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Deep urban groundwater vulnerability in India revealed through the use of emerging organic contaminants and residence time tracers☆

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A B S T R A C T

Demand for groundwater in urban centres across Asia continues to rise with ever deeper wells being drilled to avoid shallow contamination. The vulnerability of deep alluvial aquifers to contaminant migration is assessed in the ancient city of Varanasi, India, using a novel combination of emerging organic contaminants (EOCs) and groundwater residence time tracers (CFC and SF_6). Both shallow and intermediate depth private sources (<100 m) and deep (>100 m) municipal groundwater supplies were found to be contaminated with a range of EOCs including pharmaceuticals (e.g. sulfamethoxazole, 77% detection frequency, range <0.0001–0.034 μg L^{-1}), perfluoroalkyl substances (e.g. PFOS, range <0.0001–0.033 μg L^{-1}) as well as a number of pesticides (e.g. phenoxyacetic acid, range <0.02–0.21 μg L^{-1}). The profile of EOCs found in groundwater mirror those found in surface waters, albeit at lower concentrations, and reflect common waste water sources with attenuation in the subsurface. Mean groundwater residence times were found to be comparable between some deep groundwater and shallow groundwater sources with residence times ranging from >70 to 30 years. Local variations in aquifer geology influence the extent of modern recharge at depth. Both tracers provide compelling evidence of significant inputs of younger groundwater to depth >100 m within the aquifer system.

1. Introduction

Groundwater is a major source of drinking water across the Gangetic basin (Gleeson et al., 2015; MacDonald et al., 2016). It is estimated that Uttar Pradesh alone has over 4 million groundwater sources (Planning Commission, 2014). Many urban centres, such as Varanasi, are heavily reliant on groundwater for drinking water supplies. Groundwater is abstracted from shallow (typically <100 m deep) tube wells for domestic or private use and also from deeper (>100 m) municipal or industrial boreholes. Shallow urban aquifer systems are highly susceptible to contamination and potentially present risks to human health from gross microbiological contamination (Hamner et al., 2006; Hoque et al., 2014), high salinity, and elevated concentrations of arsenic and fluoride (Chakraborti et al., 2011; Farooqi et al., 2007). Together, these water quality problems constrain available groundwater resources in many parts of the Gangetic Basin (MacDonald et al., 2016; Mukherjee et al., 2011), and are a particular concern for rapidly expanding urban mega-cities in Asia (e.g. Hoque et al., 2014; Khan et al., 2016). Recent evidence from residence-time tracers and hydrochemistry in the Indo-Gangetic Basin, suggests that prolonged intensive pumping can alter natural flow regimes and lead to vertical migration of contaminants to depths >150 m (Hoque et al., 2014; Lapworth et al., 2017).

The release of partially treated or untreated waste water introduces a potentially vast array of organic contaminants such as pharmaceuticals, antimicrobials and pesticides to surface water and groundwater (Petrie et al., 2015). Concentrations of these

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contaminants in surface water are typically higher than in groundwater, though microgram levels of many compounds are still detected in groundwater (Stuart et al., 2012). The impact on aquatic ecosystems has started to be evaluated (Van Donk et al., 2016) but both the direct and indirect effects of multiple micro-organics on human health is poorly understood despite growing interest. Their occurrence in aquatic systems is also of interest due their use as tracers of waste water sources and groundwater flow processes in the subsurface (Lapworth et al., 2012). They are particularly valuable as a tracer in south Asia where there is currently limited treatment of waste water and potentially high environmental loading from emerging organic contaminants (EOCs) (Kurunthachalam, 2012).

Waste water treatment only removes some EOCs and, in many cases, EOCs can pass through the treatment process unaffected (Petrovic et al., 2003). In many parts of the world, waste water treatment is limited and there is significant direct input of waste water into surface waters and aquifers due to leakage from sewers and septic tanks (Sorensen et al., 2015). Indeed, large urban centres in Asia have been shown to be hot-spots for EOC contamination (Pal et al., 2010; Sharma et al., 2016). Due to the large volumes of waste generated and limited treatment prior to dispersal in the environment, densely populated cities in India, and elsewhere in Asia, are likely to have high EOC inputs into both surface waters and groundwater (Sharma et al., 2016; Yeung et al., 2009), with few studies in India (Bhanumathi et al., 2003; Selvaraj et al., 2014; Sharma et al., 2016).

Modern groundwater residence time tracers (such as CFC and SF_6) have been used in many settings to assess: the extent of modern contamination; groundwater flow processes; and the mean residence time of groundwater (Darling et al., 2012; Gooddy et al., 2006; Morris et al., 2006), but have not yet been used in combination with EOC tracers to understand groundwater contaminant migration in India.

