Groundwater quality in the alluvial aquifer system of northwest India: new evidence of the extent of anthropogenic and geogenic contamination

Lapworth DJ[1*], Krishan G[2], MacDonald AM[3], Rao MS[2]

[1] British Geological Survey, Maclean Building, Wallingford, UK

[2] National Institute of Hydrology, Roorkee, Uttarakhand, India

[3] British Geological Survey, Lyell Centre, Edinburgh, UK

*Corresponding author, Dan Lapworth, email: djla@bgs.ac.uk

Highlights

1. Distinct urban, agricultural and geogenic sources of groundwater contamination

2. Elevated uranium occurrence, exceeding 30 µg/L in 10% of sites

3. Shallow aquifer system have significantly enhanced salinity, and nitrate and selenium concentrations

4. There is evidence of salinity and nitrate breakthrough to depths >100 m due to pumping

Abstract

Groundwater depletion has been widely studied in northwest India, but water quality concerns are still poorly constrained. In this study, we explore the hydrochemistry of the top 160 m of the aquifer system, through detailed field studies in the Bist-Doab region, considering both anthropogenic and geogenic controls. A detailed comparison is made between sites dominated by urban and agricultural landuse. Salinity, nitrate, chloride and lead concentrations are significantly higher in the shallow (0-50 m) groundwater system due to surface anthropogenic contaminant loading from agricultural and urban sources. The widespread occurrence of oxic groundwater within the aquifer system means that denitrification potential is limited and also enhances the mobility of selenium and uranium in groundwater. Geogenic trace elements (e.g. As, Se, F), are generally found at concentrations below WHO guideline drinking water values, however elevated U concentrations (50-70 µg/L) are found within the deeper part of the aquifer and shallow urban aquifers associated with higher bicarbonate waters. Higher concentration of Se (10-40 µg/L) are found exclusively in the shallow groundwater system where Se is mobilised from soils and transported to depth in the shallow aquifer due to the prevailing oxidising aquifer conditions. New evidence from a range of environmental tracers shows elevated concentrations of anthropogenic contaminants in the deeper part of the aquifer (50-160 m deep) and demonstrates vulnerability to vertical migration of contaminants. Continued

intensive groundwater abstraction from >100 m deep means that water quality risks to the deep aquifer system need to be considered together with water quantity constraints.

Key words: groundwater, India, contamination, groundwater vulnerability, geogenic, anthropogenic

1. Introduction

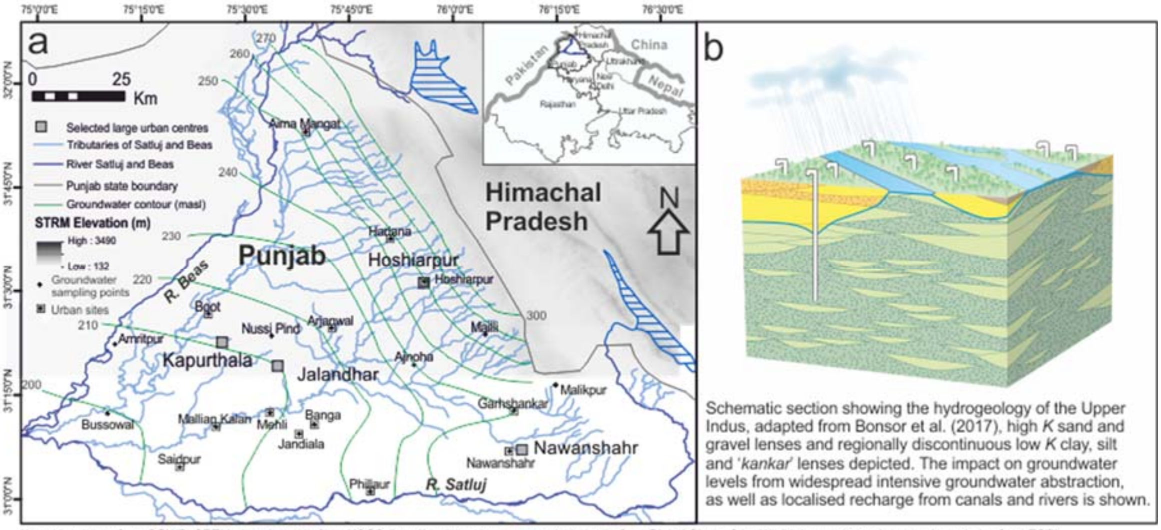
Over the last 150 years there has been growing intensification of agricultural activity in the Indo-Gangetic plain (Abrol et al., 2002). This started with the introduction of large surface water irrigation in the 19th century, and was followed by the introduction of agrichemicals in the mid-20th century and rapid growth in groundwater irrigation and urban development in the last 50 years (Mukherjee and Kuroda, 2003). Groundwater is now heavily exploited for irrigation, industry and drinking water and demands on this resource are increasing rapidly (MacDonald et al., 2016). The Punjab region of northwest India is a nationally critical source of food and this has been possible through the steady increase in surface water and more recently groundwater irrigation (Cheema et al., 2014). The Bist-Doab region of northwest India is a prime example of where there has been long term unsustainable abstraction of groundwater (CGWB, 2011; Tiwari et al., 2009). There are huge pressures on groundwater resources in this region and abstraction for irrigation and domestic use, as well as changes in rainfall patterns (Asoka et al., 2017), has led to a steady drop in groundwater levels in many regions of northern India over the last 30 years. The security of groundwater supply is often looked at from a quantity perspective (Aeschback-Hertig and Gleeson, 2012; Asoka et al., 2017; Gleeson et al., 2015; MacDonald et al., 2012). In contrast, with perhaps the exception of arsenic and fluoride contamination, the degradation of groundwater quality and aquifer vulnerability, and its impacts on water security, has received less attention globally (Foster and Chilton, 2003; Scanlon et al., 2007).

The relatively long residence times of pumped groundwater systems (e.g. $10\text{-}10^3$ y^{-1}) are able to protect groundwater sources from some surface sources of contamination, but once contaminated, steps taken to reverse this type of anthropogenic water quality degradation take considerable time (Morris et al., 2003; Visser et al., 2009). The build-up of high salinity in shallow groundwater systems driven by irrigation and abstraction practice across the Indo-Gangetic Basin is considered to pose a greater threat to groundwater degradation than aquifer storage depletion (MacDonald et al., 2016).

Geogenic contamination of shallow groundwater resources from arsenic and fluoride is well documented globally and limits the use of groundwater resources (Edmunds and Smedley, 2013; Fendorf et al., 2010; Smedley and Kinniburgh, 2002). A large number of studies have investigated geogenic contamination in the distal parts of the Indo-Gangetic basin (DPHE/BGS, 2001; Nickson et al., 1998; Ravenscroft et al., 2004), in contrast water quality constraints are relatively poorly characterised in the upper parts of the basin. While regional hydraulic anisotropy (ratio horizontal to vertical permeability) is thought to protect the deeper groundwater from being contaminated by shallow geogenic sources of arsenic contamination in the more distal parts of the Indo-Gangetic alluvial deltaic aquifer system (Bonsor et al., 2017; Hoque and Burgess, 2012; Michael and Voss, 2009), the vulnerability of the plains aquifer systems of NW India to pumping induced vertical migration of contaminants is poorly understood. Aquifer vulnerability assessment in the upper and central Indo-Gangetic basin are dominated by the use of models that consider the combined factors of intrinsic aquifer vulnerability and land use (Rahman, 2008; Raju et al., 2014).

A recent study by Lapworth et al. (2015) in NW India highlighted the low regional aquifer anisotropy through the use of modern residence time tracers (chlorofluorocarbons), and traced modern recharge from local meteoric sources using stable isotope ratios of O and H. This study showed that the shallow (0-50 m) and deeper (>75 m) aquifer system is actively recharged and renewed by local meteoric sources, and that the intensive pumping for municipal drinking water supplies from (>100 mbgl) induces vertical leakage from the shallow aquifer (Lapworth et al., 2015). This induced recharge may reduce aquifer depletion, but the presence of modern tracers within the shallow and deeper parts of the aquifer system suggests that this groundwater is perhaps regionally vulnerable to vertical contaminant migration from either anthropogenic or geogenic sources.

Depth variations in lithology within Indo-Gangetic basin are characterised by large spatial heterogeneity due to variations in depositional conditions and changes in drainage network patterns controlled by tectonics and large historical variations in the intensity of the Monsoon (Gupta, 1997; Kumar et al., 2007; Singh, 2004). Geo-mophologically the foreland basin can be divided into three zones, the Shiwalik and Kandi watershed, the interfluvial plains located between larger drainage channels e.g. R. Beas, R. Sutlej and the R. Yamuna, and floodplain areas located in close proximity to the drainage and in the confluence zones (Bowen, 1985). Recent work by van Dijk et al. (2014) shows that the geomorphic setting of the Sutlej fan system provides a primary control on the aquifer distribution and geometry, showing an overall decrease in the proportion of aquifer material downstream and an average aquifer thickness of 7 m.



Schematic section showing the hydrogeology of the Upper Indus, adapted from Bonsor et al. (2017), high *K* sand and gravel lenses and regionally discontinuous low *K* clay, silt and '*kankar*' lenses depicted. The impact on groundwater levels from widespread intensive groundwater abstraction, as well as localised recharge from canals and rivers is shown.

Water level data from CGWB, SRTM elevation data from USGS (http://earthexplorer.usgs.gov), drainage from Digital Chart of the World data, state and country boundaries from ESRI.

Figure 1. a) Study area location, groundwater sampling network and regional groundwater levels, site names were chosen based on the name of the nearest settlement, the inset shows the location of the Bist-Doab. b) Schematic hydrogeological cross section of the region, adapted from Bonsor et al. (2017).

