Environmental tracers and groundwater residence time indicators reveal controls of arsenic accumulation rates beneath a rapidly developing urban area in Patna, India

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ARTICLE INFO

ABSTRACT

Groundwater security is a pressing environmental and societal issue, particularly due to significantly increasing stressors on water resources, including rapid urbanization and climate change. Groundwater arsenic is a major water security and public health challenge impacting millions of people in the Gangetic Basin of India and elsewhere globally. In the rapidly developing city of Patna (Bihar) in northern India, we have studied the evolution of groundwater chemistry under the city following a three-dimensional sampling framework of multi-depth wells spanning the central urban zone in close proximity to the River Ganges (Ganga) and transition into peri-urban and rural areas outside city boundaries and further away from the river. Using inorganic geochemical tracers (including arsenic, iron, manganese, nitrate, nitrite, ammonium, sulfate, sulfide and others) and residence time indicators (CFCs and SF_6), we have evaluated the dominant hydrogeochemical processes occurring and spatial patterns in redox conditions across the study area. The distribution of arsenic and other redox-sensitive parameters is spatially heterogenous, and elevated arsenic in some locations is consistent with arsenic mobilization *via* reductive dissolution of iron hydroxides. Residence time indicators evidence modern ($<\sim$60–70 years) groundwater and suggest important vertical and lateral flow controls across the study area, including an apparent seasonal reversal in flow regimes near the urban center. An overall arsenic accumulation rate is estimated to be $\sim$0.003 $\pm$ 0.003 $\mu M.yr^{-1}$ (equivalent to $\sim$0.3 $\pm$ 0.2 $\mu g.yr^{-1}$), based on an average of CFC-11, CFC-12 and SF_6-derived models, with the highest rates of arsenic accumulation observed in shallow, near-river groundwaters also exhibiting elevated concentrations of nutrients including ammonium. Our findings have implications on groundwater management in Patna and other rapidly developing cities, including potential future increased groundwater vulnerability associated with surface-derived ingress from large-scale urban abstraction or in higher permeability zones of river-groundwater connectivity.

1. Introduction

Groundwater impacted by dangerous concentrations of geogenic arsenic affects the health of millions of people across the globe, especially in South and Southeast Asia (Smedley and Kinniburgh, 2002; Charlet and Polya, 2006; Ravenscroft et al., 2009; World Health Organization, 2011). Elevated groundwater arsenic has been widely reported in parts of the Ganga Basin (Chakraborti et al., 2017; Chakraborti et al.,

2018), including in the northern Indian State of Bihar (Chakraborti et al., 2003; Nickson et al., 2007; Ghosh et al., 2008; Saha, 2009; Saha et al., 2010; Saha et al., 2011; Ghosh et al., 2012; Chakraborti et al., 2018; Richards et al., 2020). Arsenic release in shallow circum-Himalayan aquifers is typically attributed to the reductive dissolution of arsenic-bearing Fe(III) minerals (Islam et al., 2004), driven by metal reducing bacteria using bioavailable organic matter (Bhattacharya et al., 1997; Islam et al., 2004; van Geen et al., 2004; Charlet and Polya, 2006; Postma et al., 2007; Rowland et al., 2009) or potentially ammonium (Xiu et al., 2020) as an electron donor. However, the sub-surface location where arsenic mobilization occurs remains vigorously debated (Harvey et al., 2002; Datta et al., 2011; McArthur et al., 2011; Neumann et al., 2011; Lawson et al., 2013; Lawson et al., 2016; Schaefer et al., 2016; Stuckey et al., 2016). Uncertainties in interpretations of arsenic mobilization arise in part because of the spatial heterogeneity of arsenic observed in affected aquifers (Richards et al., 2017; Richards et al., 2020; Chakraborty et al., 2022), the high sensitivity of arsenic mobilization to aqueous and sedimentary redox conditions (Gulens et al., 1978; Cherry et al., 1979; Smedley and Edmunds, 2002; Kocar et al., 2008; Lee et al., 2008; Mukherjee et al., 2008; Polizzotto et al., 2008; Sharif et al., 2008; Tufano et al., 2008; Ying et al., 2015; Richards et al., 2020; Vega et al., 2020; Glodowska et al., 2021; Kontny et al., 2021) and the potential co-occurrence of competing processes such as (partial) adsorption/desorption (Goldberg et al., 2007, Lalonde et al., 2012, Richards et al., 2019a) and co-precipitation (Johnson et al., 2015). Understanding the underpinning hydrogeochemical processes and the nature of organic matter implicated in arsenic release (Nickson et al., 1998; Harvey et al., 2002; McArthur et al., 2004; Gault et al., 2005; Rowland et al., 2007; van Dongen et al., 2008; Neumann et al., 2009; Rowland et al., 2009; Fendorf et al., 2010; Mladenov et al., 2010; Al Lawati et al., 2012; Al Lawati et al., 2013; Lawson et al., 2013; Neumann et al., 2014; Lawson et al., 2016) is critical to resolving these questions. The organic matter associated with arsenic mobilization is generally thought to originate, in some proportion, from (i) external, modern surface-derived sources (Harvey et al., 2002; Kocar et al., 2008; Papacostas et al., 2008; Polizzotto et al., 2008; Neumann et al., 2010; Lawson et al., 2013; Lawson et al., 2016); (ii) plant-derived sources internal to the sediment aquifers (Nickson et al., 1998; McArthur et al., 2001; McArthur et al., 2004); and/or (iii) petroleum-derived hydrocarbons from thermally mature sediments (Rowland et al., 2007; van Dongen et al., 2008; Rowland et al., 2009; Al Lawati et al., 2012; Al Lawati et al., 2013; Magnone et al., 2017). Geochemical, including isotopic, studies have probed hydrogeochemical processes in arsenic-impacted areas (Aggarwal et al., 2000; Harvey et al., 2002; van Geen et al., 2003; Lawson et al., 2008; Sengupta et al., 2008; van Dongen et al., 2008; Datta et al., 2011; McArthur et al., 2011; Neumann et al., 2011; Lawson et al., 2013; Lawson et al., 2016; Kumar et al., 2021), generally in the context of potential secular changes in arsenic hazard (Harvey et al., 2002; Polya and Charlet, 2009; Lawson et al., 2016; Nghiem et al., 2020).

The processes controlling groundwater (bio)geochemical conditions become inherently more complex in urban or heavily irrigated settings where groundwater flow paths can be perturbed by large-scale abstraction, as is common in India and other groundwater-dependent regions (MacDonald et al., 2016). The depletion of alluvial aquifers in northwest India has been reported to be extreme but spatially variable, reflecting a response to multiple drivers including abstraction, precipitation, canal irrigation and potential evapotranspiration (van Dijk et al., 2020). The potential impact of large-scale groundwater abstraction specifically on arsenic mobilization remains unresolved (Lawrence et al., 2000; Harvey et al., 2002; Aggarwal et al., 2003; Harvey et al., 2003; van Geen et al., 2003; Sengupta et al., 2008; Polya and Charlet, 2009; Neumann et al., 2010; McArthur et al., 2011; Lawson et al., 2013; Mailloux et al., 2013). In some cases, increased abstraction rates could lead to reduced groundwater arsenic concentrations *via* dilution or flushing if the timescale of transport is more rapid than arsenic

mobilization and accumulation; conversely increased abstraction (and hence increased surface-derived ingress) could stimulate higher rates of arsenic mobilization if arsenic mobilization is occurring at a faster rate than recharge (van Geen et al., 2008; Radloff et al., 2017).

Anthropogenic residence time indicators (RTIs) including substances such as chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) have been widely used as inert tracers of modern ($<$60–70 years) groundwater (Cook and Solomon, 1995; Oster et al., 1996; Beyerle et al., 1999; Gooddy et al., 2006; Plummer et al., 2006; Hinsby et al., 2007; Horneman et al., 2008; Darling et al., 2012; Jones et al., 2014), including in arsenic-impacted aquifers (Horneman et al., 2008, Lapworth et al., 2018a, 2018b, Richards et al., 2019c), providing information on subsurface residence times and mixing processes based on simplifying assumptions (Gooddy et al., 2006). The greenhouse gases CFCs were produced from the 1940s and used for refrigeration and air-conditioning; SF_6 production began later in the 1960s for use in thermal and electrical insulation (Plummer et al., 2006). Modern RTIs have been found at significant depths (*e.g.* $>\sim$30 m and deeper) in arsenic bearing aquifers (Aggarwal et al., 2000, Dowling et al., 2003, Klump et al., 2006, Lawson et al., 2008, Lawson et al., 2013, Lawson et al., 2016, Lapworth et al., 2018a, 2018b, Richards et al., 2019c), although this does not necessarily implicate modern surface-derived organic matter (or other sources of electron donors) in driving arsenic mobilization. In Cambodia, arsenic concentrations generally increase with apparent groundwater ^{3}H-^{3}He ages, especially in sand-dominated sedimentary sequences, with an estimated arsenic loading rate (also referred to as an arsenic accumulation rate) $\sim$ 0.1 μM.yr^{-1}, typically highest in shallow groundwaters (Richards et al., 2019c). Broadly comparable arsenic loading rates of $\sim$0.3 μM.yr^{-1} have been observed in Bangladesh (Radloff et al., 2007; Stute et al., 2007). Such accumulation estimates have not been made in Bihar, and mechanistic studies designed to evaluate key geochemical controls on arsenic mobilization in the context of rapidly developing urban areas (such as Patna, Bihar) in northern India remain limited.

