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

Lapworth DJ*[1], Das P[2], Ashok S[2], Mukherjee A[2], Civil W[3], Petersen JO[1], Gooddy DC[1], Wakefield O[4], Finlayson A[5], Krishan G[6], Sengupta P[2], MacDonald AM[5]

[1] British Geological Survey, Maclean Building, Wallingford, OX10 8BB, UK

[2] Department of Geology and Geophysics, IIT-Kharagpur, Kharagpur 721302, West Bengal, India

[3] National Laboratory Service, Star Cross, Exeter, EX6 8FD, UK

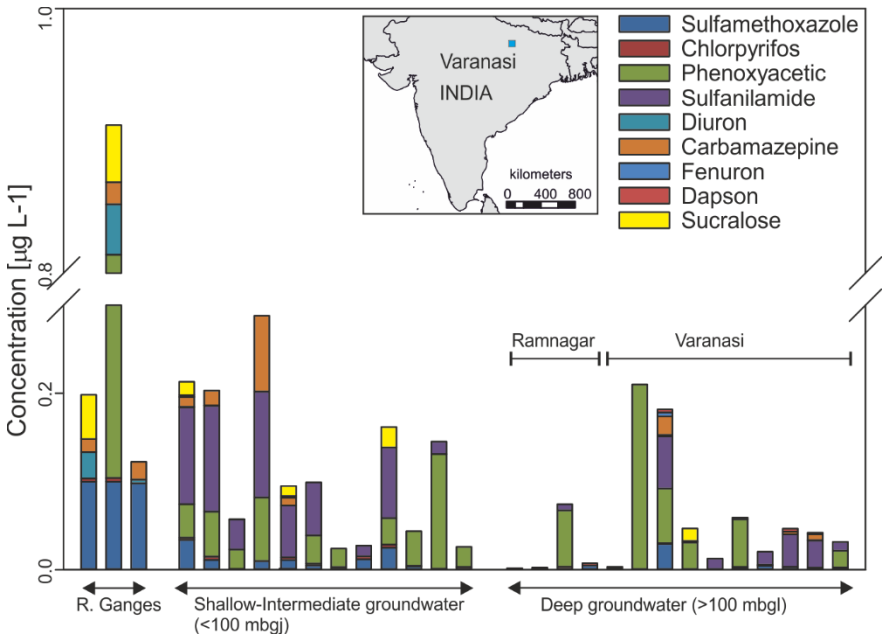
[4] British Geological Survey, Environmental Science Centre, Keyworth, NG12 5GG, UK

[5] British Geological Survey, Lyell Centre, Edinburgh, EH14 4AP, UK

[6] National Institute of Hydrology, Roorkee 247667, Uttarakhand, India

*Corresponding author djla@bgs.ac.uk

## Abstract Art



## Abstract

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.



**Keywords**. Emerging contaminants, groundwater, drinking water, water quality, India

## 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 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

64 sources and groundwater flow processes in the subsurface (Lapworth et al., 2012). They are
65 particularly valuable as a tracer in south Asia where there is currently limited treatment of
66 waste water and potentially high environmental loading from emerging organic contaminants
67 (EOCs) (Kurunthachalam, 2012).

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

78 Modern groundwater residence time tracers (such as CFC and $SF_6$) have been used in many
79 settings to assess: the extent of modern contamination; groundwater flow processes; and the
80 mean residence time of groundwater (Darling et al., 2012; Gooddy et al., 2006; Morris et al.,
81 2006), but have not yet been used in combination with EOC tracers to understand
82 groundwater contaminant migration in India.

83 The issues of contamination in the River Ganges and its tributaries have been widely reported
84 (Raju et al., 2009; Raju et al., 2014; Sharma et al., 2016). Past efforts to improve its water
85 quality have had limited success (Ahmed, 1994; Mishra, 2005; Reuters, 2017). The Ganges
86 and its tributaries remain highly contaminated. In Varanasi, surface water microbiological
87 contamination is high (Mishra et al., 2009) and only ~30% (100 ML $d^{-1}$ of the estimated 300

88 ML $d^{-1}$ of sewerage generated) is currently treated (Hamner et al., 2006). Groundwater
89 resources represent an essential source of potentially 'better' quality drinking water. It is
90 necessary to understand the vulnerability of shallow and deeper groundwater to
91 contamination in order to inform future use and management of water resources in these
92 regions. This contamination-water supply challenge is by no means unique to Varanasi and is
93 relevant across the Indo-Gangetic Basin.