Chemical properties of groundwater can be used as environmental tracers and so enable conclusions to be drawn about the water's origin, residence time and hydrogeochemical evolution (Edmunds et al., 2003). For example, tracers such as major elements and ratios (e.g. NO_3, Ca/Mg, NO_3/Cl, Cl/Br) and trace elements (e.g. Sr, Li, Rb, Mo, U, As, F, Se, Cd, Ni, Zn, B) are used as tracers in hydrogeological investigations to characterise anthropogenic and geogenic sources of contamination (Edmunds and Savage, 1991; Jaunat et al., 2012). Environmental tracers are routinely employed as proxies for assessing groundwater vulnerability to vertical leakage and microbiological contamination (Hinsby et al., 2008; Katz et al., 2011; Katz and Griffin, 2007; Lapworth et al., 2008; Morris et al., 2006). Few studies have employed direct observations such as hydrochemical profiling with environmental tracers coupled with available lithological data sets to assess aquifer vulnerability to water quality degradation in this setting.

This paper focuses on assessing the scale of current contamination in the shallow and deep aquifers and the vulnerability of the deep aquifers to vertical migration of anthropogenic contaminants and groundwater degradation risks from geogenic sources of contamination. This assessment was conducted using detailed hydrochemical profiling in a large study are in Punjab, NW India (Figure 1). Hydrochemical data from contrasting urban/peri-urban and rural settings, categorised based on field observations of the dominant land use at sample sites, are to characterise surface contaminant sources and groundwater degradation within the shallow sedimentary aquifer system from these two dominant land use types. Data from paired shallow (0-50 mbgl) and deep abstraction points (60-160 mbgl) are used to assess the impact of intensive pumping on contaminant breakthrough to depth within the aquifer system. The hydrochemical profiles will be considered for the first time with available data from detailed lithological profiles to explore regional controls on deep aquifer vulnerability to vertical contaminant migration within the sedimentary aquifer system.

2. **Methods**

2.1 Study area: hydrogeology and groundwater sampling

A hydrogeochemical sampling campaign was carried out across the Bist-Doab region of Punjab, northwest India, a 9000 km^2 area located between the River Sutlej, River Beas and the Shiwalik Hills to the north (Figure 1). See Figure S1 in supplementary information for details on surface elevation and population density across the study area. The Bist-Doab is a suitable region to understand the impacts of intensive groundwater abstraction on groundwater flow and recharge processes. It is amongst the most agriculturally productive areas in Punjab for wheat, rice, cotton and maize, with a current split of ca. 75% groundwater irrigation, 25% surface water irrigation (Lapworth et al., 2014). The Bist-Doab has seen groundwater levels fall systematically in some regions over the last two decades (Cheema et al., 2014; Lapworth et al., 2014).

Thick sequences of Pleistocene to Recent sediments derived from erosion of the Himalayas and lower lying foothills have formed the deep multi-layered sedimentary alluvial plain aquifer system we find today. Within the Bist-Doab study area (Figure 1) the major lithologies and sequences in order of increasing age and depth comprise: i) Recent surface deposits, ii) Holocene Sirowal sediments and occasional gravels with inter-bedded coarse clastics from the Kandi belt and red clay beds and iii) Pleistocene boulder beds and inter-bedded clays (Bowen, 1985; Khan, 1984).

Figure 1b shows a schematic hydrogeological section for the Upper Indus, a brief summary of the hydrogeology is provided in the subsequent section. For a comprehensive description see

Bonsor et al. (2017). The Upper Indus sedimentary aquifer is characterised by highly permeable sand and gravel lenses interlayered with laterally discontinuous lower permeability silt, clay and '*kankar*' (carbonate) deposits. The groundwater resources are highly exploited with many tube wells (typically <100 m), hand dug wells and an ever growing number of deeper tube wells, typically >100 m; CGWB (2010). For example Punjab, India, is estimated to have around 1 million tube wells. Groundwater is abstracted using handpumps and motorised diesel and electric submersible pumps. The aquifer anisotropy ratio (ratio of vertical vs horizontal hydraulic conductivity, Kv/Kh) for the Upper Indus is typically <25 (Bonsor et al., 2017). The regional groundwater piezometric head decreases and flattens in a NE-SW direction (CGWB, 2007), with little or no regional flow within the central and SW part of the study area. Recent groundwater dating work has shown that the regional groundwater flow is now highly modified by vertical leakage due to both shallow pumping for irrigation and and abstraction at depth for drinking water (Lapworth et al., 2015). Regionally the groundwater recharge is dominated by meteoric rainfall (Lapworth et al., 2015), however in close proximity to surface water sources including canal leakage and surface water exchange have been shown to be important (Rao et al., 2017). Irrigation in this region is both from shallow groundwater sources and the Bist-Doab canal system diverted from the Sutlej River.

An array of 19 sites distributed across the study area was selected to characterise a range of hydrogeological settings including conventional recharge zones, the mid plains as well as discharge zones close to the confluence of the R. Satluj and Beas and included sites dominated by urban and rural landuse. Sites were classified as urban (n=12) or rural-agricultural (n=7) based on field observations of dominant landuse around sampling sites undertaken in 2013. Field measurements of dissolved oxygen (DO), pH, specific electrical conductance (SEC) and temperature were made at the wellhead using a flow-through cell. Hydrochemical sampling was carried out only after stable instrument readings were obtained for the field parameters and a minimum of three borehole volumes had been purged. These were sampled for a full suite of inorganic hydrochemistry to characterise the top 160 m of the alluvial aquifer system.

At 19 locations paired shallow (8-50 mbgl) and deep (60-160 mbgl) were sampled from aquifers (sand and gravels) which were separated in places by thick (typically several, 10-20 m) but regionally discontinuous lower permeability horizons.. Shallow sites were a sampled using a combination of hand pumps and submersible motorised pumps, deep samples were taken from municipal abstraction sites using submersible pumps. Sampling for groundwater was carried out both pre- and post-monsoon (2013-2014) to characterise temporal variability.

2.2 Hydrochemistry

Field alkalinity was determined by duplicate titration of 50 mL of sample with 1.6N sulphuric acid using a bromocresol green pH indicator. Samples for anion determination were filtered (<0.45 μm) in the field, stored in Nalgene™ bottles and refrigerated prior to analysis by ion chromatography. Samples for cations were filtered in the field using cellulose nitrate filters and stored in Nalgene™ bottles. These were preserved by acidifying using 0.5% v/v HCl and 0.5%v/v HNO_3 (Aristar™ grade). Allanalysis was carried out atat BGS laboratories using UKAS accredited methods. Field blanks were taken through the same sampling procedure and the ICP-MS and IC results were validated using Aquacheck™ standards. Daily calibration of field probes (SEC, DO, pH) were carried out, Eh probes values were checked using Zobell solution in the field. All raw Eh values were temperature corrected.

2.3 Lithological profiles

Lithological records were compiled for 30 locations within the study area from a range of sources including the Central Ground Water Board database (CGWB, 2014), Bowen (1985 and six newly installed (2013) National Institute of Hydrology groundwater monitoring sites. The fraction of aquifer and non-aquifer thickness within the shallowest 50 metres was calculated. Fifty meters is is locally considered the depth above which the shallow aquifer system is found. Aquifer units were identified as micaceous sands of varying grades, fine-coarse grained, as well as selected cobble, pebble and angular gravel sized quartzite sequences. Non-aquifer deposits were typically plastic clays (brown and green) as well as non-plastic yellow clays found at a few locations. The identified aquifer layers were numbered from shallowest to deepest at each site as a measure of the vulnerability of the deeper aquifers to vertical migration of recharge (See Table S1 in supplementary information for compiled summary results).

3. Results

3.1 Hydrochemical depth profiles

Results from pre and post monsoon sampling at each paired site are not differentiated in this study. While statistically significant differences between shallow and deep samples were found for a range of hydrochemical parameters, no statistically significant differences in either shallow and deep groups were detected using a Wilcoxon rank sum test ($p>0.1$), when hydrochemistry results were compared pre and post monsoon.

Figure 2 shows hydrochemical depth profiles for a range of key water quality parameters and environmental tracers including electrical conductivity, nitrate ($NO_{3)}$, and selected trace elements (selenium (Se), arsenic (As), lead (Pb) and fluoride (F)) grouped by sites dominated by either urban or agricultural landuse. Overall there is a decrease in concentration with depth for all parameters except As for urban sites. For agricultural sites broad decreases in concentrations with depth are observed for all parameters except F, Se and As which had no clear trend with depth. Highest concentrations for a range of trace elements including As, Pb, Se, uranium (U) and F were found in sites dominated by urbanland use, and with the exception of U (Figure 3),Pb and NO_3 these were below the WHO guideline value and Indian standard for drinking water . Molybdenum (Mo) shows an increase in concentration with depth irrespective of land use type, some sites between 50-150 m show higher concentrations between 10-20 μg/L.