Recent estimates based on machine learning geospatial modelling suggest that $\sim$1.2–4.6 million people in Bihar and $\sim$3–12% of land area in Bihar (Podgorski et al., 2020) are potentially exposed to concentrations of arsenic above the World Health Organization (WHO) provisional guideline value for drinking water of 0.13 μM (10 μg.L^{-1}) (World Health Organization, 2011). Whilst Bihar is centrally located in the arsenic-enriched belt of the Indo-Gangetic Plain (Mukherjee et al., 2014), spatially representative sampling of groundwater arsenic in Bihar has been limited (Richards et al., 2020) as is detailed systematic investigations probing the underpinning geochemical controls impacting arsenic mobilization into groundwater. This is particularly important in the context of rapidly developing urban areas, such as Patna, where population densities and groundwater demand is generally highest. This study aims to elucidate the hydrogeochemical processes impacting arsenic mobilization in Patna, India as an exemplar rapidly developing city in the circum-Himalayan region. Using a complementary suite of geochemical tracers (*e.g.* major and trace inorganic tracers and residence time indicators), our objectives are to: (i) develop profiles of the evolution of groundwater geochemistry along inferred groundwater flow-paths following an urban to rural transition; (ii) determine associations and/or spatial co-variance between arsenic and other redox-sensitive inorganics (*e.g.* iron, manganese, nitrate, nitrite, ammonium, sulfate, sulfide) and residence time indicators to identify key transport and transformation processes; (iii) estimate the extent of seasonal monsoonal influence on key redox zones and hydrogeochemical conditions including apparent flow regimes; and (iv) estimate arsenic accumulation rates in Patna including in comparison to other shallow, circum-Himalayan groundwaters.

2. Methods

2.1. Study area

The field research of this study was focussed around Patna, the capital city of the State of Bihar, India, in the Middle Gangetic Plain. Patna is a rapidly developing "Smart City" with a dense urban population (Government of India, 2011; Saha et al., 2014), heavily centered within relatively close proximity (within ~5 km) to the River Ganga. Intensive groundwater pumping in urban areas of Patna has drastically increased with rapid urbanization and associated water demand (Saha et al., 2014). The climate is sub-tropical to sub-humid with an annual monsoon season from around June to September. Groundwater sampling sites (Richards et al., 2020; Richards et al., 2021) were systematically selected to target the transition from dominantly urban zones to peri-urban and rural areas with increasing distance from the River Ganga, running in transects broadly parallel to inferred dominant groundwater flowpaths (Fig. 1). The overall average density of sampling sites was approximately one site per ~10 km², a density which was higher in the urban center and near the River Ganga, in a sampling area of ~480 km², a sampling density which is much higher than typically used for groundwater monitoring in the area (Central Ground Water Board, 2013). In general, the dominant groundwater flow direction is oriented towards the River Ganga, contributing to its baseflow (Central Ground Water Board, 2015). However, a monsoonal reversal in groundwater flow direction can occur if the river stage is higher than the hydraulic heads of adjacent aquifers (Shamsudduha et al., 2011, Das et al., 2021, Lu et al., 2022).

Two major Quaternary aquifers are present in Patna within the top ~300 m, separated by a clay/sandy clay layer of variable thickness (~15–30 m) (Saha, 2009; Saha et al., 2011; Saha et al., 2014; Central Ground Water Board, 2015). Typical groundwater level depth in the study area is ~5–10 m below ground surface (Central Ground Water Board, 2015). Further information on hydrogeological setting and hydrological conditions in selected areas of the wider Patna District is provided in reports by other authors (Saha et al., 2014, Central Ground Water Board, 2015), noting that detailed or high resolution information on the hydrogeological substructure under Patna, including for the particular sampling sites, is not available.

2.2. Water sample collection

Groundwater was sampled during two sampling seasons: (i) pre-monsoon in June/July 2019 (n = 44 samples) and (ii) post-monsoon in November/December 2019 (n = 44). Groundwater was collected from existing private or public wells (predominantly used for drinking), from multiple sampling depths (ranging from ~6–120 m), using hand-pumps or submersible pumps (Richards et al., 2020). Screening lengths
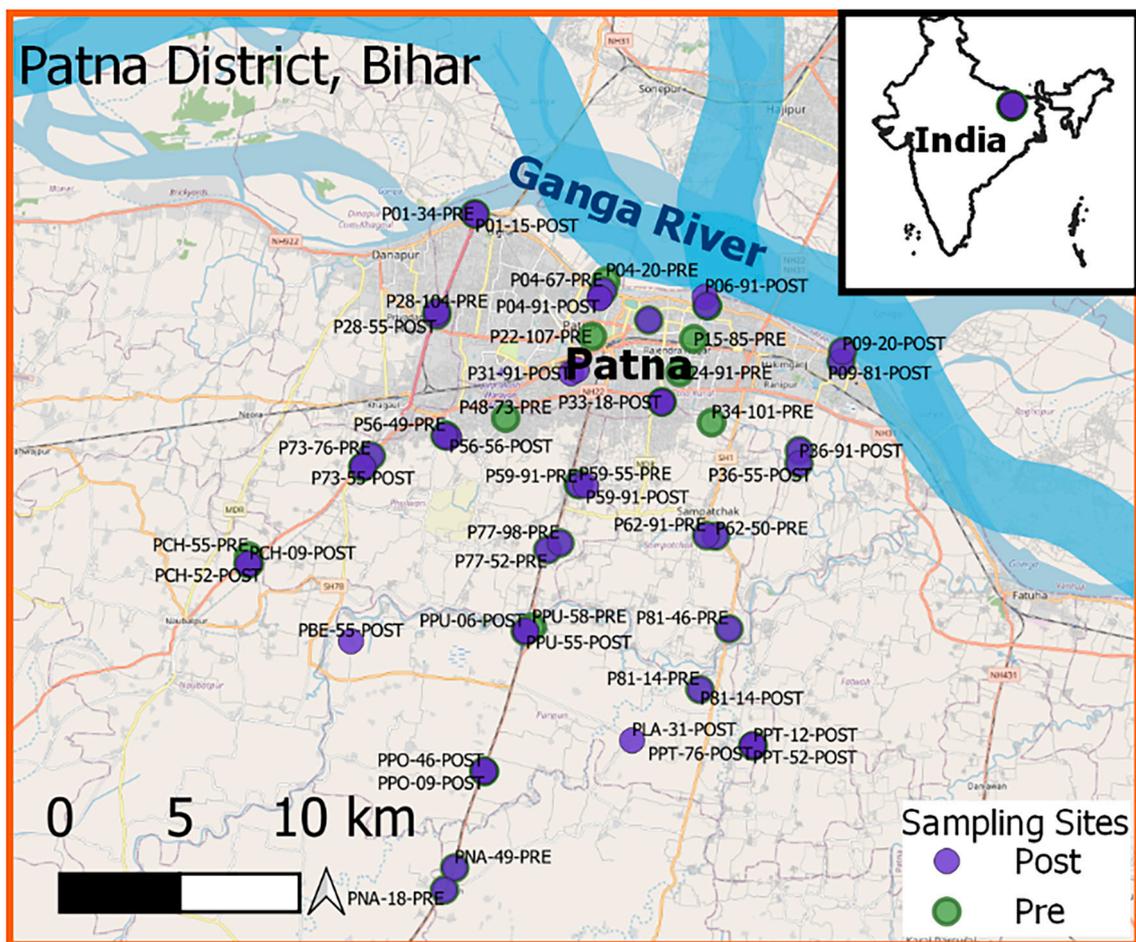

Fig. 1. Field site map of sampling locations in Patna District, Bihar, northern India (adapted from (Richards et al., 2021)). Sample IDs are XXX-YY where XXX is a site ID and YY is depth (m); "POST" or "PRE" indicates post-monsoon (purple symbol, *n* = 44) and pre-monsoon (green symbol, n = 44) sampling respectively (some points are overlapping as many identical wells were sampled). River centerlines are exaggerated and do not necessarily represent width. Red and yellow lines are major and minor roads, respectively. Population density is generally highest towards the urban center of Patna (where the highest density of sampling sites as well as roads are located); for sample sites overlain with population density information see (Richards et al., 2021). Details of layer data sources are provided in Supplementary Information. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

were not always known and were reported to vary depending on installation and intended purpose. Based on hydrogeological characterization reported elsewhere in the Patna District (Central Ground Water Board, 2015) and locally reported information, we expect that two aquifers are likely found within this depth range. Site/sample IDs are coded as XXX-YY-(PRE), where XXX is a site code, and YY is well depth (in m); "PRE" or "POST" indicates pre- and post-monsoon respectively.