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

101 # Methods

102 ## Study site and drinking water sources

103 Varanasi, one of India's oldest cities, is situated in the middle section of the Ganges Basin,
104 Uttar Pradesh, India. With a population of 1.4 million (2011 Census) Varanasi is situated on
105 the west bank of the River Ganges, Ramnagar is situated on the east bank (Figure 1). The
106 Ganges basin is estimated to receive around 12,000 ML $d^{-1}$ of waste water (Mohan et al.,
107 2011; Mondal et al., 2010), and the worst contamination is reported upstream of Varanasi
108 (Sharma et al., 2016). Groundwater samples (n=26) were collected in Varanasi and Ramnagar
109 as well as surface water samples from the River Ganges (n=3), see Figure 1. Municipal
110 drinking water for Varanasi is supplied locally from the River Ganges and local deep
111 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 et al., 2010). Municipal boreholes are up to 200 m deep and completed within thick, high-permeability horizons. These sources are cased down to between 90-110 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 20-30 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 10-50 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.

## 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 Figure 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 Figures 1a and 1c, 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 (Figure 1c).

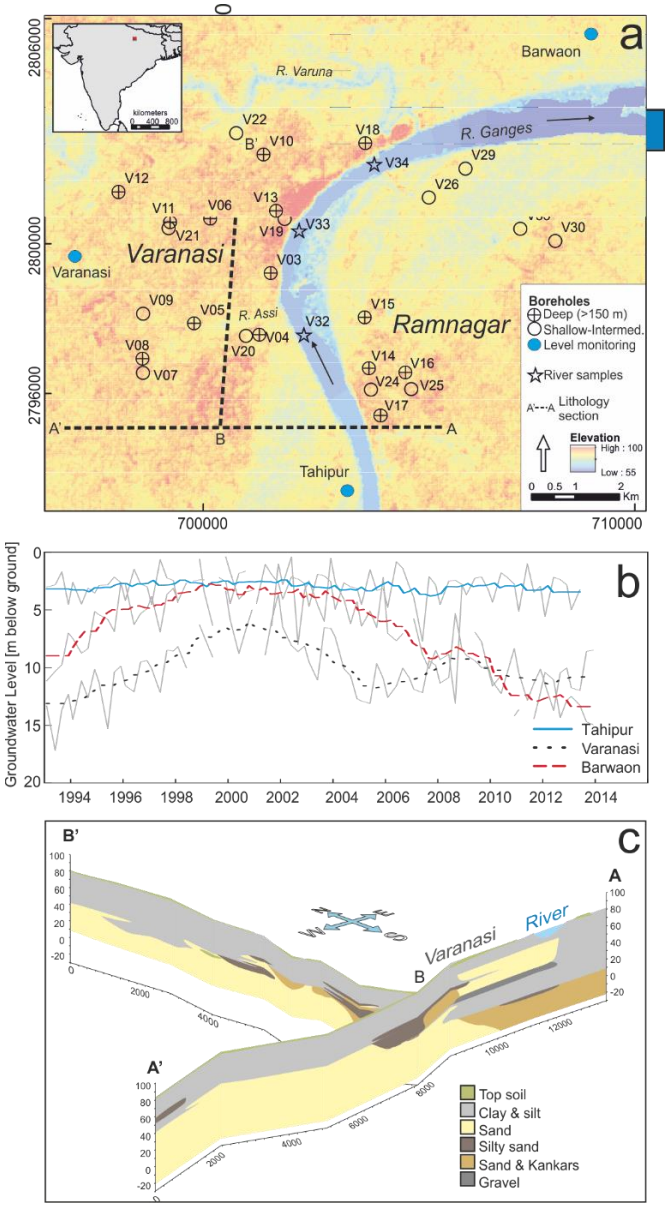



**Figure 1.** Study area and hydrogeology, a) location and elevation map showing groundwater and surface-water sampling sites, b) long-term groundwater level results (1994-2014) from

three representative sites for urban (Varanasi) and rural (Barwaon) land use and surface water (Tahipur) controlled sites (CGWB 2016), seasonal dips (grey lines) and running mean (bold lines) shown, c) schematic lithological cross section West-East (A-A' and B-B', see Figure 1a), datum is Mean Sea Level, from Ramnagar to Varanasi. The sand aquifers extend deeper on both sides of the Ganges River (Jal-Kal, 2016; Kumar et al., 2014; Nandimandalam, 2012).

