respectively (estimated exposure 3.70, 0.41, 0.57, 19.61, 103.22, 324.05, 10.53, 32.21 and 287.90 µg per kg bw, respectively). Twelve of 15 cooked rice contained high As concentration compared to uncooked rice. Water contributes (67%) considerable As to daily exposure followed by rice and vegetables. Whereas food is the major contributor of other elements to the dietary exposure. Correlation and principal component analysis (PCA) indicated natural source for As but for other elements, presence of diffused anthropogenic activities were responsible. The chronic daily intake (CDI) and health risk index (HRI) were also estimated from the generated data. The HRI were >1 for As in drinking water, vegetables and rice, for Mn in drinking water, vegetables, rice and wheat, for Pb in rice and wheat indicated the potential health risk to the local population.

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**Educational History:**

| | |
|---|---|
| 2012 onwards | Ph.D Pursuing (Environmental Sciences), School of Environmental Sciences, Jawaharlal Nehru Univeristy, New Delhi. |
| 2010 – 2012 | M.Phil (Environmental sciences), First Class (8.21/9.00, CGPA) ~ 87.1%, School of Environmental Sciences, Jawaharlal Nehru university, New Delhi, India. |
| 2008 – 2010 | M.Sc. (Environmental Sciences), First Class (7.18/9.00, CGPA) ~ 76.8%, School of Environmental Sciences, Jawaharlal Nehru University. |
| 2005 – 2008 | B.Sc (Chemistry, Zoology and Botany), First Class (67 %), CCS,University Meerut, Meerut, India. |
| 2001 – 2003 | Class XII, with First Class (66%), U. P. Board, Uttar Pradesh. |
| 2001 – 2000 | Class X with First Class (61%), U.P.Board, Uttar Pradesh. |

**Awards and Achievements:**

- Recipient Senior Research Fellowship (SRF) (July 2012 to July 2015) a National level Research fellowship from CSIR-UGC.
- Visiting Research Student at Environmental Risk Assessment & Remediation (CERAR) at the University of South Australia (UniSA), Australia, for four months from 10th July 2013 to 10th November, 2013 supported by Crawford Fund (A prestigious award, Australian Government).
- A member of consortia of scientist working on Arsenic problem in Groundwaters for preparing detail science plan for deploying a specialized drilling rig in developing countries, ICDP workshop held at Hanoi, Vietnam (24 april-28 April, 2011). Travelling and lodging supported by US National Science Foundation.
- Secured 094/0264 ranks in Council of Scientific & Industrial Research (CSIR), for Junior Research Fellowship a National level Research fellowship exam conducted by CSIR-UGC in Earth, Atmospheric, Ocean & Planetary Sciences held on December, 2009.

- Qualified University Grants Commission (UGC), in Environmental Sciences for Junior Research Fellowship (JRF), a national level Research fellowship exam conducted by UGC held on December 2011. Electronic Certificate No.: 112003159.

- Won best poster presentation in national seminar on Past and Present Geochemical Processes-Impacts on Climate Change by Indian Society of Applied Geochemists, Hydrabad, 22nd –23rd December, 2015 organized by SES, JNU, New Delhi.

**Publications**: please *see* list of publications inserted in thesis.

**Teaching Experience:**

- Valued trainer cum volunteer in the INSPIRE (Innovation in Science Pursuit for Inspired Research) internship programme sponsored by the Department of Science and Technology, Government of India, conducted by School of Environmental Sciences, JNU, New Delhi, from 17th -21st February, 2014.

**Seminar attended and Paper Presentations:**

- Manoj Kumar, Al. Ramanathan, Naveen Kumar, poster presented entitled "Arsenic mobilization and enrichment in the subsurface waters, Ballia, Central Gangetic Plain, India" in International Association for Mathematics Geosciences (IAMG), 16th conference, October, 2014, JNU, New Delhi.

- Manoj Kumar, Mukesh Kumar, Alok Kumar, AL. Ramanathan, paper presented entitled "Arsenic distribution and mobilization in three districts of Central Gangetic Plain" in the Indo-Australian workshop on arsenic, October 3rd – 4th, 2012, JNU, New Delhi, India.