Subsamples for major and trace inorganic analyses were filtered (0.45 μm cellulose and polypropylene syringe filters, Minisart RC, UK) in the field directly into 60 mL amber glass bottles (acid-washed and furnaced). Due to transport restrictions on nitric acid, samples for major and trace elemental analysis (excluding subset for anion analyses) were acidified upon arrival at the Manchester Analytical Geochemical Unit (MAGU) laboratories at the University of Manchester. Subsamples for CFCs and SF_6 analyses were collected in 60 and 500 mL glass bottles, respectively, using motorbike innertubes and the USGS single bottle 'diffusion barrier' method to avoid atmospheric contact (Plummer et al., 2006; Darling et al., 2012).

2.3. Chemical and data analysis

The Supplementary Information contains details of *in-situ* analysis, laboratory analysis (inorganic, organic, CFCs and SF_6), analytical quality assurance/quality control, software packages and data analysis, including estimation of arsenic accumulation rates based on measured concentrations of groundwater arsenic and apparent ages derived from groundwater residence time indicators.

3. Results and discussion

3.1. Dominant groundwater geochemical conditions

The major element groundwater chemistry in Patna is dominated by, in order of decreasing median concentrations, bicarbonate, calcium, sodium, magnesium, silicon, chloride, nitrate, potassium and sulfate (Fig. S2). Calcium, magnesium and sodium contribute a maximum of 77%, 48% and 37% of the bulk cationic charge. The bulk anionic charge is strongly dominated by bicarbonate, contributing a maximum of ~100% of the bulk anionic charge, followed by chloride and sulfate, with maximum contributions 36% and 25% respectively. The groundwater is mostly a calcium-magnesium-carbonate type (Fig. S3), with samples with relatively high (*e.g.* >~1000 mg L^{-1}) total dissolved solids (TDS) trending towards a calcium-magnesium-sulfate type near the Ganga river and a sodium-carbonate type at greater distance from the river and urban center. Most groundwaters are of circum-neutral pH (range 5.9–7.7; median 7.2), spanning a wide range of redox potential (*Eh* range 30–430 mV; median 240 mV), electrical conductivity (EC; range 120–2200 μS cm^{-1}; median 240 μS cm^{-1}) and temperature (range 22–31 °C; median 26 °C). The Patna groundwater chemistry is similar to previously characterized across Bihar (Richards et al., 2020) and broadly typical of other arsenic-bearing groundwaters in South and Southeast Asia (Berg et al., 2001; McArthur et al., 2001; Smedley and Kinniburgh, 2002; Polizzotto et al., 2008; Buschmann and Berg, 2009; Lawson et al., 2013; Richards et al., 2017; Pincetti Zúñiga et al., 2020). Summary statistics and sample-specific selected compositions are in Supplementary Information (Tables S3 & S4).

3.2. Concentrations of arsenic and other health-relevant elements in groundwater

Dissolved arsenic concentrations in the studied groundwater range from below detection to 0.88 μM (~<1–70 μg.L^{-1}), with ~2% of samples exceeding the World Health Organization (WHO) provisional guideline value for drinking water of 0.13 μM (10 μg.L^{-1}) (World Health Organization, 2011), and ~55% of samples exceeding 0.013 μM (1 μg.

L^{-1}) (Fig. S4). Other exceedances are described in Supplementary Information.

3.3. Arsenic and related inorganic hydrogeochemical parameters

3.3.1. Relationship between arsenic and inorganic hydrogeochemical parameters

Arsenic is positively correlated with iron (Fig. 2A; $t_{86} = 4.8; p < 0.01$) and manganese (Fig. 2B, $t_{86} = 3.8; p < 0.01$) in Patna, consistent with arsenic mobilization *via* reductive dissolution of iron (hydr)oxides (Nickson et al., 2000; Islam et al., 2004; Lawson et al., 2013; Yadav et al., 2015; Richards et al., 2017; Richards et al., 2020). A broadly inverse relationship between arsenic and sulfate (Fig. 2C; $t_{85} = -1.0; p = 0.32$, noting a linear relationship is not statistically significant at the 0.05 level) shows that elevated arsenic usually corresponds to low sulfate and indicates that high sulfate waters are not consistently favorable to support arsenic reduction and mobilization. Redox conditions are variable, noting the presence of sulfide suggests sulfate reduction, even if the relationship between sulfide and arsenic is not statistically significant (Fig. 2D; $t_{42} = -0.7; p = 0.48$). Further, arsenic concentrations are not significantly correlated with nitrate (Fig. 2E; $t_{42} = -0.8; p = 0.44$) nor nitrite (Fig. 2F; $t_{42} = -0.7; p = 0.52$) concentrations, although they are strongly and positively correlated with ammonium (Fig. 2G; $t_{42} = 4.7; p < 0.01$), which is stable typically under strongly reducing conditions. The presence of ammonium suggests that nitrate and nitrite have started to be reduced and that conditions are sufficiently reducing to support arsenic release; ammonium inputs may also be river or surface-derived. Pyrite oxidation is not expected to be the dominant arsenic mobilization mechanism, given that elevated arsenic occurs in low sulfate waters, iron and sulfate are not positively correlated ($t_{43} = -1.4, p = 0.15$), and that the iron:sulfate molar ratios are usually much less than ~0.5 (McArthur et al., 2001).

3.3.2. Spatial distribution of arsenic and related hydrogeochemical parameters

The relationship between depth below land surface and arsenic concentration (and other associated parameters) shows that relatively shallow groundwater (~15 to 20 m in depth) is typically characterized by the highest observed concentrations of arsenic, sulfate, sulfide, nitrate, nitrite and ammonium (Fig. S5, noting the log scale). A similar depth profile of arsenic concentrations has been observed previously in Bangladesh (Harvey et al., 2002) and elsewhere (Erban et al., 2013). Elevated arsenic, iron and sulfate tends to occur mostly in relatively shallow groundwaters, noting the overall relationship between depth with arsenic, iron and sulfate is not statistically significantly at the 0.05 level ($p = 0.36$, $p = 0.37$ and $p = 0.08$, respectively) when combined across seasons. Notably, a strong and significant inverse relationship between sulfate and depth is observed exclusively in the post-monsoon season dataset ($t_{42} = -2.1; p < 0.05$) indicating rapid ingress of oxic recharge during the monsoon. This input might be masked by confounding factors (*e.g.* mixing, intensive pumping) if the entire annual dataset is considered. The highest concentrations of sulfide occur at a similar depth as the peak in sulfate concentrations (~15 m).