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 monsoon. The connectivity between the River Ganges and the adjacent aquifer system is poorly constrained, and a topic of future research. The shallow lithology in the vicinity of the Ganges channel is highly variable and the increased prevalence of sand and gravel lenses below the channel base may provide hydraulic connectivity between the River Ganges and the Varanasi groundwater system.

**Sampling**

All sampling was undertaken during a single campaign in March 2016. Samples from actively pumped sites across the study area were obtained (Fig 1a) and include 13 deep municipal sources with total borehole depths (>150 mbgl) which are typically cased to a depth of >100 m and 13 shallow-intermediate private sources with total depths between 20-100 mbgl which have much shallower casing, typically between 10 and 50 m, depending on local lithology and total borehole depth. Specific electrical conductivity and pH were measured on site and stable readings obtained prior to sampling. Groundwater residence-time

samples were taken from a total of 25 sites. Three surface water samples for EOCs were taken, one upstream, one mid Varanasi and one downstream of Varanasi from the middle of the River Ganges.

Specific electrical conductivity (SEC) and pH readings were taken in the field and allowed to stabilise before sampling for residence time tracers and EOCs were undertaken. All sites were operational and fully purged before sampling. Care was taken to ensure that a direct raw water sample was taken from the abstraction boreholes from each site, i.e. that it was not dosed with chlorine or had undergone temporary storage prior to sampling. In addition, any plastic tubing was removed prior to sampling for EOCs. Particular attention was paid when taking the EOC samples to minimise the possibility of contamination from the sampler, i.e. no creams, spays or other skin products were used by the sampler during the fieldwork. The sampler at no point made any contact with the inside of the bottle or cap during the sampling.

For EOC samples, new 500 mL glass bottles were used which were cleaned and rinsed with ultra-pure water (ASTM type I reagent grade water, including a UV cracker). Prior to sampling, bottles were rinsed three times with the sample water and stored in the dark before extraction (White et al., 2017). Solid-phase extraction (SPE, pre-conditioned sorbent Oasis® HLB cartridges) of the unfiltered sample was undertaken within 2-6 hours of sampling. See supporting information for further details. Prior to CFC (CFC-11 and CFC-12) and $SF_6$ sampling for residence time estimation, an air-tight seal between the borehole outlet and the sample container was ensured. CFC and $SF_6$ samples were collected unfiltered and without atmospheric contact in sealed air-tight containers by the displacement method outlined in Gooddy et al. (2006). Further details on the use of residence time tracers is provided in the supporting information.

## Groundwater residence time tracers

While any one of the residence time tracers described above can in principle be used to provide a mean residence time (MRT) of groundwater, when two or more are used in combination the potential exists to identify different modes of flow and/or mixing processes operating within the aquifer or at the borehole (Darling et al., 2012). The mean residence time of a groundwater sample can be obtained by reading across the year of recharge from input concentration curves for a particular flow model, once these have been adjusted for local recharge temperatures. In reality groundwaters are usually mixtures of waters with different ages, which either mix during flow in the aquifer, or more likely mix during pumping from boreholes with a wide screen interval. Lumped- parameter models (LPM) are typically used to explain variations observed in groundwater mixtures, these include the piston flow model (PFM), exponential mixing model (EMM), exponential flow model (EFM), as well as binary mixing models (BMM), i.e. the combined use of two different flow models (Zuber 1986, Maloszewski and Zuber 1996, Cook and Böhlke 2000). These mixing models derive from different conceptual models describing underlying groundwater flow processes. Deciding which LPMs are appropriate to estimate MRTs can be resolved by plotting groundwater concentrations obtained for two tracers, and comparing these to various LPM input curves, often referred to as a 'bow plot' (Darling et al., 2012). CFC-12 vs $SF_6$ results were used as they have sufficiently different input functions to be able to distinguish between different LPMs..