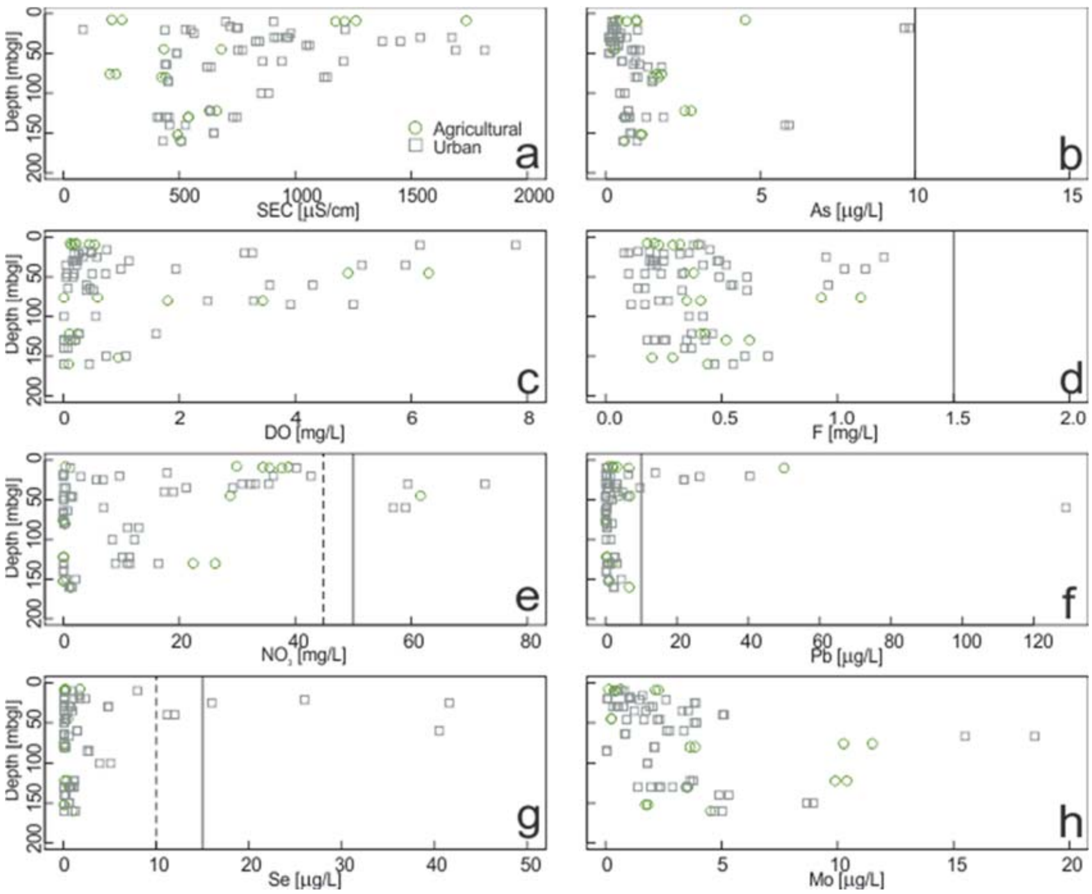


Figure 2. Depth profiles for selected hydrochemistry for different land use a) SEC (μS/cm), b) As (μg/L), c) DO (mg/L), d) F (mg/L), e) NO_3 (mg/L), f) Pb (μg/L), g) Se (μg/L), h) Mo (μg/L). Solid line shows WHO drinking water guideline values (WHO 2011), dashed line shows permissible India drinking water standard (IS, 2012) if they differ from WHO standard.

Figure 3 shows depth profiles for U (Figure 3a) and key geochemical parameters that control U concentrations in groundwater, including pH (Figure 3b), Eh (Figure 3c), alkalinity (Figure 3d). Elevated concentrations of U are found in both the shallow and deep aquifers, with mean and median concentrations of 17 and 16 μg/L respectively.

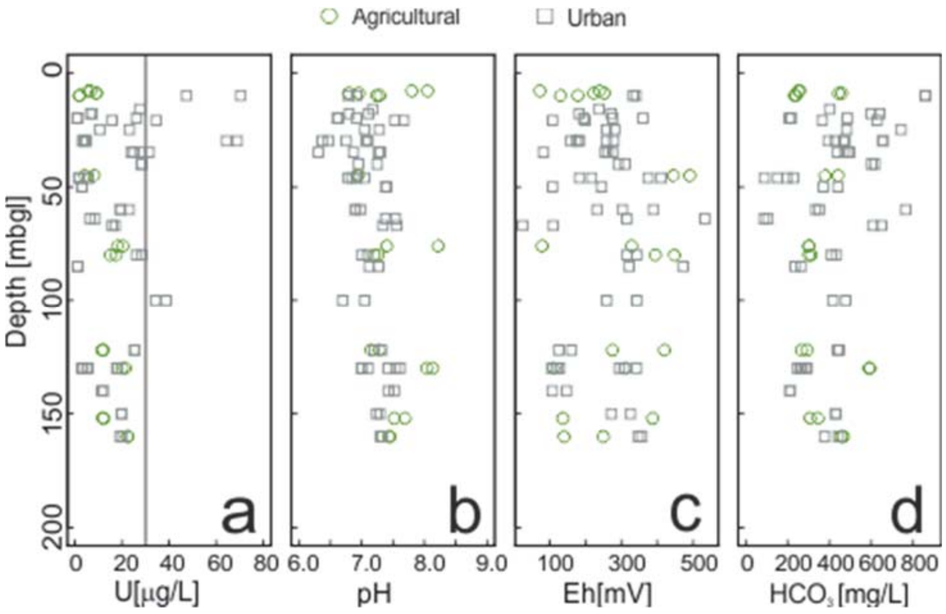


Figure 3. Depth profiles of Uranium and key hydrogeochemical parameters for different land use a) U (μg/L), b) pH, c) Eh (mV), d) HCO_3 (mg/L). Solid line shows WHO drinking water guideline value of 30 μg/L for Uranium (WHO 2011).

3.2 Hydrochemical changes with land use, lithology and historical groundwater trends

Statistical summaries, shown as box plots and cumulative frequency plots, are presented in Figures 4 and 5 for key selected water quality parameters, with results grouped by depth and landuse type. Shallow groundwaters from urban and agricultural land use have comparable median values for SEC and show significantly elevated SEC values compared to deep sites. Nitrate distributions were significantly higher for shallow agricultural groundwater compared to urban land use, and elevated in concentration compared to deep groundwater, only a few outliers were found above the WHO guideline values of 50 mg/L. Higher Cl concentrations were observed in shallow groundwater compared to deep groundwater although median values are all below 50 mg/L. Median U concentrations were >15 μg/L for all groups except shallow agricultural sites where concentrations were significantly lower with median values of c. 6 μg/L. Arsenic concentrations were below 10 μg/L, with median concentrations for all groups below 2 μg/L. Shallow groundwaters had higher Pb concentrations and larger interquartile ranges compared to deep groundwater, and a number of outliers that were above the WHO guideline value of 10 µg/L (Figure 5d). Fluoride concentrations were all found to be below 1.5 mg/L. Significantly higher HCO_3 concentrations were found in shallow urban groundwater compared to other groups. Median DO and concentrations and distributions were comparable across all groups and depths (Figure 4c and Figure 5h). Groundwater is generally oxic, but sub-oxic and more reducing conditions are found in all groups and depths. Higher pH values (median of 7.5) were found in deep agricultural groundwater compared to other groups.

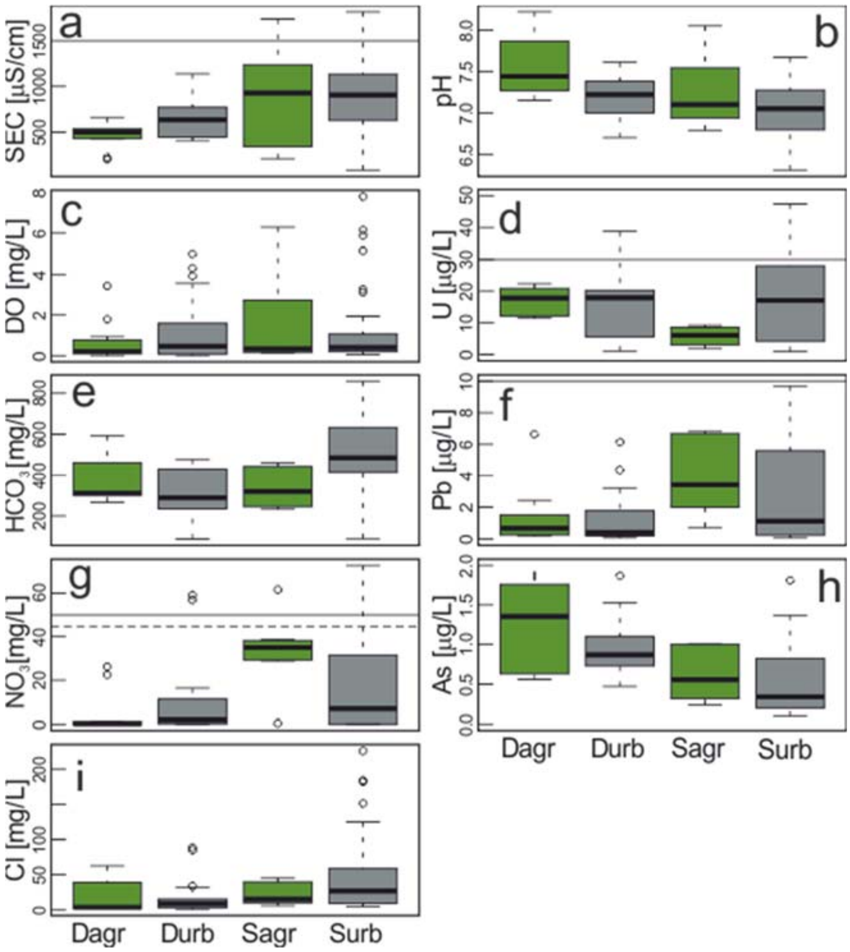


Figure 4. Box-plot of selected hydrochemical parameters by land use and borehole depth a) SEC (µS/cm), b) pH, c) DO (mg/L), d) U (µg/L), e) HCO_3 (mg/L), f) Pb (µg/L), g) NO_3 (mg/L), h) As (µg/L), i) Cl (mg/L). DAgr = deep agricultural, DUrb = deep urban, SAgr = Shallow agricultural, SUrb = shallow urban. Solid lines show WHO drinking water guideline values (WHO 2011), dashed line shows permissible India drinking water standard (IS, 2012) if they differ from WHO standard.