In-situ measurements of nitrogen species reflect a strong vertical control on the distribution of surface-derived constituents. Significant inverse correlations with depth for both nitrate ($t_{42} = -2.9, p < 0.01$; Fig. S5E) and nitrite ($t_{42} = -2.9, p < 0.05$; Fig. S5F) are observed, as well as broadly for ammonium although not statistically significant at the 0.05 level ($t_{42} = -1.7, p = 0.10$; Fig. S5G). Interestingly, post-monsoon nitrate and nitrite both reach peak values at the shallow depth of ~15 m, which is slightly shallower in comparison to the ammonium peak ~20 m, suggesting the development of a depth-controlled redox front likely impacted by monsoonal ingress, and which plausibly might be exacerbated by intensive pumping in urban areas. The ammonium concentration peak at a depth of ~20 m is located around the same depth where peak arsenic and elevated iron occur; a
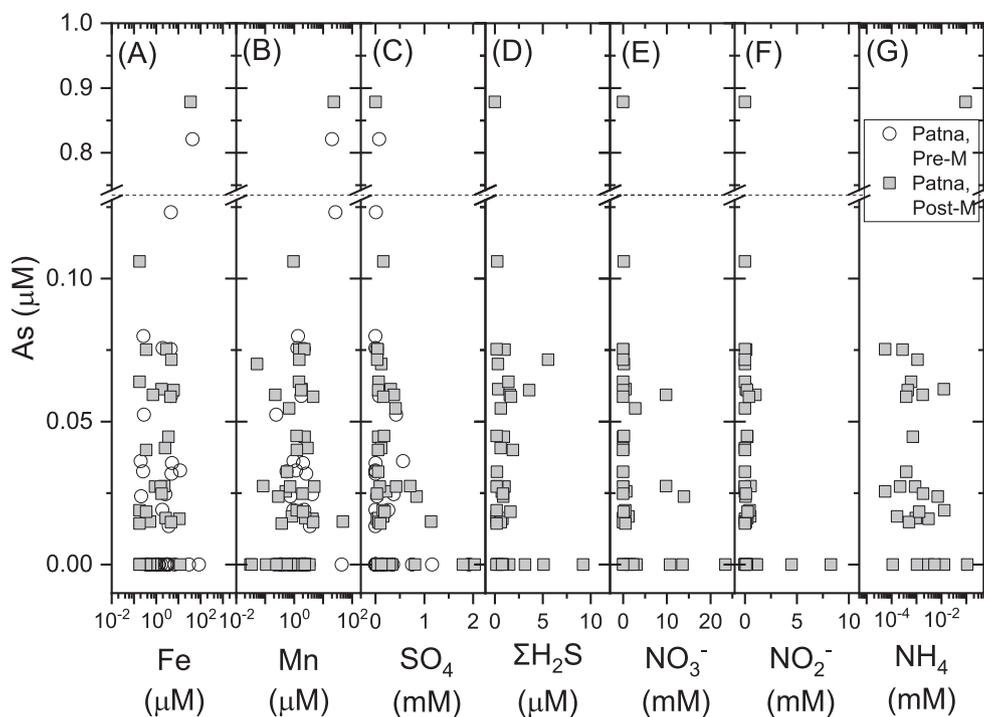
Fig. 2. Groundwater arsenic *versus* inorganic parameters (A) Fe*; (B) Mn*; (C) SO₄*; (D) ΣH₂S §; (E) NO₃⁻§; (F) NO₂⁻§; (G) NH₄§. Some parameters shown as log-scale. Data notes: *based on laboratory analysis; § *in-situ* measurements post-monsoon only. Circle (open) and square (grey fill) symbols are for Patna pre- and post-monsoon, respectively. Dashed line is WHO provisional guideline for arsenic (World Health Organization, 2011).

similar spatial correlation was previously noted in Bangladesh (Harvey et al., 2002). The co-occurrence of maximum arsenic and ammonium is notable as ammonium has been postulated as an electron donor to induce arsenic mobilization from the reduction of iron oxide minerals in the Hetao Basin in China (Xiu et al., 2020), noting however that there are also groundwaters present in Patna which contain relatively high ammonium but low arsenic.

Geochemical conditions in groundwater under Patna are characterized by substantial spatial heterogeneity, laterally as well as vertically (Fig. 3). The highest arsenic concentrations are detected in very shallow groundwaters in close proximity to the River Ganga. In the pre-monsoon season, a front of higher arsenic groundwater appears to develop at greater depths near the urban center of Patna (within ~5 km of the River Ganga) and at intermediate depths in the expanding urban/peri-urban area (within ~5–15 km of the River Ganga) (Fig. 3A). These patterns are broadly mirrored by observed Fe distributions (Fig. 3C & D). Interestingly, the distributions of *Eh* (Fig. 3E & F) and sulfate concentrations (Fig. 3G & H) strongly suggest the ingress of oxic groundwater recharge both from the surface across the field area and in areas in close proximity (within ~1 km) of the River Ganga. In the dry pre-monsoon season, the most oxidized groundwaters are found at depths > ~60 m under urban areas, suggesting that urban groundwater abstraction is drawing down oxic groundwater at a faster rate than would occur naturally under areas less impacted by pumping (*e.g.* in peri-urban and rural areas > ~15 km from the River) (Fig. 3E & G). The greater depth of the unsaturated zone during this period (due to drawdown) may also facilitate oxic conditions at this time. In the post-monsoon season, rapid surface-derived ingress likely occurs across the field area, refreshing an input of oxic groundwater recharge and contributing to water table rebound. In this case, the impact of urban pumping becomes masked, and more oxidizing groundwaters are observed throughout the depth profile in urban areas, whilst at greater distance from highly urbanized areas they only appear near the surface (Fig. 3F & H). Higher *Eh* and sulfate are both observed across the field area in the post-monsoon season (see Section 3.5 on seasonal changes).

Importantly, however, the observed trends are very spatially heterogeneous. Whilst the highest concentrations of arsenic occur at shallow depths and near the River Ganga, for example, not all shallow groundwaters near the Ganga exhibit high arsenic concentrations. The lateral variation of various hydrogeochemical parameters reveals spatial bands of broadly similarly characterized groundwater throughout the study area (Fig. S6). This helps to explain some of the variability which is not fully explained by depth or perpendicular distance from the River or urban center. These bands, mostly oriented in a similar direction in increasing distance from the river, are indicative of zones where redox conditions are systematically shifting. Some parameters, like nitrate, nitrite and ammonium have clear areas of elevated concentrations very near the river (and in shallow depths, as shown on Fig. S5), which then decrease with increasing distance, before increasing again in the south east part of the field area. Other parameters, like arsenic and iron, also exhibit a near river/city elevated band before decreasing beyond the outskirts of the city. These patterns and consistency between them suggest that lateral flow controls are also very important across the study area. As many of the patterns seem to span the entire distance along the river covered in the field area, this seems to suggest that at least some of the observed trends are attributed to river-groundwater interactions; this is consistent with the relatively high hydraulic conductivities (~150 m.day⁻¹) reported near the River Ganga in the upper aquifer (~30–130 m depth) near Patna (Central Ground Water Board, 2015). Systematic patterns (*e.g.* zones of developing redox fronts) specifically surrounding the urban center of Patna, like as observed beneath Hat Yai, Thailand (Lawrence et al., 2000), are less clear, which is likely due to the confounding variables including diffuse sources and the wide distribution of municipal pumping wells (Central Ground Water Board, 2015). Influences from the river as compared to the urban center are not necessarily mutually exclusive as urban pumping may increase the extent of river-groundwater interactions (Lu et al., 2022). Detailed geochemical modelling of the evolution of redox zones under Patna is the subject of ongoing investigation by co-authors.
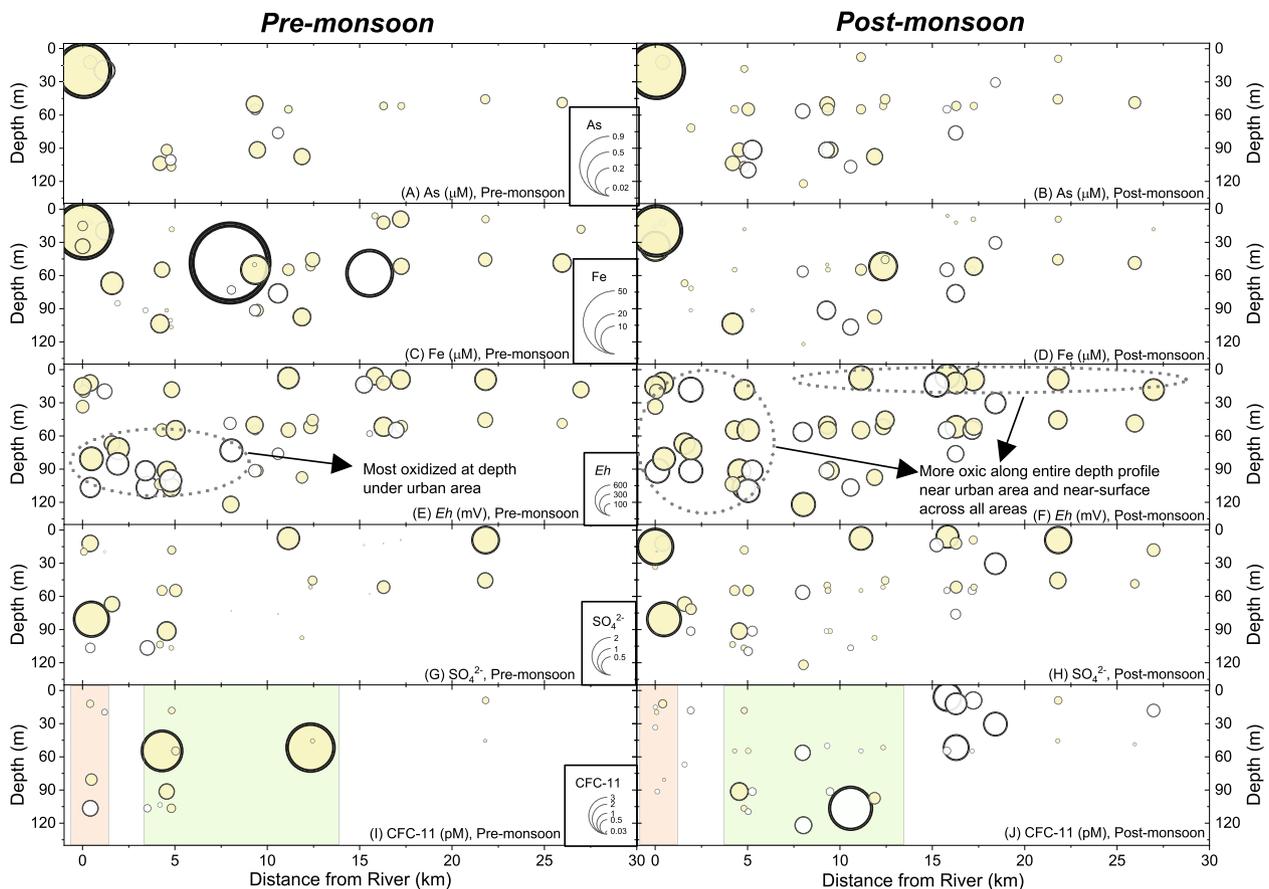
Fig. 3. Bubble plot with depth and distance from River Ganga for pre-monsoon (left panels) and post-monsoon (right panels) groundwater from Patna for (A & B) As; (C & D) Fe, (E & F) *Eh*; (G & H) SO_4^{2-} and (I & J) CFC-11 concentrations. Very small symbols represent low (or below detection) measured concentrations according to the legends shown. Yellow fill indicates identical wells were sampled for a particular analyte in pre- and post-monsoon seasons. Peach and green boxes on I and J represent areas of directional changes in seasonal flow regimes (see also Fig. 5). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. Residence time indicators/CFC and SF_6 groundwater signatures