## Analytical methods

Broad screening for micro-organics was carried out using pre-concentrated SPE followed by target based liquid chromatography/mass spectrometry (LCMS) screening. A Time-of-Flight

(Q-TOF) LC/MS method was used to screen for 686 polar organic compounds in each sample. An isotopically labelled internal standard Carbutamide-d9 (CAS 1246820-50-7) was added to each of the pre-conditioned SPE cartridges to assess instrument performance. Target compounds have been analysed in a blank and at a concentration of 0.1µg/l, the response factor obtained is used to create a single point calibration curve. Estimate of concentration is based on quant ion response and response of the internal standard. Detection limits are compound specific but are typically between 0.001-0.1 µg/L for the vast majority of compounds. Target compound identification is made by retention time, accurate mass and by Isotope distribution patterns (mass, ratio, spacing). The combined results contribute to an overall match score.

A full procedural blank sample (using ultra-pure water) was processed in the field to quantify any procedural contamination. An internal AQC containing 9 target compounds is analysed with each sample batch, at a concentration of 0.01µg/l. Prior to analysing the results all compounds (n=7) that were detected in the blank were first screened for and removed from the results (see Supporting Information for details on procedural blank results). Analysis took place at the UK National Science Laboratories at Star Cross. For further details on the analytical method see supporting information.

CFCs and $SF_6$ were measured by gas chromatography with an electron capture detector after cryogenic pre-concentration based on the methods of (Busenberg and Plummer, 2000). Measurement precision was within and ±5% for the CFCs and 10% for $SF_6$, with detection limits of 0.01 pmol/L (CFC-12), 0.05 pmol/L (CFC-11) and 0.1 fmol/L ($SF_6$). A recharge temperature of 28° C was assumed for calculating the recharge year, based on field results (mean 28±1° C), and relative fractions of modern water. $SF_6$ data were corrected for excess air at 3 cc/L. Analysis took place in the BGS Wallingford groundwater tracer laboratory, UK.