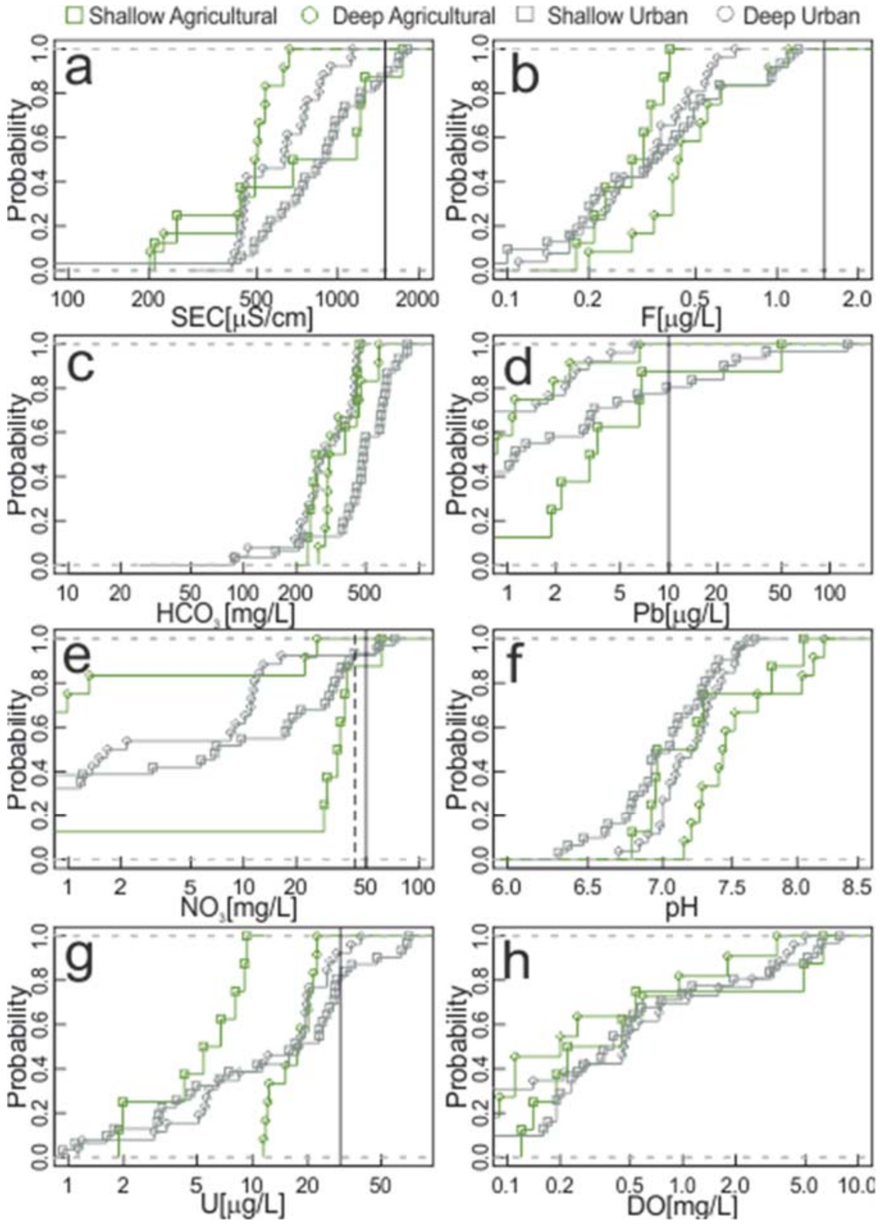


Figure 5. Cumulative probability plots for hydrochemistry a) SEC (µS/cm), b) F (mg/L), c) HCO_3 (mg/L), d) Pb (µg/L), e) NO_3 (mg/L), f) pH, g) U (µg/L) and h) DO (mg/L). Solid lines show WHO drinking water guideline values (Orgnaisation, 2011), dashed line shows permissible India drinking water standard (IS, 2012) if they differ from WHO standard.

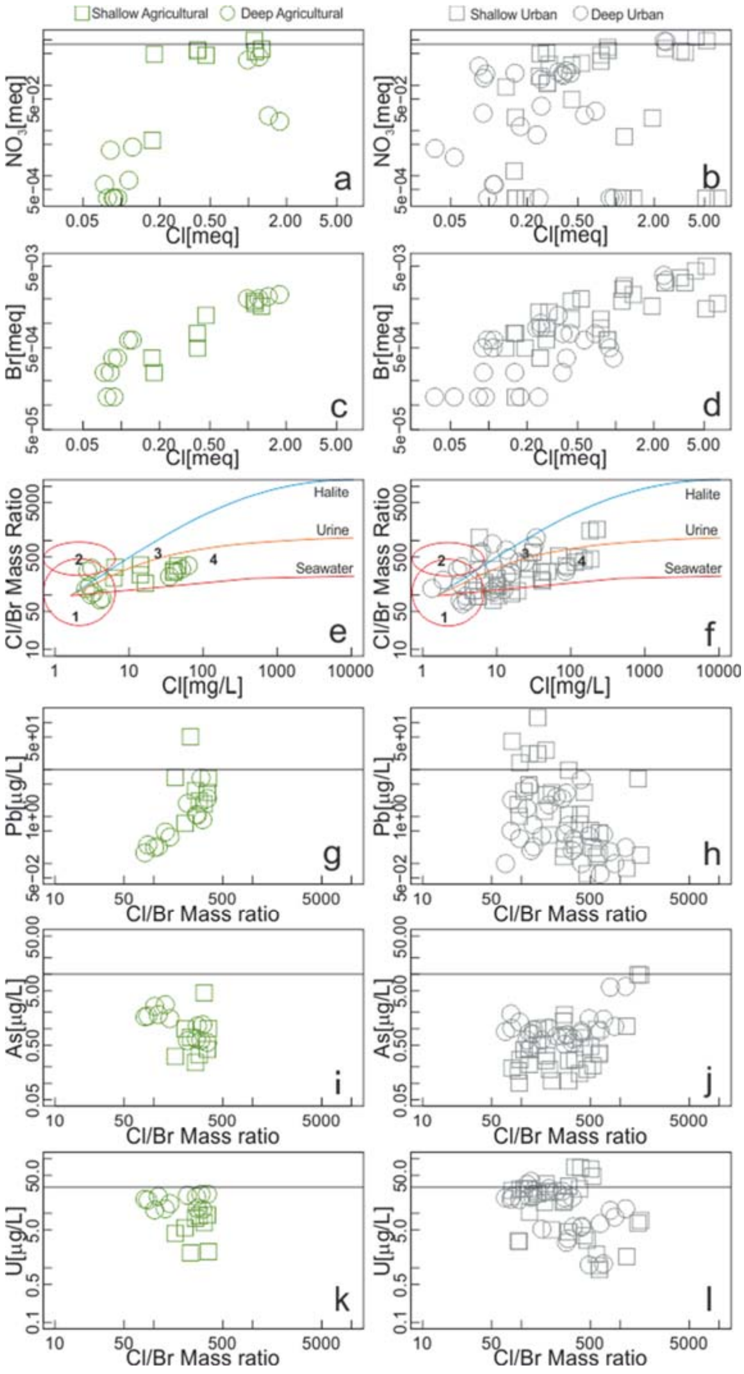


Figure 6. Cross plots of: Cl (meq) for agricultural (agr) and urban (urb) sites vs a) $NO_{3(agr)}$, b)$NO_{3(urb)}$, c) $Br_{(agr)}$, d) $Br_{(urb)}$; cross plots of Cl/Br Mass Ratio vs e) $Cl_{(agr)}$, f) $Cl_{(urb)}$, 1=Dilute (i.e. low total dissolved solids (TDS)) groundwater (Davis et al., 2004), 2=Bulk precipitation (Alcalá and Custodio, 2008), 3=Septic tank leachate (Panno et al., 2006), 4=Sewage (Vengosh and Pankratov, 1998), marine and halite binary mixing lines shown (Katz et al., 2011), urine binary mixing line for West Bengal, India (McArthur et al., 2012); cross plots of Cl/Br Mass Ratio vs g) $Pb_{(agr)}$, h) $Pb_{(urb)}$, i) $As_{(agr)}$, j) $As_{(urb)}$, k) $U_{(agr)}$, l) $U_{(urb)}$. WHO guideline drinking water values are shown as black horizontal lines (Orgnaisation, 2011).

Cross plots for selected parameters (Cl vs NO_3, Br and Cl/Br and Cl/Br vs Pb, As, U) are shown in Figure 6. These plots can be used to distinguish between different sources of contamination as well as key geochemical controls. There is a positive correlation between Cl and NO_3 (Figures 6a and 6b) for both agricultural ($R^2=0.2$, $p<0.001$) and urban land use ($R^2=0.16$, $p=0.07$) and several shallow sites within urban settings show evidence of denitrification. A strong positive correlation is observed between Cl and Br shown in Figures 6c for agricultural land use ($R^2=0.9$, $p<0.001$) and urban land use in Figure 6d ($R^2=0.5$, $p<0.001$). Figure 6e and 6f show cross plots of Cl (mg/L) against Cl/Br mass ratio, which can be used to distinguish between different sources of Cl. Deep sites are characteristic of more pristine and dilute (low TDS) groundwater and bulk precipitation, and some plot between the mixing line of dilute unaltered groundwater and halite end members, the latter being significant only for urban land use, suggesting that halite is not naturally occurring in the Bist-Doab. Shallow groundwater sources area dominated by samples that plot along the dilute groundwater-urine mixing line for both land uses. Overall, there is a positive correlation between log (Pb) and log (Cl/Br mass ratios) for agricultural sites ($R^2=0.4$, $p<0.001$) and a weak negative correlation for urban sites ($R^2=0.2$, $p<0.001$), as shown in Figures 6g and 6h. The sign is in reverse for As and Cl/Br mass ratios (Figures 6i and 6j), suggesting different sources and controls. There is a weak negative correlation between log(U) and log(Cl//Br mass ratios) with higher U concentrations in shallow urban groundwater with urine and halite signatures (Cl/Br mass ratio >400), shown in Figures 6k and 6l.