Apparent ages based on CFC-11, CFC-12 and SF_6 signatures indicate that most groundwater in the study area is modern (less than ~60–70 years) and mostly within the age range of ~40–70 years (Fig. 4). Independent age indicators are generally consistent, with CFC-11 ages being well correlated with CFC-12 ages ($t_{43} = 7.4$, $p < 0.01$) and SF_6 ages ($t_{28} = 2.3$, $p < 0.05$) (when over-modern and below detection values are excluded). The presence of modern groundwater is also qualitatively consistent with emerging organic contaminants in the study area (Richards et al., 2021). The distributions of pre-monsoon groundwater ages are statistically similar to post-monsoon groundwater ages, noting although the youngest ages are observed post-monsoon which is consistent with monsoonal ingress of young recharge. Two groups appear to be following contrasting systematic patterns (Fig. 4B & D) as groundwater evolves from relatively young to relatively old along separate flowpaths.

As there is some evidence of slight excess in CFC-12, plausibly deriving from air conditioning units and refrigerators in the area, much of the detailed interpretation will focus on CFC-11 rather than CFC-12 data. No statistically significant relationship is observed between concentrations of CFC-11, CFC-12 and SF_6 with *Eh* nor Fe (Fig. S7) suggesting that potential degradation of CFCs, particularly CFC-11, under reducing conditions (Hinsby et al., 2007, Sebol et al., 2007, Lapworth et al., 2018a, 2018b), is not the dominant control on CFC-11 concentrations observed. This is consistent with the relatively low groundwater DOC concentrations observed (usually <2 mg.L^{-1} observed; Table S3),

suggesting that the reducing conditions are likely not dominantly attributed to organic carbon degradation which would likely co-metabolize with CFC-11, noting, however, that this does not preclude that organic degradation may still be an important process in some cases.

Although the groundwater throughout the study area is consistently modern, there is no apparent overall, systematic relationship between groundwater age and depth (Fig. S8). In the pre-monsoon season, there is a broadly inverse relationship between depth and CFC-11 age, with the youngest pre-monsoon waters found at relatively deep depths (~90–110 m depth), although the overall relationship is not statistically significant at the 0.05 level ($t_{11} = -1.5$, $p = 0.16$; over-modern and below detection values excluded). This could possibly be explained by upwelling of younger water in some locations in the hyporheic zone (Klump et al., 2006; Hester et al., 2013; Krause et al., 2013; Gomez-Velez and Krause, 2014), arising from a zone of relatively deep hyporheic water with high hydraulic connectivity with the river, more apparent in the drier pre-monsoon season. In contrast, and interestingly, in the post-monsoon season, depth and age switch to a positive correlation which is statistically significant for SF_6-based ages ($t_{26} = 2.3$, $p < 0.05$) although not CFC-11-based ages ($t_{30} = 0.85$, $p = 0.40$) (Fig. S8). This suggests a monsoonal reversal in groundwater flow direction, consistent with modelled lateral flow path predictions based on particle tracking (Lu et al., 2022). The observation that shallow groundwater is typically younger than deeper groundwater in the post-monsoon season is consistent with monsoonal ingress of surface-derived recharge. The lack of overall age-depth relationship observed is likely due to a number of
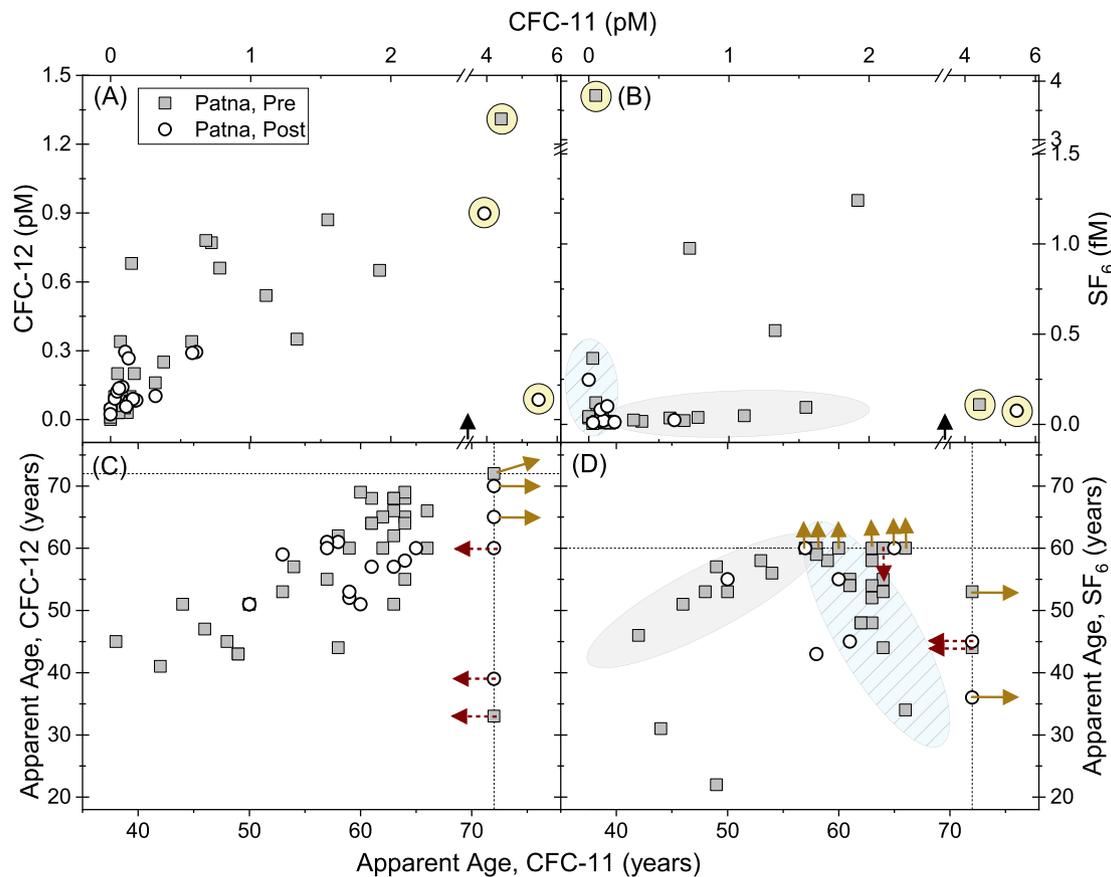
Fig. 4. Residence time indicator concentrations of groundwater CFC-12 and SF_6 against CFC-11 (A & B, respectively) with yellow circles indicating "over modern" signatures (indicative of contamination). Apparent groundwater age (2020 basis, in years) based on (A) CFC-12 and (B) SF_6 piston flow ages against CFC-11 apparent age. Brown arrows indicate groundwater is older than the estimated maximum model age (*e.g.* 72 years for CFC-11 and CFC-12, and 60 years for SF_6, indicated by dashed line); maroon dotted arrows indicate "over modern" signatures and thus represent a maximum age estimate. Light blue (dashed) and grey circles show systematic groupings. Circle (open) and square (grey fill) symbols are for Patna pre- and post-monsoon, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

confounding factors including these seasonally-dependent flow patterns impacting groundwater-surface water exchange, perturbations due to pumping, subsurface heterogeneity and other factors such as leaky well construction and likely variation in well screening length between sampling wells. These factors are difficult to isolate given the co-variances and complexity of the groundwater system studied. However, regardless of the numerous factors potentially contributing to the controls on these processes, the presence of modern age indicators at depths >100 m strongly suggests that groundwater at all depths may be vulnerable to the influence of modern recharge at some locations. These findings are consistent with those within a comparable setting in Varanasi (Lapworth et al., 2018a).