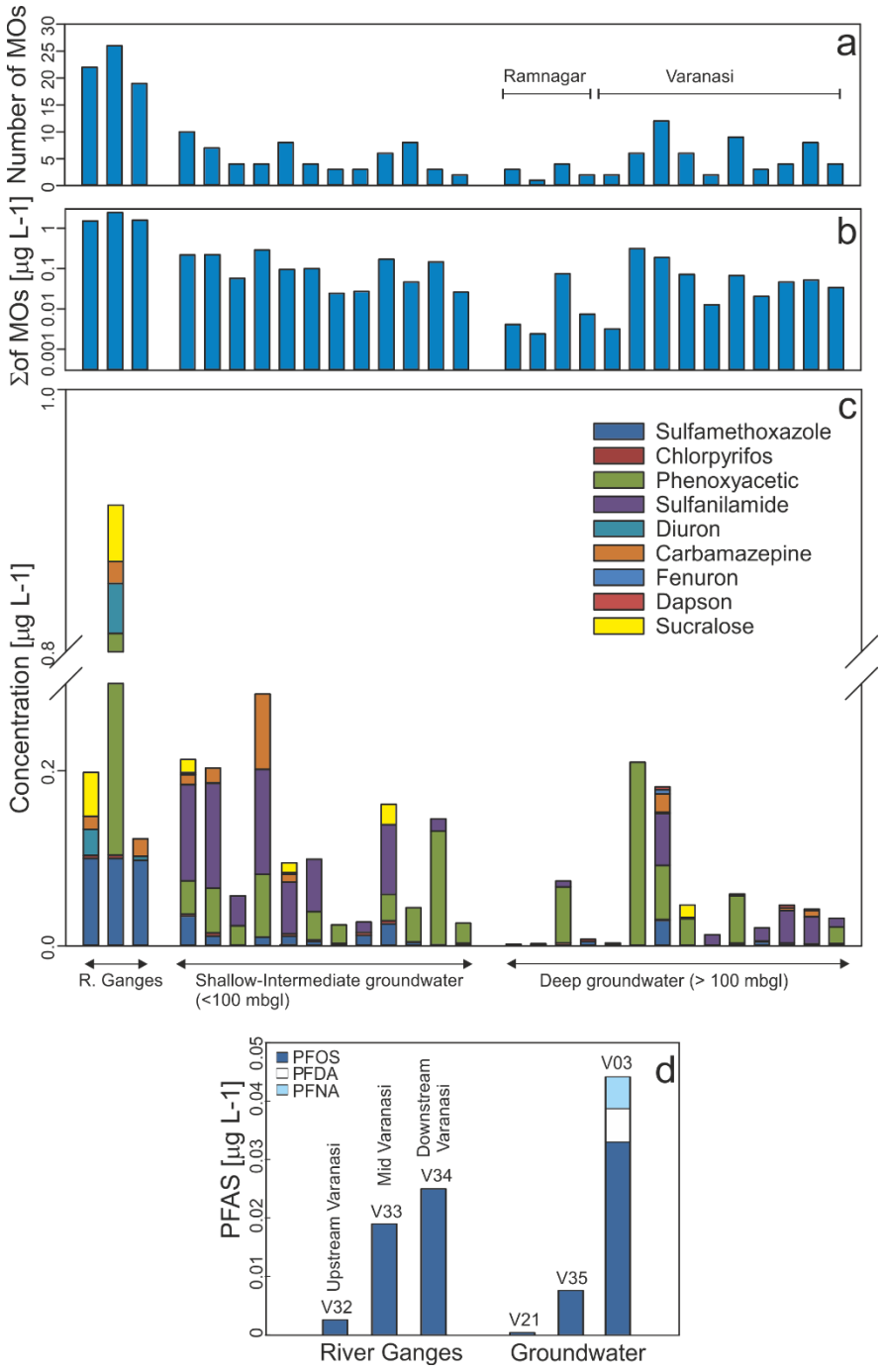
For details on the methods used in this study to characterise groundwater residence time and mixing processes please refer to the Supporting Information.

# Results

## Micro-organic Contaminants

Forty micro-organic contaminants were detected across all samples including 21 pesticides and transformation products (TPs), 14 pharmaceuticals, 3 perfluoroalkyl substances (PFAS), one industrial compound and the artificial sweetener, sucralose (Table S1). The number and total concentrations of compounds in the Ganges were higher than those found in groundwater (Figures 2a and 2b). Samples from the Ganges had between 19-26 detected compounds, shallow groundwaters (<50 mbgl) between 4-10 compounds and deeper groundwater (>100 mbgl) between 1 and 12 compounds (see Figure 2a). Figure 2c shows the concentrations of the 9 most frequently detected EOC compounds in groundwater and the 3 samples collected from the R. Ganges. This included frequent detection in groundwater of the following compounds (see Table S1): antimicrobials sulfamethoxazole (77% of samples), sulfanilamide (62%) and dapson (19%); the anticonvulsant carbamazepine (27%) and the artificial sweetener sucralose (15%).