3.3 Spatial variations in hydrochemistry

Figures 7a and 7b show the spatial variability in long term groundwater levels and the fraction of low *K* horizons in the top 50 m below ground level across the study area. There is considerable variability in the average aquifer layer thickness (6.8 m, range 0-23.7 m) and average number (2, range 0-6) of non-aquifer units found in the top 50 m below ground level for individual lithologs across the study area. No clear spatial correlation in the fraction of low *K* horizons across the study area is observed; sites in close proximity have significantly different profiles. The average fraction (cumulative depth) of non-aquifer sequences for the top 50 meters was 0.3 (range 0-0.9) (See Table S1 for details). Spatial variability for selected hydrochemistry (SEC, NO_3, CFC-12 and U), is also presented in Figures 7c-7f. Overall, the highest SEC and NO_3 groundwaters are clustered in the central plains and distal part of the Bist-Doab; deep groundwaters are typically below 600 μS/cm and 10 mg/L as NO_3. Uranium concentrations greater than 10 μg/L are found across the study area, the two sites with the lowest U concentrations in both shallow and deep sites (Nawanshahr and Aima Mangat, see Figure 7f). Both also have high NO_3 and CFC-12 concentrations (Figure 7d and 7e) indicating shorter residence times which suggests that U concentrations may increase with longer residence times.

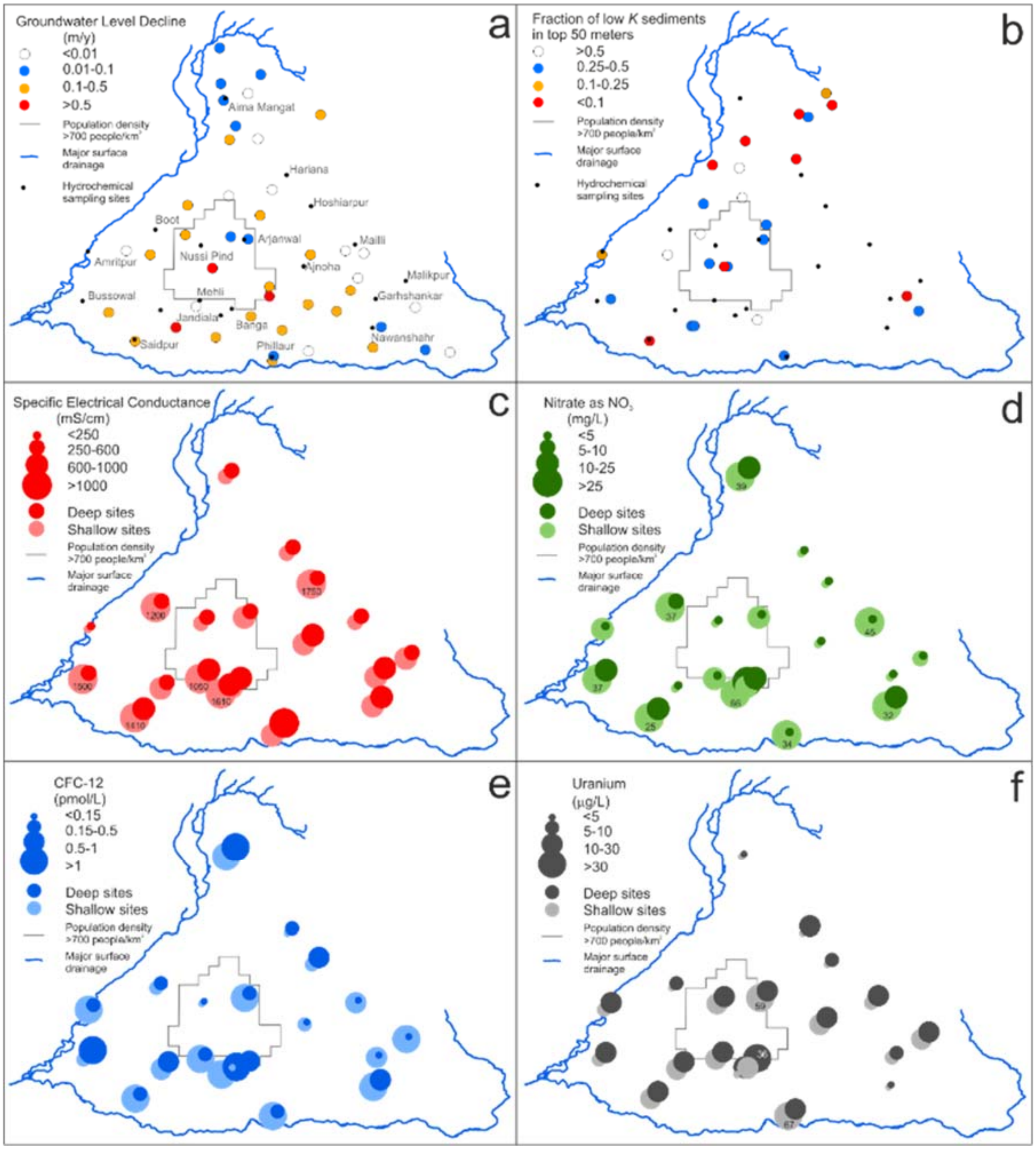


Figure 7. Spatial variation in a) long-term groundwater level trends (1985–2012), data source CGWB from Lapworth et al. (2015), site location names for groundwater sites are shown , b) fraction of low *K* lithology (plastic clay sediments) in the top 50 m below ground surface, and hydrochemistry (average of pre and post monsoon): c) SEC (μS/cm), d) NO_3 (mg/L), e)

Chloroflurocarbon-12 (pmol/L), data from (Lapworth et al., 2015), and f) Uranium (μg/L). The highlighted region in the centre of the study area shows region with highest population density (>700/km^2).

4. Discussion

4.1 Hydrochemical depth profiles

4.4.1 Anthropogenic sources of contamination

Significantly higher SEC and NO_3 concentrations are found in the shallow aquifer system, compared to the deeper aquifer systems, and this observation is consistent for groundwaters located in both urban and rural settings (Figure 7). This finding is consistent with other studies in India which show similar vertical variation in groundwater SEC (Misra and Mishra, 2007) and NO_3 concentrations (Agrawal et al., 1999; Suthar et al., 2009) and references therein. In the Bist-Doab this reflects anthropogenic inputs to the shallow groundwater system as there is no evidence, based on stable isotope data, for significant enrichment due to evapotranspiration in this study area (Lapworth et al., 2015). In the shallow agricultural areas, the data are consistent with irrigation returns flushing nitrate and chloride (Cl) into the aquifer (O Dochartaigh et al., 2010) and the use of fertilizers. In the urban areas, widespread contamination from sanitation is a more likely explanation. The presence of DO and the high Eh values for the majority of samples suggest that NO_3 reduction is probably not regionally significant (Rivett et al., 2008). However, at some sub-oxic sites the reducing conditions may lead to NO_3 reduction hot-spots within the shallow aquifer system where shallow groundwater tables are present or dissolved organic carbon concentrations are higher (Seitzinger et al., 2006).

In sites where agricultural land use dominates there is a good correlation between NO_3 and Cl (Figure 6). For some urban sites this relationship breaks down, and there are very low NO_3: Cl mass ratios, indicating denitrification processes and may result from the supply of organic carbon from urban waste-water sources (McCray et al., 2005). This assertion is further corroborated by the Cl:Br mass ratios for urban sites, which largely fall on a waste water mixing line in Figure 6 (Katz et al., 2011). At some sites shallow and deep groundwaters have low Cl and low Cl:Br mass ratios and low NO_3 and Cl concentrations that suggest rainfall dominated low TDS groundwater samples (Alcalá and Custodio, 2008; Davis et al., 2004). This inference is further supported by Rao et al. (2014) who use major ion chemistry (i.e. Gibb plots and

Ca/Na vs Mg/Na cross plots) which reveals that groundwater composition in this region is dominated by carbonate and silicate weathering processes but that in some instances shallow groundwaters show rainfall signatures. High Pb (>10 μg/L) concentrations are found in the shallow groundwater in urban sites, as has been reported in other urban aquifers in India (e.g. Somasundaram et al., 1993) and elsewhere (Navarro and Carbonell, 2007; Rivett et al., 2011).

4.1.2 Geogenic contamination

Potential geogenic contaminants such as selenium, arsenic, fluoride and uranium show contrasting trends with depth, though in the case of As and U they are subtle. Observed fluoride concentrations are below 1.5 mg/L for all samples in this study (see Figure 5) comparable to other studies undertaken within the Shiwalik hills in close proximity to Bist-Doab, to the north of this study area (Singh et al., 2010). There is a general trend of increasing F concentrations, up to 0.6 mg/L, with depth, pH, HCO_3 and groundwater residence time (Figure 2), irrespective of land use. There is a distinct group of shallow groundwater samples with F concentrations between 0.9-1.2 mg/L.

The highest Se groundwaters are found at shallow depths within the generally more oxic part of the aquifer and consistent with other published studies (Weres et al., 1990), which have observed high Se in groundwater associated with oxidising conditions and high NO_3 concentrations (Figure 2). Selenium appears to have a shallow source and enhanced regional Se concentrations in soils are thought to be the source of elevated Se in shallow groundwaters in Punjab (Bajaj et al., 2011; Dhillon and Dhillon, 2003). In semi-arid areas, such as the southern parts of the Bist-Doab, Se can build up over time in the soil and once irrigated can leach soluble Se from the soils leading to elevated Se in shallow groundwater (Deverel and Fio, 1991). Under oxidising conditions the more mobile Se (VI) is leached and this can be enhanced by the presence of oxyanions such as NO_3, sulphate and phosphate (Wright, 1999). Selenium concentrations found in this study (0.01-40 μg/L) are comparable with a recent study undertaken across Punjab, NW India (Dhillon and Dhillon, 2003; Dhillon and Dhillon, 2016), which found a significant relationship with depth, NO_3 and SEC suggesting a shallow source of Se.