CFC-11 and SF_6 signatures are compared to simple theoretical mixing models to disentangle apparent dominant hydrogeochemical controls across the study area (Fig. S9). In brief, the highest proportion of samples are consistent with a piston flow model (PFM, ~47% of samples), suggesting the dominance of young recharge from a consistent source and location. The observation that CFC-11 and SF_6 data does not consistently fall below the piston flow line further indicates that potential degradation of CFCs is not the dominant control on CFC-11 concentrations. Other groundwater samples are consistent with a binary mixing model (BMM) or an exponential mixing model (EMM); see Supplementary Information.

Patterns in the spatial distribution of CFC-11 (Fig. 5) are consistent with those observed for other geochemical parameters (Fig. 3; Fig. S6). At locations farthest from both the River Ganga and urban center (>~20 km away from river), younger groundwater is found at shallower

depths. This is as expected and consistent with a dominant vertical flow control and the main source of recharge being monsoonal, surface-derived ingress from precipitation and/or flooded areas. In these locations far from the river, perturbations both due to urban pumping and direct river-groundwater interactions are expected to be minimal, and thus the conditions are controlled mostly by natural factors (such as the subsurface lithological structure). The downwards trend in groundwater age is also observed very near the river in the post-monsoon season (peach box, Fig. 5B) consistent with vertical recharge from the surface and/or river-groundwater interactions at shallow depths. Importantly, however, some reversals in these patterns were also observed. In urban areas in the post-monsoon season (green box, Fig. 5B), an opposite trend occurs; here the youngest groundwaters are seen in the deepest samples. This could perhaps be explained by upwelling of younger groundwaters from deeper depths (possibly associated with high permeability zones from old river channel paths) or by the combination of monsoonal ingress and urban pumping which draws in a higher proportion of well oxygenated recharge that would occur simply by pumping alone. This also may be reflected in the pre-monsoon sites very near the river (peach box, Fig. 5A) if there is a time delay between observation and flow reversal due to the transport times. The pre-monsoon groundwater in the urban area is likely a mixture of these impacts, with the youngest groundwaters at middle depths – these samples are plausibly impacted by a combination of monsoonal recharge, river-surface water interactions and urban pumping. The majority of samples in the post-monsoon season are consistent with a piston flow mechanism, suggesting point sources of young recharge which control the distribution of
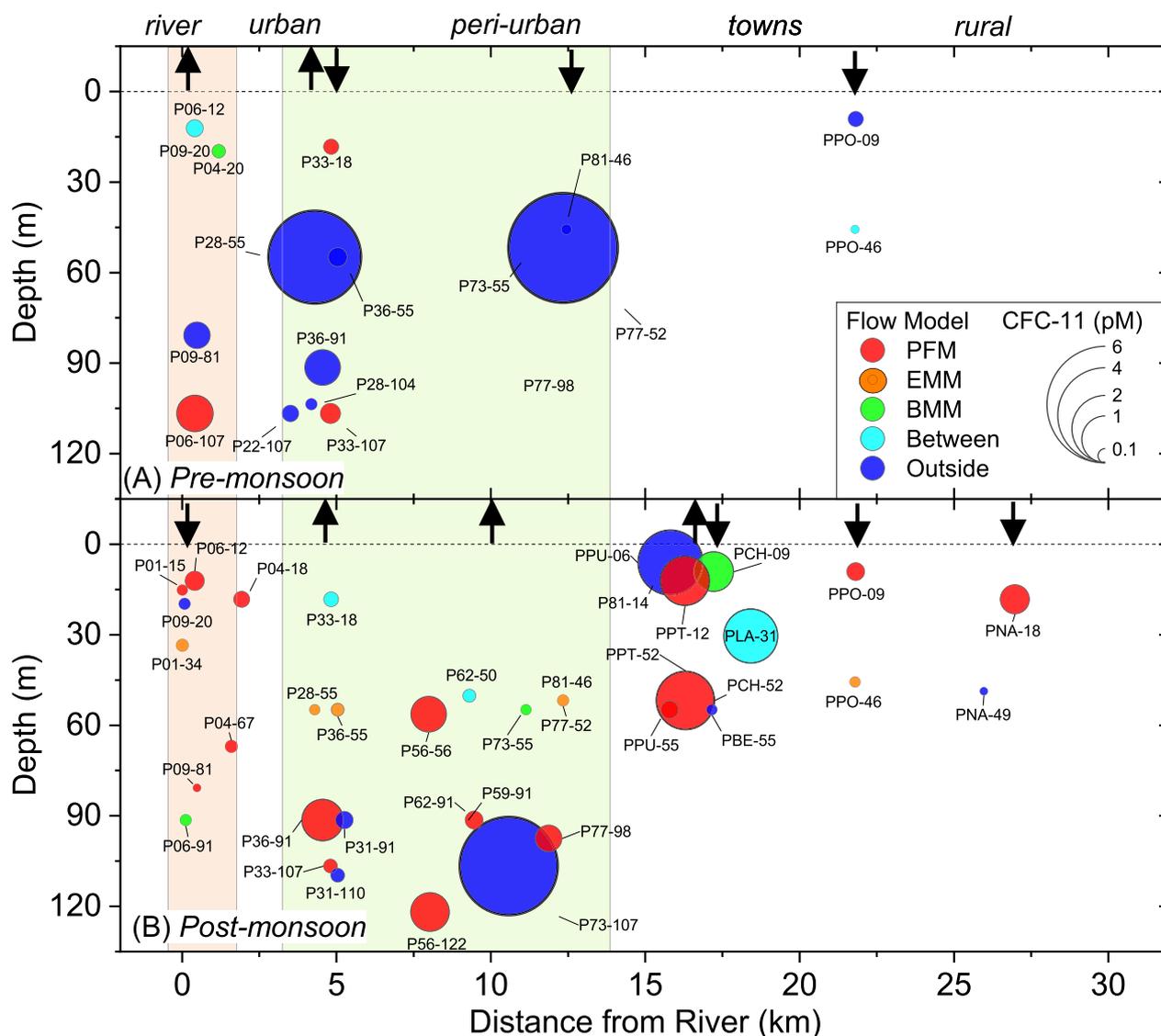
Fig. 5. Bubble plot of CFC-11 concentrations (pM) with depth and approximate distance from the River Ganga for (A) pre-monsoon and (B) post-monsoon groundwater. Colors correspond to groupings according to CFC-11 and SF_6 mixing lines: red = piston flow (PFM); orange = exponential mixing (EMM); green = binary mixing (BMM) turquoise = between models (*e.g.* no apparent dominant fit); and blue = outside other mixing lines; see bow plots on Fig. S9). Black arrows indicate direction of apparent dominant vertical flow as inferred by CFC-11 concentration distribution. Peach and green boxes represent areas of apparent changing directions of seasonal flow regimes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

groundwater ages. These seasonal shifts in direction of flow regimes likely reflect the combined influence of multiple factors, likely both geogenic (*e.g.* monsoonal ingress, river-groundwater interactions, changing hydraulic gradients) and anthropogenic (*e.g.* pumping induced perturbations, surface inputs of organic carbon), which control the groundwater chemistry in and around Patna.

3.5. Seasonal variation in groundwater composition

Direct seasonal comparisons of identically paired pre- and post-monsoon groundwater samples is shown in Fig. S10. Generally there is strong seasonal agreement with the major element composition, although there are some parameters (*e.g.* sulfate and chloride) which are substantially different in a limited number of shallow samples indicative of localized point inputs (Fig. S10D & H). Seasonal differences are systematically apparent and statistically significant for physico-chemical parameters pH and *Eh*, showing lower pH and higher *Eh* in the post-monsoon season (Fig. S10F & G), consistent with rapid monsoonal ingress of oxic recharge across the field area. More details are provided

in Supplementary Information.