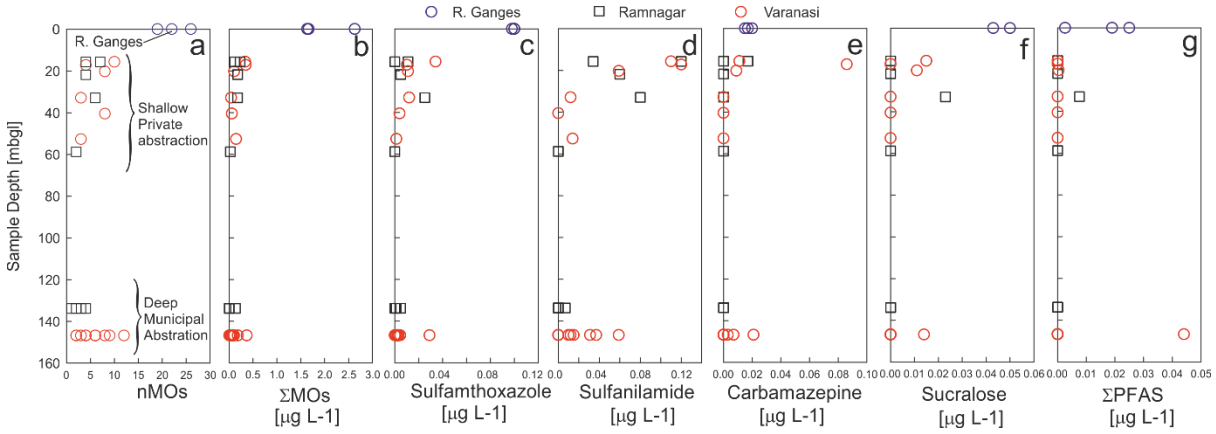
Figures 3 and 4 show the depth profile of some of the most frequently detected EOCs and most frequently detected pesticides respectively. Overall, greatest waste water contamination is found in surface waters and shallow groundwater samples; lower contaminant concentrations and frequency of detections are found at intermediate depths (>50 m) from private sources of abstraction. High concentrations and detection frequencies are then found deeper (>100 m) from some large municipal sources which have a long history (> 30 years in these cases) of intense pumping (Figure 3 and 4).




268

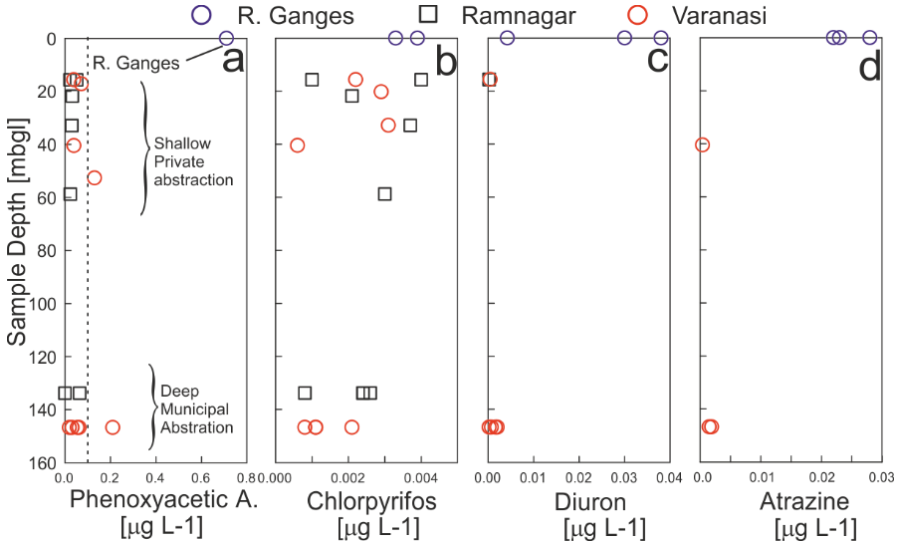
269 **Figure 2.** Micro-organic contamination in the River Ganges and groundwater in Varanasi and
270 Ramnagar, India. a) number of micro-organic compounds (MO), b) sum of MO compounds
271 (µg/L) and c) stacked bar plot of frequently detected MOs including EOCs, d) stacked bar
272 plot of detected perfluoroalkyl substances (PFAS).

273




274

275 **Figure 3.** Emerging organic contaminant depth profiles, a) number of micro-organic
276 compounds detected, b) total concentration of MOs. Selected EOCs; c) Sulfamethoxazole, d)
277 Sulfanilamide, e) Carbamazepine, f) Sucralose, g) ΣPFAS (Σ PFOS+ PFNA + PFDA). Blue
278 circles show results for R. Ganges. Sites from Varanasi shown with a circle, sites from
279 Ramnagar shown with a square symbol. Upper screen is typically at 10-50 m for shallow-
280 intermediate sites (<100 m deep), and is typically >100 m for deep sites. Sample depth is
281 plotted as the mid-point in the screened section of the borehole.