Uranium concentrations ranged between 0.9-70 μg/L and concentrations in deep groundwater are significantly higher compared to shallow groundwater ($p<0.05$), with median values >15 μg/L. Significantly higher Mo concentrations were also found in deeper sites compared to shallow sites (Figure 2). WHO provisional guideline value for U is 30 μg/L, a guideline value for U that is based on daily water consumption of 2 L/day. Comparable concentrations of U have also been reported in the shallow hard-rock ("basement") groundwater of Andhra Pradesh, where U mineralisation is present (Brindha et al., 2011). The highest Se and U concentrations are observed in urban/peri-urban sites, which suggests that fertilisers are probably not a major source of Se and U in this area as has been hypothesised for other regions globally (Schnug and Lottermoser, 2013), it is likely that geogenic sources of U (e.g. U minerals and iron oxide coatings on aquifer grains, the prevailing oxic and alkaline conditions and carbonate complexation with U (VI)) that facilitates U mobilisation and result in high median U concentrations (Barnett et al., 2002; Kumar et al., 2011). The elevated U concentrations in the top 30 m in urban/peri-urban sites could be related to carbonate or organic matter U complexation, possibly from waste water sources, another possible process that could enhance in-situ U mobility is NO_3 fertilisation which was recently proposed by Banning et al. (2013).

Arsenic concentrations were found below the WHO guideline drinking water value of 10 μg/L for all of the samples in this study (n=76), and showed an inverse relationship with SEC, DO and the CFC-12, a groundwater age tracer, and a positive relationship with pH (see Figure 4). The overall increase in arsenic concentration with depth (see Figure 2) and bulk groundwater residence time (Lapworth et al., 2015) and correlation with pH and DO suggest that redox-speciation controls may be important for desorption of AsV from iron oxy-hydroxide surfaces leading to the release of higher arsenic concentrations into solution under alkaline conditions (Jain et al., 1999; Masscheleyn et al., 1991). Concentrations are generally below 3 μg/L even in the deepest sites where median concentrations are 1.5 μg/L. There are three anomalously high sites that fall between 3-9 μg/L which are found in the shallow part of the aquifer system, and these higher concentrations could be related to recent Holocene deposits and/or regions of lower aquifer flushing (Shamsudduha et al., 2015). In contrast, much higher arsenic concentrations in groundwater have been reported for parts of southern Punjab and Chandigarh, to the southeast of the study area (Chakraborti et al., 2016) and over much of the region (Hundal et al., 2009; Kumar et al., 2016; Sharma et al., 2013)

4.2 Vertical contaminant migration and vulnerability of deep groundwater sources

Natural flow regimes and recharge in the groundwater system are highly perturbed by the sustained pumping for irrigation and drinking water supply. A conceptual diagram showing a schematic of the contrasting groundwater flow regimes pre and post pumping and the migration of anthropogenic contaminants within the aquifer system is shown in Figure 8. There is evidence of NO_3 breakthrough from the shallow groundwater to depth (Figure 2 and 7) and this is likely to be enhanced in the future if the current increases in pumping from the shallow and deep aquifers continue. There is clear evidence from historical groundwater-level records that there has been a large decline in groundwater levels in shallow aquifers used for irrigation at a regional scale (ca. 20-25% of the Bist-Doab) over the last 20 years (Lapworth et al., 2015).

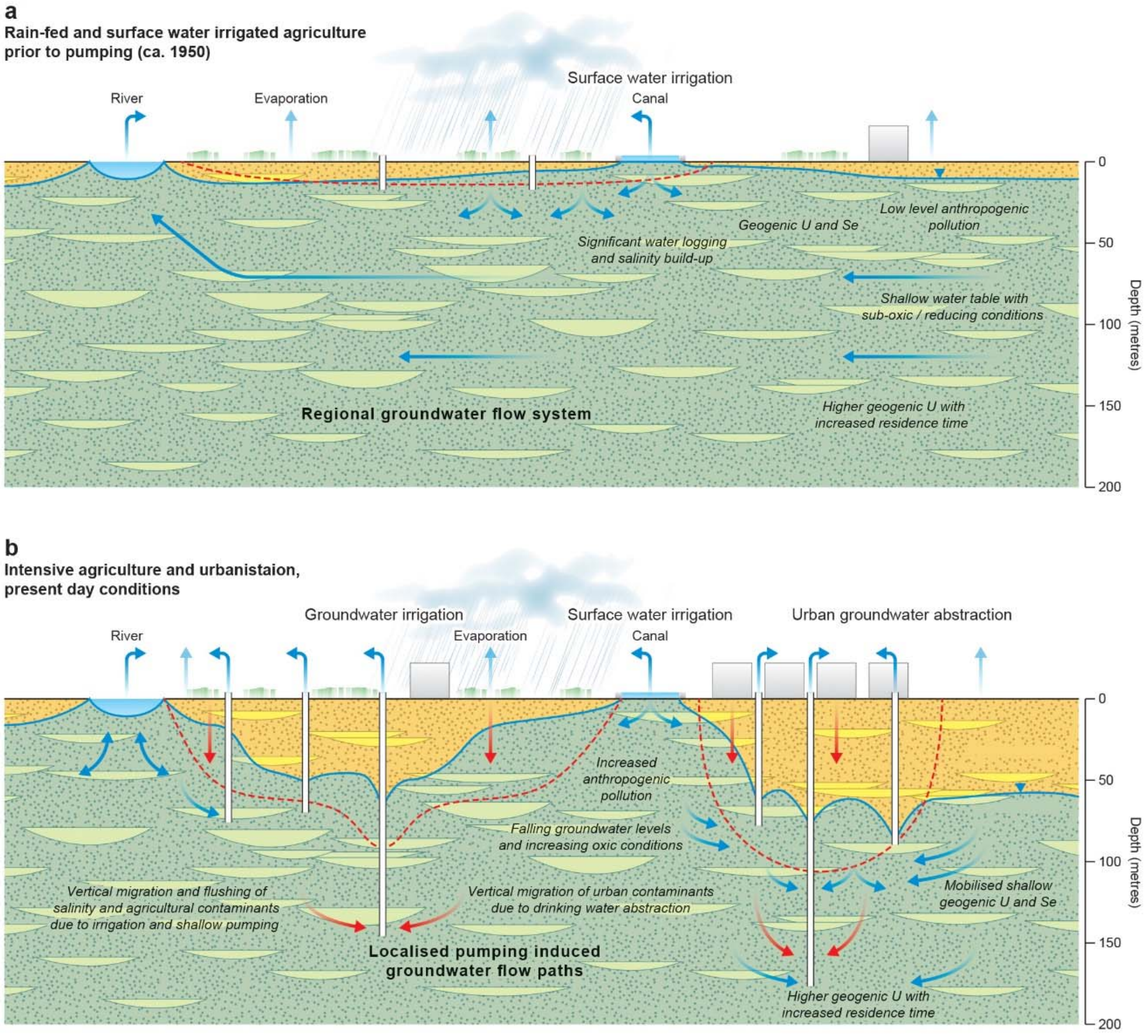


Figure 8. Conceptual model of changes in the hydrogeology and groundwater contaminant sources and migration in the Upper Indus aquifer system as a result of intensive pumping and anthropogenic pollution, a) pre-pumping conditions ca. 1950s, b) present day conditions with intensive pumping for irrigation and domestic drinking water

No obvious relationship exists between deep groundwater CFC-12 and distance from the recharge zone at the foot of the Shiwalik hills. Further, there is no clear spatial pattern in fraction of low K horizons in the upper 50 m of the aquifer (Figure 7). However, the poor spatial continuity of low *K* layers and the existence of high concentrations of CFC-12 and NO_3 in some deep groundwater points suggests that the aquifer has some vertical continuity enabling pumping induced flow. Under a natural groundwater flow regime pre-pumping groundwater residence times of the order of ca.10^2-10^3 years or more might be expected at 100-150 m deep within the aquifer (Figure 8). This is due to the vertical stratification in lithology,high aquifer storage and the low hydraulic gradients.

The aquifers in this region are vulnerable to contamination from anthropogenic agricultural (e.g. NO_3) urban sources (e.g. NO_3, Pb) and natural geogenic sources (e.g. Se and U). In some shallow groundwaters these contaminants are approaching or exceeding WHO guideline drinking water limits (e.g. NO_3, Pb and Se). These results show the potential for contaminants from surface and shallow sources to be flushed deeper into the aquifer, exceeding the capacity of the shallow aquifer to fully attenuate these contaminants through natural mechanisms such as sorption, dilution and denitrification. The enhanced pumping and resulting decline in water levels has meant that net potential recharge to the shallow aquifer has been enhanced (MacDonald et al., 2016; Shamsudduha et al., 2011), facilitating the rapid migration of recharge to depth within the aquifer system. Observed arsenic concentrations in the shallow aquifers in this region were all found to be below 10 μg/L, and it is possible that this can be attributed to the oxidising conditions, low anisotropy and higher rates of flushing in the aquifer system compared with the distal parts of the Indo-Gangetic Basin and elsewhere (Shamsudduha et al., 2015; Smedley et al., 2003; Van Geen et al., 2008).

In contrast to the deltaic parts of the Indo-Gangetic Basin, the regionally low anisotropy within the multi-layered aquifer system in the Bist-Doab, demonstrated in this paper using a range of environmental tracers, reveal that the deeper groundwater system is potentially vulnerable to vertical breakthrough of mobile contaminants from shallow parts of the aquifer system. This finding has important implications for the management of groundwater in this region and risks posed by geogenic and other anthropogenic contaminants (Chakraborti et al., 2011) including pesticides which are used intensively in this region (Ali et al., 2014) and have been shown to contaminate the shallow groundwater system (Tariq et al., 2004). The oxic and HCO_3 enriched hydrochemistry of the deeper aquifer and shallow urban groundwater system facilitates the mobility of uranium and occurrence of elevated uranium in groundwater, in some cases exceeding 50 μg/L, in a significant proportion of sites (median value of 15 μg/L). Together these findings show that it is vital to continue to monitor the evolution of water quality within the top 200 m of this critical drinking and agricultural water resource. Indeed, deep groundwater pumping will continue to increase in the future to supply the growing demand for drinking water. The findings from this study are expected to be relevant across the Indo-Gangetic Basin, a large and densely populated area, where similar hydrogeological typologies are found (Bonsor et al., 2017). Evidence from this region, which has a long history of intensive pumping, is useful to inform the groundwater management in regions which are likely have an intensification of groundwater use in the future.