3.6. Implications on controls on arsenic mobilization and groundwater vulnerability

Arsenic concentrations are compared to apparent CFC-11 years (Fig. 6A), with maximum concentrations of arsenic substantially increasing in older groundwater ($t_4 = 1.8$, $p = 0.14$, below detection CFC-11 excluded). The envelope relationship suggests that although the maximum concentrations are associated with age, other geochemical processes (*e.g.* adsorption/desorption (Goldberg et al., 2007, Lalonde et al., 2012, Richards et al., 2019a), co-precipitation (Johnson et al., 2015)) and/or physical processes (*e.g.* flushing), plausibly contribute to the range observed. The overall relationship between arsenic concentrations and CFC-11 ages allows for a rough estimation of an overall arsenic accumulation rate in Patna of ~0.002 ± 0.003 $\mu M.yr^{-1}$ (~0.2 ± 0.2 $\mu g.L^{-1}.yr^{-1}$). If apparent CFC-12 ages are used to estimate an overall arsenic accumulation rate rather than CFC-11 ages, a stronger and statistically significant relationship is observed in the dataset (~0.005 ±
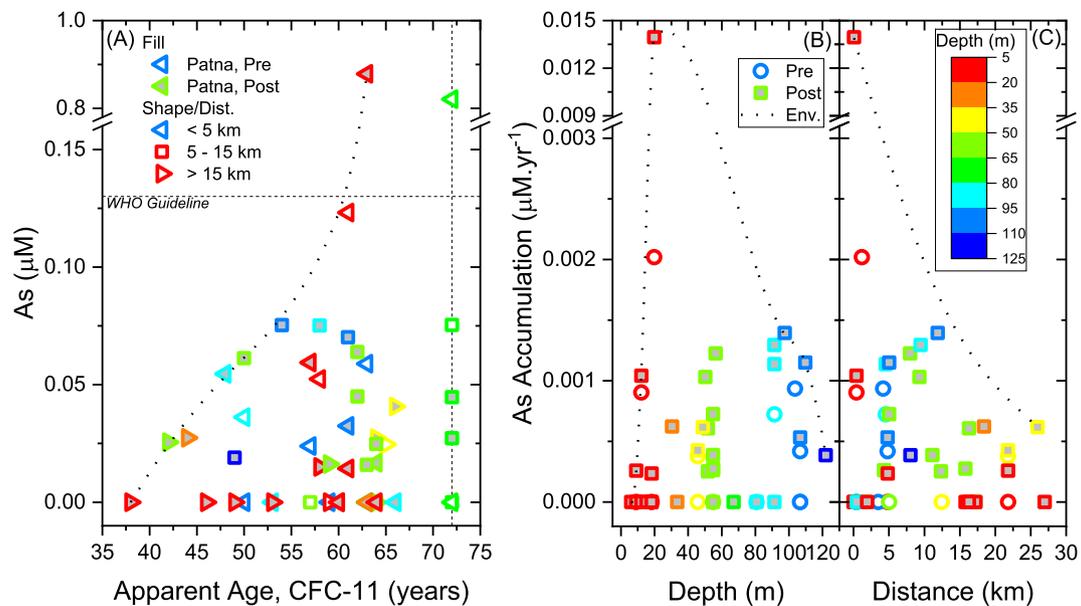
Fig. 6. (A) Groundwater arsenic *versus* apparent CFC-11 age (2020 basis, in years) for Patna. Symbol shape represents proximity to River Ganga (left triangle ≤ 5 km; square = 5–15 km; right triangle ≥ 15 km. The horizontal dashed line is WHO provisional guideline for arsenic (World Health Organization, 2011) and the vertical short dotted line is the estimated maximum CFC-11 model age (*e.g.* 72 years). Groundwater arsenic accumulation rate on the basis of CFC-11 apparent age (μM.yr^{-1}) for Patna against (B) depth and (C) distance from river. Edge colour represents groundwater depth and grey fill indicates post-monsoon season. Fitted dotted lines represent approximate envelope relationships estimated based on maximum concentration at a given CFC-11 age (for A) or maximum arsenic accumulation at a given depth or distance (for B & C respectively) observed.

0.003 μM.yr^{-1}; $t_{49} = 2.1$, $p < 0.05$). Arsenic accumulation rates based on SF$_6$ ages (~0.002 ± 0.002 μM.yr^{-1} or ~0.2 ± 0.2 μg.L^{-1}.yr^{-1}; $t_{33} = 1.0$, $p = 0.3$) are very similar to the CFC-11 based estimation. The average overall accumulation rate, based on a combined average of CFC-11, CFC-12 and SF$_6$ based estimations, is ~0.003 ± 0.003 μM.yr^{-1} (~0.3 ± 0.2 μg.L^{-1}.yr^{-1}). The maximum observed rates based on each residence time indicator are very consistent across tracers and are ~0.014 μM.yr^{-1}, ~0.013 μM.yr^{-1} and ~0.015 μM.yr^{-1} for CFC-11, CFC-12 and SF$_6$, respectively, with an average maximum rate across the age models being ~0.014 μM.yr^{-1} (~1 μg.L^{-1}.yr^{-1}). The arsenic accumulation rates do not strongly depend on season, as the distributions of pre- and post-monsoon rates are not significantly different.

The maximum arsenic accumulation rate in groundwater of ~0.014 μM.yr^{-1} and other elevated rates are clearly observed at relatively shallow depths (~20 m) and at locations in near proximity to the River Ganga (<~1 km) (Fig. 6B & C), particularly in urban areas in the eastern part of Patna (Fig. S6L). A broad decrease in accumulation rates is observed with regard to both increasing depth and distance from the River Ganga in envelope-type relationships. Importantly, however, these relationships are heterogeneous, and an overall dependence of accumulation rate on both depth ($t_{43} = -0.65$, $p = 0.52$) and distance from River Ganga ($t_{43} = -1.3$, $p = 0.21$) is not statistically significant. Nevertheless, the observation of elevated arsenic accumulation at some shallow depths in close proximity to the River Ganga suggests there are particular zones which provide an important control on arsenic mobilization processes. The presence of near-river fast-track zones in some locations would facilitate high groundwater-surface water connectivity, leading to the ingress of young, oxic recharge, particularly to relatively shallow groundwater. The observation that the site of highest arsenic and arsenic accumulation is also characterized by highest ammonium concentrations and elevated iron (Fig. 2 & Fig. S5) suggests that nutrient-bearing sewage may ingress into groundwaters in this area, possibly *via* groundwater-river connectivity, which in turn could induce iron reduction and arsenic release if ammonium is used as a potential electron donor (Xiu et al., 2020). This has important implications for groundwater management, including siting of pumping locations, particularly as urban abstraction in relatively vulnerable locations may

exacerbate surface-groundwater interactions leading to geochemical conditions which are more favorable for arsenic release and hence future accumulation in groundwater.

The overall estimated arsenic accumulation rate in Patna of ~0.003 ± 0.003 μM.yr^{-1} is more than an order of magnitude lower than similarly estimated rates in Cambodia (~0.08 ± 0.03 μM.yr^{-1} (Richards et al., 2019c)) and two orders of magnitude lower than suggested in Bangladesh (estimates between ~0.28 ± 0.05 and 0.31 ± 0.08 μM·yr^{-1} (Radloff et al., 2007) and ~0.26 ± 0.03 and 0.32 ± 0.04 μM·yr^{-1} (Stute et al., 2007)). Even the maximum value ~0.014 μM.yr^{-1} observed in Patna are lower than these rates reported elsewhere. The much lower arsenic accumulation rates observed in Patna as compared to other arsenic-impacted areas in the circum-Himalayan region raises a number of interesting questions regarding these differences and wider implications including on future groundwater vulnerability. A systematic investigation of the nature of organic matter in the study area, and its potential role (or otherwise) as an electron donor in arsenic mobilization, including in comparison to trends observed in arsenic-impacted Bengali (Kulkarni et al., 2017; Vega et al., 2017; Kulkarni et al., 2018) or Cambodian (Richards et al., 2019b) aquifers, is currently being undertaken by co-authors. Further a reactive transport model is under development to better understand the changing redox conditions, hydrological controls and groundwater-surface water dynamics in relation to groundwater arsenic release. Interpreting the potential geochemical interactions between recently characterized surface water in the Ganga River Basin (Richards et al., 2022) and groundwater in Patna is an important next step, including to inform future predictions of groundwater vulnerability, especially given insight provided by other investigations demonstrating the importance of the riverbed-aquifer interface as a hotspot for biogeochemical interactions influencing arsenic mobilization in high abstraction zones of the Red River Basin in Vietnam (Wallis et al., 2020).