- Manoj Kumar, AL. Ramanathan, Naveen Kumar, paper presented entitled "Arsenic mobilization and enrichment in the subsurface waters, Ballia, Central Gangetic Plain, India in "International Conference on Interface between Chemistry and Environment (ICICE) held on 13th – 14th December, 2012, organized by Department of Chemistry, Ramjas College University of Delhi, Delhi, India.

- Al. Ramanathan, Manoj Kumar, Parijat Tripathi, Pankaj Kumar, Alok Kumar, Prosun Bhattacharya, Manish Kumar, presented paper entitled "Arsenic in the central Gangetic Plain region in India" in the National conference on sustainable Development of Groundwater resources in Industrial Regions, SDGRIR 2012.

- National seminar on, "Modern and Palaeo Sediments: Implication to Climate change, Water Resources and Environmental Changes & XXVIII Convention of Indian Association of Sedimentologists" School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, from 24th -26th November, 2011.

**Training Programme:**

- EAW Intensive Summer Programme, "From Synopsis to Thesis Writing" from 1st May to 10th May, Winter Semester 2013-14 Organized by Linguistic Empowerment Cell, Jawaharlal Nehru University, New Delhi.

- Two weeks workshop on "Hydrogeochemical modelling using PHREEQC and MODFLOW" from 21st to 31st January, 2013 at Annnamalai University, Annamalai Nagar, Tamil Nadu, India.

- One week Summer School on “Digital Image Processesing (DIP)” Organized by TERI University, New Delhi. July 20-24, 2009.

- Training Programme on “GIS Application in Hydrology and Environmental Geology” by Prof. Wolfgang Goessel, Martin Luther University, Germany Feb. 2010, at SES, Jawaharlal Nehru University, New Delhi. 16-18 February 2010.

- Training course on “Hydrological Investigations for Conservation and Management of Lakes” organized by National Institute of Hydrology, Roorkee (Uttaranchal) during March 1-3, 2011.

- One week “National workshop on Advance Soft computing Techniques in Hydrology and its Applications” Jointly Organized by NIH & IAH Roorkee at National Institute of Hydrology, Roorkee, Uttaranchal, India. June 20-24, 2011.

- One week “Training program on Hydro geochemical modeling assessment and management of urban and coastal groundwater” from 17-23 rd October 2011 at SES, JNU, New Delhi.

- One week, DST-SERC sponsored training workshop on "Isotope hydrology" at NIH, Roorkee during 19-24 December, 2011.

**Research Experience:**

- Four months training title *“Analysis of arsenic and other elements in various environmental samples using advanced analytical techniques”* at Environmental Risk Assessment & Remediation (CERAR), University of South Australia, from 10 July-10 November, 2013.

- *M.Phil.(2012)* dissertation entitled *“Geochemical assessment of the aquifer sediments of Ballia, Central Gangetic Plain with the special reference to As mobilization and enrichment in to groundwater.”*

- *M.Sc.*( 2010) dissertation entitled *“Preliminary studies on the Hydrogeochemical evolution of meltwaters in Gangotri glacier, Uttranchal, India”* under the supervision of *Prof. AL Ramanathan.*

**Techniques known and Instrumentation handling:**

- Analytical techniques like ICP-MS, HPLC-ICP-MS, TOC analyser, $NH_4$ and $NO_2$+$NO_3$ analyser, Spectrophotometer, Atomic Absorption Spectrometer, Flame photometer, Ion Chromatography Water testing kits (including pH & conductivity meters), GPS locators etc.

**Computer Knowledge:**

- Basic knowledge of computer operations, Operating system: Linux and Windows, Software: MS Office, Hands on experience of GIS software ArcGIS, ERDAS and hydro-geological software’s like Surfer, SPSS, WATCLAST, AQUA.

**Personal Traits:**

- Good communication skills, command over English (both written & spoken)

- Strong analytical aptitude, innovative & creative by nature, like research works in a team and individual as well.

**Personal Details:**

Name : Manoj Kumar

Father’s name : Bhagwat Singh

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