5. Conclusions

- Evidence from a range of tracers (e.g. NO_3, SEC and CFC-12) demonstrate that there is low regional anisotropy within the multi-layered aquifer system in this region and a significant component of vertical leakage can penetrate to deeper aquifers (>100 m) due to intensive pumping within the deeper part of the aquifer system.
- Some shallow groundwaters have SEC >1500 μS/cm, and nitrate concentrations >50 mg/L, with potential implications for the use of this water for irrigation in the long-term due to the build-up of dissolved constituents in the shallow aquifer and unsaturated zone.
- Naturally occurring contaminants arsenic and fluoride were present in concentrations below WHO guideline drinking water limits for all sites in this study with median concentrations below 2 μg/L and 0.4 mg/L respectively.
- Uranium concentrations in deeper groundwater are significantly higher, >30 μg/L, compared to shallow groundwater, and overall median values are >15 μg/L. Enhanced uranium concentrations, >50 μg/L, are also observed in urban areas where higher HCO_3 concentrations are found due to urban waste water sources.
- There is evidence of NO_3 breakthrough from the shallow groundwater to depth and this may to be enhanced in the future if the current increases in pumping from the deep aquifers continue. This also has implications for the vulnerability of deep drinking water sources to contamination by pesticides and other anthropogenic contaminants.

6. Acknowledgments

This work was jointly funded by the UK Department for International Development (Grant 202125-108) and the British Geological Survey (NERC). However, the views expressed do not necessarily reflect the UK Government’s official policies. Authors acknowledge the support of the Director of National Institute of Hydrology, Roorkee. This paper is published with the permission of the Executive Director of the British Geological Survey (NERC). A full set of groundwater chemistry results are available in the supplementary information.

7. References

Abrol YP, Sangwan S, Dadhwal VK, Tiwari MK. Land-use Land-cover in Ido-Gangetic Plains - history of changes, present concerns and future approaches. In: Land Use--Historical Perspectives: Focus on Indo-Gangetic Plains. Eds: Abrol, Y. P., Sangwan, S., Tiwari, M. K. Allied Publishers. 2002: 1-28.

Aeschback-Hertig W, Gleeson T. Regional strategies for the accelerating global problem of groundwater depletion. Nature Geoscience 2012; 5: 853-861.

Agrawal GD, Lunkad SK, Malkhed T. Diffuse agricultural nitrate pollution of groundwaters in India. Water science and technology 1999; 39: 67-75.

Alcalá FJ, Custodio E. Using the Cl/Br ratio as a tracer to identify the origin of salinity in aquifers in Spain and Portugal. Journal of Hydrology 2008; 359: 189-207.

Ali U, Syed JH, Malik RN, Katsoyiannis A, Li J, Zhang G, et al. Organochlorine pesticides (OCPs) in South Asian region: a review. Sci Total Environ 2014; 476-477: 705-17.

Asoka A, Gleeson T, Wada Y, Mishra V. Relative contribution of monsoon precipitation and pumping to changes in groundwater storage in India. Nature Geoscience 2017.

Bajaj M, Eiche E, Neumann T, Winter J, Gallert C. Hazardous concentrations of selenium in soil and groundwater in North-West India. Journal of hazardous materials 2011; 189: 640-646.

Banning A, Demmel T, Rude TR, Wrobel M. Groundwater uranium origin and fate control in a river valley aquifer. Environ Sci Technol 2013; 47: 13941-8.

Barnett MO, Jardine PM, Brooks SC. U (VI) adsorption to heterogeneous subsurface media: application of a surface complexation model. Environmental Science and Technology 2002; 36: 937-942.

Bonsor HC, MacDonald AM, Ahmed KM, Burgess WG, Basharat M, Calow RC, et al. Hydrogeological typologies of the Indo-Gangetic basin alluvial aquifer, South Asia. Hydrogeology Journal 2017: 1-30.

Bowen R. Hydrogeology of the Bist Doab and adjacent areas. Nord. Hydrol. 1985; 16: 33-44.

Brindha K, Elango L, Nair RN. Spatial and temporal variation of uranium in a shallow weathered rock aquifer in southern India. Journal of earth system science 2011; 120: 911-920.

CGWB. Ground water scenario, India. Central Ground Water Board, Ministry of Water Resources, New Delhi, 2007.

CGWB. Ground Water Scenario of India 2009-10. CGWB, 2010.

CGWB CGWB-. Dynamic Groundwater Resources of India. CGWB, Ministry of Water Resources, Government of India, Delhi, India 2011: 243.

CGWB CGWB. Databse of borehole lithology, accessed in June 2014. 2014.

Chakraborti D, Bhaskar D, Murrill M. Examining India’s Groundwater Quality Management. Environmental Science & Technology 2011; 45: 27-33.

Chakraborti D, Rahman MM, Chatterjee A, Das D, Das B, Nayak B, et al. Fate of over 480 million inhabitants living in arsenic and fluoride endemic Indian districts: Magnitude, health, socio-economic effects and mitigation approaches. J Trace Elem Med Biol 2016; 38: 33-45.

Cheema MJ, Immerzeel WW, Bastiaanssen WG. Spatial quantification of groundwater abstraction in the irrigated Indus basin. Ground Water 2014; 52: 25-36.

Davis SN, Fabryka-Martin JT, Wolfsberg LE. Variations of bromide in potable groundwater in the United States. Ground Water 2004; 42: 902-909.

Deverel SJ, Fio JL. Groundwater flow and solute movement to drain laterals, western San Joaquin Valley, California: 1. Geochemical assessment. Water Resources Research 1991; 27: 2233-2246.

Dhillon KS, Dhillon SK. Quality of underground water and its contribution towards selenium enrichment of the soil–plant system for a seleniferous region of northwest India. Journal of hydrology 2003; 272: 120-130.

Dhillon KS, Dhillon SK. Selenium in groundwater and its contribution towards daily dietary Se intake under different hydrogeological zones of Punjab, India. Journal of Hydrology 2016; 533.

DPHE/BGS. Arsenic contamination of groundwater in Bangladesh. In: Kinniburgh D, Smedley P, editors. British Geological Suevey, Keyworth, 2001.

Edmunds WM, Savage D. Geochemical characteristics of groundwater in granites and related crystalline rocks. In: Downing, R.A., Wilkinson, W.B. (Eds.), Applied Groundwater Hydrology. Clarenden Press, Oxford 1991: 266-282.

Edmunds WM, Shand P, Hart P, Ward RS. The natural (baseline) quality of groundwater: a UK pilot study. Science of The Total Environment 2003; 310: 25-35.

Edmunds WM, Smedley P. Fluoride in natural waters. In: Essentials of medical geology. Springer Netherlands, 2013, pp. 311-336.

Fendorf S, Michael HA, Van Geen A. Spatial and temporal variations of groundwater arsenic in South and Southeast Science 2010; 328: 1123-1127.

Foster SS, Chilton PJ. Groundwater: the processes and global significance of aquifer degradation. Philos Trans R Soc Lond B Biol Sci 2003; 358: 1957-72.

Gleeson T, Befus KM, Jasechko S, Luijendijk E, Cardenas MB. The global volume and distribution of modern groundwater. Nature Geoscience 2015; 9: 161-167.

Gupta S. Himalayan drainage patterns and the origin of fluvial megafans in the Ganges foreland basin. Geology 1997; 25: 11-14.

Hinsby K, Purtschert R, Edmunds WM. Groundwater age and quality. In: Groundwater Science and Policy-An International Overview, Ed: Quevauiller P 2008: 217-239.

Hoque MA, Burgess WG. 14C dating of deep groundwater in the Bengal Aquifer System, Bangladesh: Implications for aquifer anisotropy, recharge sources and sustainability. Journal of Hydrology 2012; 444-445: 209-220.

Hundal HS, Singh K, Singh D. Arsenic content in ground and canal waters of Punjab, North-West India. Environ Monit Assess 2009; 154: 393-400.

IS. Indian drinking water standards. IS 10500, 2012, pp. 1-18.

Jain A, Raven KP, Loeppert RH. Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH-release stoichiometry. Environmental Science and Technology 1999; 33: 1179-1184.

Jaunat J, Huneau F, Dupuy A, Celle-Jeanton H, Vergnaud-Ayraud V, Aquilina L, et al. Hydrochemical data and groundwater dating to infer differential flowpaths through weathered profiles of a fractured aquifer. Applied Geochemistry 2012; 27: 2053-2067.

Katz BG, Eberts SM, Kauffman LJ. Using Cl/Br ratios and other indicators to assess potential impacts on groundwater quality from septic systems: A review and examples from principal aquifers in the United States. Journal of Hydrology 2011; 397: 151-166.

Katz BG, Griffin DW. Using chemical and microbiological indicators to track the impacts from the land application of treated municipal wastewater and other sources on groundwater quality in a karstic springs basin. Environmental Geology 2007; 55: 801-821.

Khan AU. Report on the Qyaternary geological and geomorphological mapping and study of fluvial pocesses in Satluj river basin in parts of Ropar and Hosiarpur districts Punjab Geologocal Survey of India (Lucknow, India) 1984.