A simplified conceptual schematic illustrates some of the key geochemical conditions and interactions which appear to be occurring in the groundwater under Patna (Fig. 7). In areas away from the river and Patna urban center, the dominant flow control is vertical and the main source of recharge is monsoonal, surface-derived ingress. Flow
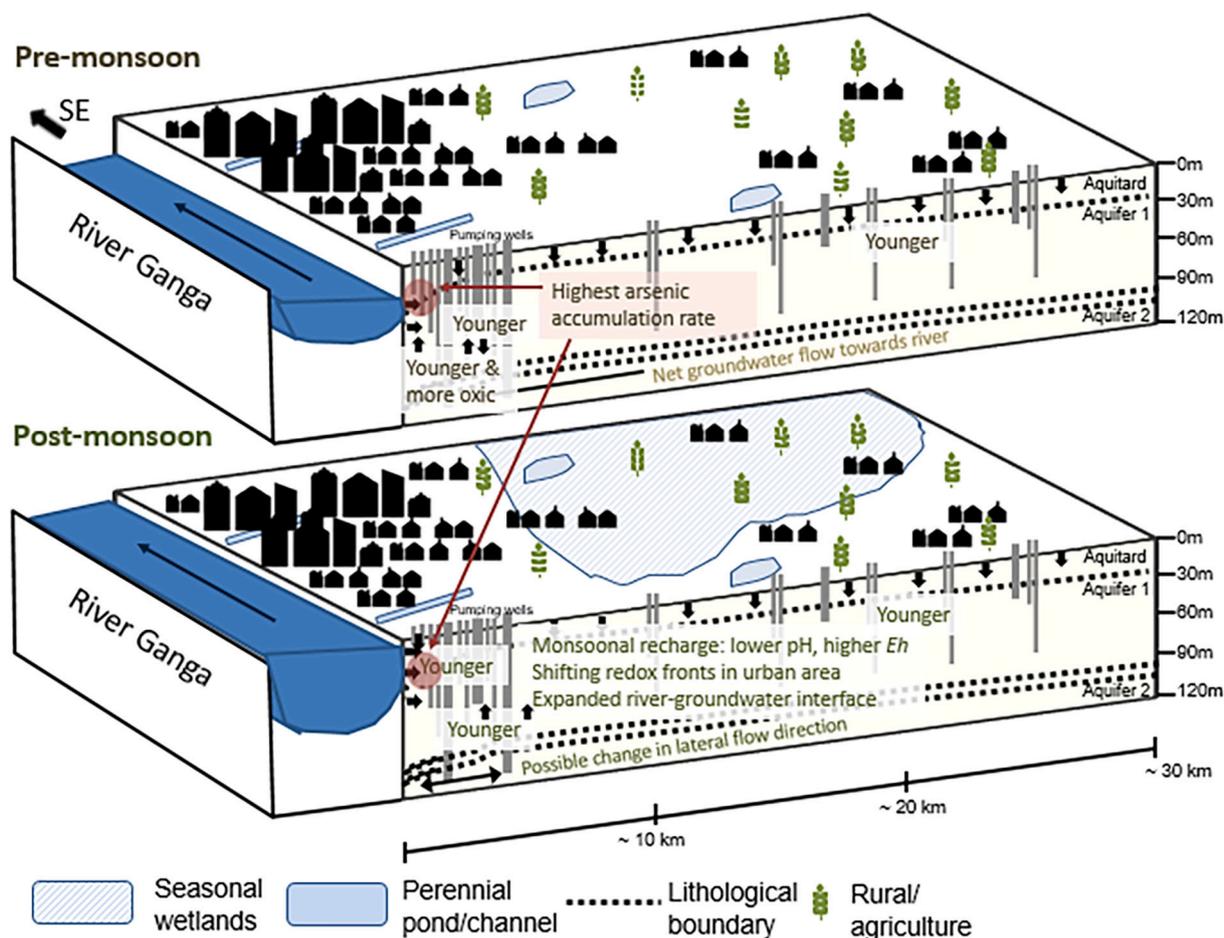
Fig. 7. Simplified conceptual schematic of field area and dominant processes in the pre- and post-monsoon seasons indicating vertical and lateral flow controls across the study area, shifting monsoonal flow regimes and shallow, near-river location of highest observed arsenic accumulation rates. Note locations of actual sampling points are shown on Fig. 1 and a three-dimensional bubble plot of arsenic concentrations on Fig. 3A and B.

regimes and chemical groundwater signatures become more complex near the central urban areas, likely attributed to the combined influence of extensive urban pumping and river-groundwater interactions. This leads to a spatially-dependent redox front where patterns in the behaviour of redox sensitive parameters (*e.g.* sulfate, nitrate, nitrite, ammonium) are observed. The river is likely contributing nutrients to the groundwater, especially during periods of flow reversal during or after the monsoon. However, regardless of season, the highest arsenic concentrations and arsenic accumulation rates are observed in shallow samples very near the river and are also associated with elevated iron and ammonium. Zones of relatively high extents of surface-groundwater interactions are the most vulnerable and are likely to be the most sensitive of pumping related vertical drawdown as well as lateral connectivity. There are likely multiple processes occurring, particularly under the urban center where pumping regimes and proximity to the River Ganga lead to more complex hydrochemical conditions.

4. Conclusions

Here we have studied the spatial distribution and evolution of inorganic groundwater chemistry under the rapidly developing city of Patna, India using a suite of inorganic hydrochemical parameters and residence time indicators. The groundwater is mostly a Ca-Mg-HCO$_3^-$ type, and concentrations of dissolved arsenic are highly heterogeneous, ranging from below detection to ~0.88 μM (~70 μg.L^{-1}). Arsenic is positively associated with iron, manganese and ammonium, and broadly inversely correlated with nitrate and nitrite, consistent with arsenic

mobilization *via* the reductive dissolution of arsenic-bearing iron hydroxide minerals. Arsenic and other redox-sensitive species are depth dependent and reveal systematic spatial patterns. CFCs and SF$_6$ evidence modern groundwater ($<$~60–70 years) throughout the depth profile, although there is no apparent overall relationship between groundwater age and depth. There is evidence of both vertical and lateral flow controls across the study area, with the dominant flow control being vertical particularly at distances relatively far from the river. Although seasonal changes in major element groundwater geochemistry are generally not significant, an observed decrease in pH and increase in *Eh* in the post-monsoon season are consistent with an overall monsoonal flushing and dilution impact from monsoonal recharge across the study area. Seasonal patterns in residence time indicators suggest that there is a seasonally inversion of flow patterns particularly near the urban center and the River Ganga. Apparent groundwater ages are used to derive an overall estimated arsenic accumulation rate in Patna of ~0.003 ± 0.003 μM.yr^{-1} (~0.3 ± 0.2 μg.L^{-1}.yr^{-1}), based on an average of CFC-11, CFC-12 and SF$_6$-derived models, a rate which is an order of magnitude lower than previously estimated in Cambodia (Richards et al., 2019c) and two orders of magnitude lower than previously estimated in Bangladesh (Radloff et al., 2007; Stute et al., 2007). Arsenic accumulation rates are highest (maximum ~0.014 μM.yr^{-1} or ~1 μg.L^{-1}.yr^{-1}) in shallow groundwaters located near the River Ganga, suggesting these groundwaters are particularly vulnerable to the impacts of nutrient-bearing ingress which may induce arsenic mobilization in particular locations. This has important implications on water management (*e.g.* on siting of large-scale groundwater pumping infrastructure and on long-term

groundwater vulnerability) in Patna and other similar rapidly developing cities in the Middle Gangetic Basin and more widely.

Data access statement

Data supporting this study are provided in the manuscript and accompanying Supplementary Information.

CRediT authorship contribution statement

Laura A. Richards: Formal analysis, Investigation, Data curation, Visualization, Supervision, Conceptualization, Project administration, Methodology, Funding acquisition, Writing – original draft. **Rupa Kumari:** Investigation, Writing – review & editing. **Neha Parashar:** Investigation, Writing – review & editing. **Arun Kumar:** Investigation, Writing – review & editing. **Chuanhe Lu:** Writing – review & editing, Formal analysis. **George Wilson:** Writing – review & editing, Formal analysis. **Dan Lapworth:** Conceptualization, Funding acquisition, Writing – review & editing. **Vahid J. Niasar:** Conceptualization, Funding acquisition, Writing – review & editing. **Ashok Ghosh:** Conceptualization, Funding acquisition, Writing – review & editing. **Biswajit Chakravorty:** Conceptualization, Funding acquisition, Writing – review & editing. **Stefan Krause:** Conceptualization, Funding acquisition, Writing – review & editing. **David A. Polya:** Conceptualization, Methodology, Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing. **Daren C. Gooddy:** Conceptualization, Methodology, Investigation, Resources, Project administration, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jconhyd.2022.104043.

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