282

283 **Figure 4.** Selected pesticides depth profiles, a) Phenoxyacetic acid, b) Chlorpyrifos, c)
284 Diuron, d) Atrazine. Blue circles show results from R. Ganges. Sites from Varanasi shown
285 with a circle, sites from Ramnagar shown with a square symbol. WHO drinking water
286 standards of 0.1 µg $L^{-1}$ for pesticides are shown as a vertical line. Upper screen is typically at
287 10-50 m for shallow- intermediate sites (<100 m deep), and is typically >100 m for deep
288 sites. Sample depth is plotted as the mid-point in the screened section of the borehole.

## Groundwater residence time tracers

Figure 5 shows variations in groundwater residence-time tracer concentrations and estimated MRT with depth for all samples. A cross-plot of CFC and $SF_6$ is shown in Figure 6, in relation to a range of likely theoretical flow mixing model curves (BMM, EMM, EFM) for the two tracers. MRTs in Figure 5d were estimated using the most appropriate mixing model based on an assessment of results from Figure 6 (see Table S3 in supporting information). Overall, comparable MRTs are found in both shallow private groundwater supplies and deeper municipal supplies.

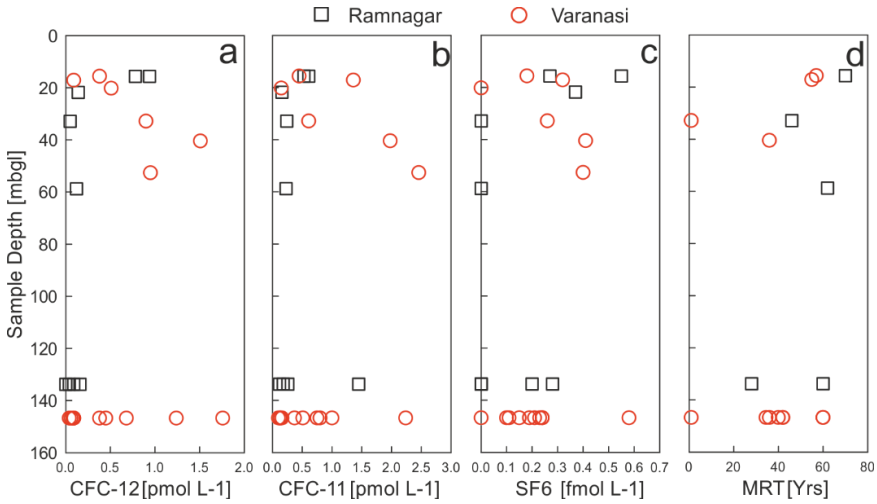
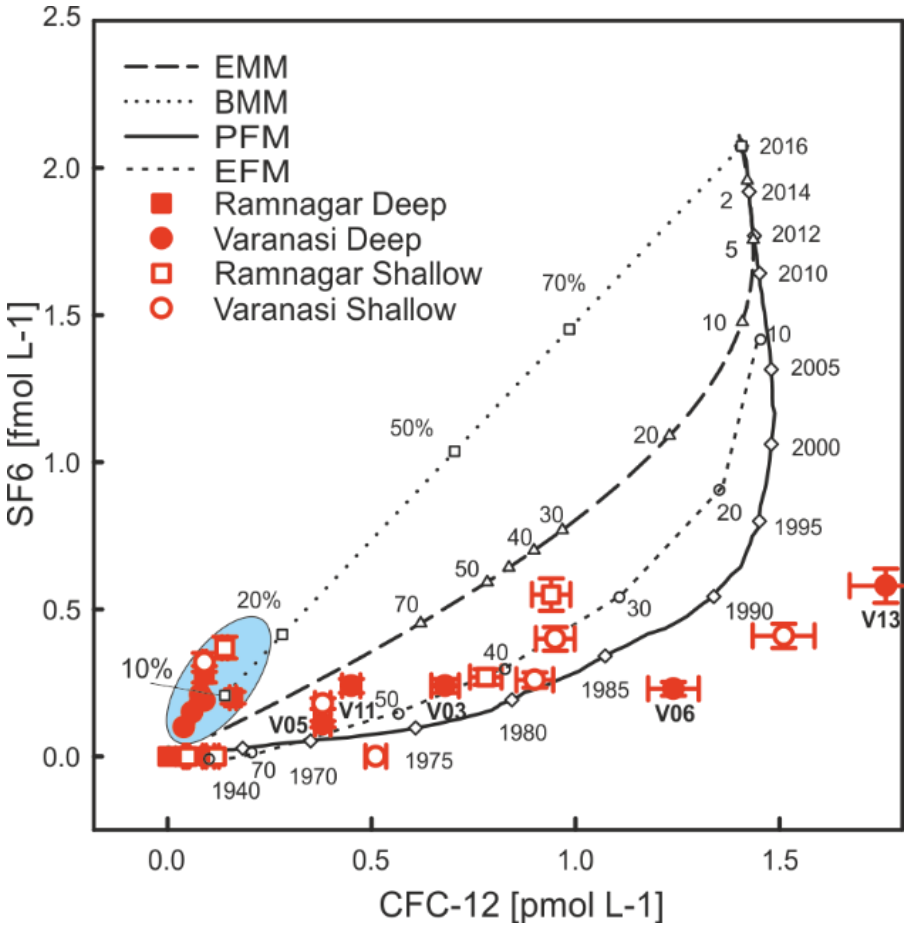