Kumar A, Rout S, Narayanan U, Mishra MK, Tripathi RM, Singh J, et al. Geochemical modelling of uranium speciation in the subsurface aquatic environment of Punjab State in India. Journal of Geology and Mining Research 2011; 3: 137-146.

Kumar M, Kumari K, Ramanathan A, Saxena R. A comparative evaluation of groundwater suitability for irrigation and drinking purposes in two intensively cultivated districts of Punjab, India. Environmental Geology 2007; 53: 553-574.

Kumar R, Kumar R, Mittal S, Arora M, Babu JN. Role of soil physicochemical characteristics on the present state of arsenic and its adsorption in alluvial soils of two agri-intensive region of Bathinda, Punjab, India. Journal of Soils and Sediments 2016; 16: 605-620.

Lapworth DJ, Gooddy DC, Butcher AS, Morris BL. Tracing groundwater flow and sources of organic carbon in sandstone aquifers using fluorescence properties of dissolved organic matter (DOM). Applied Geochemistry 2008; 23: 3384-3390.

Lapworth DJ, Gopal K, Rao MS, MacDonald AM. Intensive groundwater exploitation in the Punjab: an evaluation of resource and quality trends. British Geological Survey Open Report 2014; OR14068: 45.

Lapworth DJ, MacDonald AM, Krishan G, Rao MS, Gooddy DC, Darling WG. Groundwater recharge and age-depth profiles of intensively exploited groundwater resources in northwest India. Geophysical Research Letters 2015; 42: 7554-7562.

MacDonald AM, Bonsor HC, Ahmed KM, Burgess WG, Basharat M, Calow RC, et al. Groundwater quality and depletion in the Indo-Gangetic Basin mapped from in situ observations. Nature Geoscience 2016; 9: 762-766.

MacDonald AM, Bonsor HC, Dochartaigh BÉÓ, Taylor RG. Quantitative maps of groundwater resources in Africa. Environmental Research Letters 2012; 7: 024009.

Masscheleyn PH, Delaune RD, Patrick WH. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environmental Science and Technology 1991; 25: 1414-1419.

McArthur JM, Sikdar PK, Hoque MA, Ghosal U. Waste-water impacts on groundwater: Cl/Br ratios and implications for arsenic pollution of groundwater in the Bengal Basin and Red River Basin, Vietnam. Sci Total Environ 2012; 437: 390-402.

McCray JE, Kirkland SL, Siegrist RL, Thyne GD. Model parameters for simulating fate and transport of on-site wastewater nutrients. Ground Water 2005; 43: 628-639.

Michael HA, Voss CI. Estimation of regional-scale groundwater flow properties in the Bengal Basin of India and Bangladesh. Hydrogeology Journal 2009; 17: 1329-1346.

Misra AK, Mishra A. Study of quaternary aquifers in Ganga Plain, India: focus on groundwater salinity, fluoride and fluorosis. J Hazard Mater 2007; 144: 438-48.

Morris BL, Darling WG, Gooddy DC, Litvak RG, Neumann I, Nemaltseva EJ, et al. Assessing the extent of induced leakage to an urban aquifer using environmental tracers: an example from Bishkek, capital of Kyrgyzstan, Central Asia. Hydrogeology Journal 2006; 14(1-2).

Morris BL, Lawrence AR, Chilton PJC, Adams B, Calow RC, Klinck BA. Groundwater and its susceptibility to degradation: a global assessment of the problem and options for management (Vol. 3). United Nations Environment Programme 2003: 126.

Mukherjee AN, Kuroda Y. Productivity growth in Indian agriculture: is there evidence of convergence across states? Agricultural Economics 2003; 29: 43-53.

Navarro A, Carbonell M. Evaluation of groundwater contamination beneath an urban environment: the Besos river basin (Barcelona, Spain). J Environ Manage 2007; 85: 259-69.

Nickson RT, McArthur JM, Burgess WG, Ahmed KM, Ravenscroft P, Rahmann M. Arsenic poisoning of Bangladesh groundwater. Nature 1998; 395: 338-338.

O Dochartaigh BE, MacDonald AM, Darling WG, Hughes AG, Li JX, Shi LA. Determining groundwater degradation from irrigation in desert-marginal northern China. Hydrogeology Journal 2010; 18: 1939-1952.

Orgnaisation WH. Guidelines for drinking water quality. 2011.

Panno SV, Hackley KC, Hwang HH, Greenberg SE, Krapac IG, Landsberger S, et al. Characterization and identification of na-cl sources in ground water. Ground Water 2006; 44: 176-87.

Rahman A. A GIS based DRASTIC model for assessing groundwater vulnerability in shallow aquifer in Aligarh, India. Applied Geography 2008; 28: 32-53.

Raju NJ, Ram P, Gossel W. Evaluation of groundwater vulnerability in the lower Varuna catchment area, Uttar Pradesh, India using AVI concept. Journal of the Geological Society of India 2014; 83: 273-278.

Rao MS, Krishan G, Kumar CP, Purushothaman P, Kumar S. Observing changes in groundwater resource using hydro-chemical and isotopic parameters: a case study from Bist Doab, Punjab. Environmental Earth Sciences 2017; 76.

Rao MS, Purushothaman P, Krishan G, Rawat YS, Kumar CP. Hydrochemical and isotopic investigation of groundwater regime in Jalandhar and Kapurthala districts, Punjab, India. Int J Earth Sci Eng, 2014; 7: 6-15.

Ravenscroft P, Burgess WG, Ahmed KM, Burren M, Perrin J. Arsenic in groundwater of the Bengal Basin, Bangladesh: Distribution, field relations, and hydrogeological setting. Hydrogeology Journal 2004; 13: 727-751.

Rivett MO, Buss SR, Morgan P, Smith JW, Bemment CD. Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. Water Res 2008; 42: 4215-32.

Rivett MO, Ellis PA, Mackay R. Urban groundwater baseflow influence upon inorganic river-water quality: The River Tame headwaters catchment in the City of Birmingham, UK. Journal of Hydrology 2011; 400: 206-222.

Scanlon BR, Jolly I, Sophocleous M, Zhang L. Global impacts of conversions from natural to agricultural ecosystems on water resources: Quantity versus quality. Water Resources Research 2007; 43: n/a-n/a.

Schnug E, Lottermoser BG. Fertilizer-derived uranium and its threat to human health. Environ Sci Technol 2013; 47: 2433-4.

Seitzinger S, Harrison JA, Böhlke JK, Bouwman AF, Lowrance R, Peterson B, et al. Denitrification across landscapes and waterscapes: a synthesis. Ecological Applications 2006; 16: 2064-2090.

Shamsudduha M, Taylor RG, Ahmed KM, Zahid A. The impact of intensive groundwater abstraction on recharge to a shallow regional aquifer system: evidence from Bangladesh. Hydrogeology Journal 2011; 19: 901-916.

Shamsudduha M, Taylor RG, Chandler RE. A generalized regression model of arsenic variations in the shallow groundwater of Bangladesh. Water Resour Res 2015; 51: 685-703.

Sharma C, Mahajan A, Garg UK. Assessment of arsenic in drinking water samples in south-western districts of Punjab-India. Desalination and Water Treatment 2013; 51: 5701-5709.

Singh CK, Shashtri S, Mukherjee S. Integrating multivariate statistical analysis with GIS for geochemical assessment of groundwater quality in Shiwaliks of Punjab, India. Environmental Earth Sciences 2010; 62: 1387-1405.

Singh IB. Late Quaternary history of the Ganga plain. Geological Society of India 2004; 64: 431-454.

Smedley PL, Kinniburgh DG. A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry 2002; 17: 517-568.

Smedley PL, Zhang M, Zhang G, Luo Z. Mobilisation of arsenic and other trace elements in fluviolacustrine aquifers of the Huhhot Basin, Inner Mongolia. Applied Geochemistry 2003; 18: 1453-1477.

Somasundaram MV, Ravindran G, Tellam JH. Ground-Water Pollution of the Madras Urban Aquifer, India. Groundwater 1993; 31: 4-11.

Suthar S, Bishnoi P, Singh S, Mutiyar PK, Nema AK, Patil NS. Nitrate contamination in groundwater of some rural areas of Rajasthan, India. J Hazard Mater 2009; 171: 189-99.

Tariq MI, Afzal S, Hussain I. Pesticides in shallow groundwater of Bahawalnagar, Muzafargarh, D.G Khan and Rajan Pur districts of Punjab, Pakistan. Environment International 2004; 30: 471-479.

Tiwari VM, Wahr J, Swenson S. Dwindling groundwater resources in northern India, from satellite gravity observations. Geophysical Research Letters 2009; 36.

van Dijk WM, Densmore AL, Sinha R, Gupta S, Mason PJ, Singh A, et al. Geomorphic Controls on Aquifer Geometry in Northwestern India. American Geophysical Union, Fall Meeting 2014; abstract EP13B-3512.

Van Geen A, Zheng Y, Goodbred S, Horneman A, Aziz Z, Cheng Z, et al. Flushing history as a hydrogeological control on the regional distribution of arsenic in shallow groundwater of the Bengal Basin. Environmental Science and Technology 2008; 42: 2283-2288.

Vengosh A, Pankratov I. Chloride/bromide and chloride/fluoride ratios of domestic sewage effluents and associated contaminated ground water. Ground Water 1998; 36: 815-824.

Visser A, Dubus I, Broers HP, Brouyere S, Korcz M, Orban P, et al. Comparison of methods for the detection and extrapolation of trends in groundwater quality. Journal of Environmental Monitoring 2009; 11: 2030-2043.

Weres O, Bowman HR, Goldstein A, Smith EC, Tsao L, Harnden W. The effect of nitrate and organic matter upon mobility of selenium in groundwater and in a water treatment process. Water, Air, and Soil Pollution 1990; 49: 251-272.

Wright WG. Oxidation and mobilization of selenium by nitrate in irrigation drainage. Journal of Environmental Quality 1999; 28: 1182-1187.