The issues of contamination in the River Ganges and its tributaries have been widely reported (Raju et al., 2009, 2014; Sharma et al., 2016). Past efforts to improve its water quality have had limited success (Ahmed, 1994; Mishra, 2005; Reuters, 2017). The Ganges and its tributaries remain highly contaminated. In Varanasi, surface water microbiological contamination is high (Mishra et al., 2009) and only ~30% (100 ML d^{-1} of the estimated 300 ML d^{-1} of sewerage generated) is currently treated (Hamner et al., 2006). Groundwater resources represent an essential source of potentially 'better' quality drinking water. It is necessary to understand the vulnerability of shallow and deeper groundwater to contamination in order to inform future use and management of water resources in these regions. This contamination-water supply challenge is by no means unique to Varanasi and is relevant across the Indo-Gangetic Basin.

In this paper a novel multi-tracer approach is presented to assess deep groundwater vulnerability in an urban setting in India. This study, the first of its kind in India, employs a broad screening approach for EOCs and residence time gases as tracers in shallow and deep and groundwater beneath Varanasi and the neighbouring city of Ramnagar. The objectives are to: i) characterise the occurrence of emerging organic contaminants in groundwater; ii) explore the depth relationship between EOCs, residence-time tracers; and iii) assess the vulnerability of deep groundwater to contaminant migration.

2. Methods

2.1. Study site and drinking water sources

Varanasi, one of India's oldest cities, is situated in the middle section of the Ganges Basin, Uttar Pradesh, India. With a population of 1.4 million (2011 Census) Varanasi is situated on the west bank of the River Ganges, Ramnagar is situated on the east bank (Fig. 1). The Ganges basin is estimated to receive around 12,000 ML d^{-1} of waste water (Mohan et al., 2011; Mondal and Rashmi Dasgupta, 2010), and the worst contamination is reported upstream of Varanasi (Sharma et al., 2016). Groundwater samples ($n = 26$) were collected in Varanasi and Ramnagar as well as surface water samples from the River Ganges ($n = 3$), see Fig. 1. Municipal drinking water for Varanasi is supplied locally from the River Ganges and local deep groundwater sources. Private self-supply is from groundwater. In total, it is estimated that around 60% of municipal supply is from groundwater (Mohan et al., 2011). Municipal groundwater supplies occur via 125 deep boreholes situated on both sides of the River Ganges (Mondal and Rashmi Dasgupta, 2010). Municipal boreholes are up to 200 m deep and completed within thick, high-permeability horizons. These sources are cased down to between 90 and 110 m below ground level (mbgl), with most cased >100 mbgl and screened below this to the full depth of the well (Jal-Kal, 2016). Pumping is intense (typically between 20 and 30 L s^{-1}) from these municipal sources (based on field observations). Private sources abstract from the shallow-intermediate (0–100 mbgl) aquifers using smaller motorised pumps as well as hand pumps in at two sites and are cased down to between 10 and 50 mbgl depending on borehole depth. The use of groundwater has increased significantly over the past 30 years, with a proliferation in private sources and significant numbers of new municipal sources to meet growing demand and meet the shortfall in municipal supply.

2.2. Hydrogeology

The Mid Ganges sedimentary aquifer system is characterised by highly permeable sand and gravel lenses interlayered with laterally discontinuous lower permeability silt, clay and 'kankar' (carbonate) deposits (Bonsor et al., 2017). Aquifer properties can vary over short distances and low permeability layers are rarely continuous over more than a few kilometres. Detailed information is available for the study area and two cross-sections showing the lithology (top 100 m) of the groundwater system below Varanasi and Ramnagar are shown in Fig. 1c. Based on geophysical assessments by Kumar et al. (2014) and selected borehole logs available from the municipal water company (Jal-Kal, 2016), relatively-high permeability sands are more common in the deeper parts of the Pleistocene aquifer (100–200 m). The deeper part of the aquifer system can be locally confined although piezometric head gradients are generally downwards within the aquifer system (Mohan et al., 2011). Overall the deeper aquifer system is more poorly characterised compared to the shallow aquifer system. The thickness of the unconsolidated deposits is c. 100 mbgl in the vicinity of the Banaras University campus (Kumar et al., 2014), B on Fig. 1a and c, but it is poorly constrained elsewhere. The top 40 m is dominated by low-permeability mud and silt, with isolated shallow sand bodies (e.g. situated near the Ganges River). There is a greater thickness of low permeability deposits (mud and silt) on the Ramnagar side compared to the Varanasi side (Fig. 1c).

Three typical hydrographs which show long term groundwater trends are shown in Fig. 1b; one from a the peri-urban village outside Varanasi (Barwaon), one close to the River Ganges (Tahipur) and one on the western side of Varanasi (Varanasi). Tahipur shows relatively supressed seasonal signals compared to Varanasi and Barwaon. Varanasi and Tahipur show no long term trends (1994–2014), in contrast to the rural site (Barwaon) which shows a downward trend in groundwater levels (2000–2014) at an average rate of 0.7 m a^{-1}. All show a seasonal recharge signal from the