**Figure 5**. Groundwater residence-time tracer depth profiles, a) CFC-12, b) CFC-11, c) $SF_6$, d) and Mean Residence Time (MRT) groundwater age estimates calculated using $SF_6$ results and suitable LPMs. For samples which plotted close to the BMM line, i.e. a mixture of tracer 'dead'(i.e. groundwater recharged >70 years) and modern recharge, see Figure 6, MRTs were not calculated. Sites from Varanasi shown with a circle, sites from Ramnagar shown with a square symbol. Upper screen is typically at 10-50 m for shallow- intermediate sites (<100 m deep), and is typically >100 m for deep sites. Sample depth is plotted as the mid-point in the screened section of the borehole.




308

309 **Figure 6**. Cross-plot of CFC-12 vs $SF_6$ with LPM results shown for BMM, PFM, EFM and
310 EMM. Residence time (EMM, EFM), year of recharge (PFM) or % modern recharge (BMM)
311 are shown on the LPM input curves. Sites from Varanasi shown with a circle, sites from
312 Ramnagar shown with a square symbol. Points which fall close to the BMM (i.e. a mixture of
313 tracer 'dead' and modern recharge) are highlighted in the blue area.

314 # Discussion

315 ## Occurrence of micro-organics in urban groundwater

316 ### *Emerging organic contaminants*

317 The most frequently detected EOCs (sulfamethoxazole, sulfanilamide, carbamazepine and
318 sucralose) are common markers of waste water inputs to surface water (Buerge et al., 2009;
319 Pal et al., 2010; Richardson, 2009) and groundwater (Lapworth et al., 2012; Stuart et al.,
320 2012; Stuart et al., 2014; White et al., 2016), and have been used to understand rapid flow

and recharge pathways in the subsurface (Ascott et al., 2016; Sorensen et al., 2015; White et al., 2016).

Maximum concentrations for most pharmaceuticals and other EOCs were higher for surface waters compared to groundwaters; the exception is sulfanilamide which was only detected in groundwater. Concentrations of all pharmaceuticals and other EOCs were below 0.1 $\mu g\ L^{-1}$ except sulfanilamide which was detected above 0.1 $\mu gL^{-1}$ on three occasions in shallow groundwater (Figure 3). Sulfamethoxazole is detected in much higher concentrations in the River Ganges compared to groundwaters, (see Figure 2c and Figure 3). Sulfamethoxazole and carbamazepine are two of the most frequently detected EOCs in groundwater (Focazio et al., 2008; Lapworth et al., 2012) and they have been recently detected in waste water effluent in India (Anumol et al., 2016). Sulfamethoxazole has been shown to have adverse effects on the natural bacterial flora in groundwater and can supress biologically mediated processes such as denitrification (Haack et al., 2012; Underwood et al., 2011). Pathogens resistant to commonly used antibiotics including sulfamethoxazole have been recently isolated from both the River Ganges (Soni et al., 2013) as well as shallow groundwater in Varanasi (Bhanumathi et al., 2003). Antibiotic resistance is a growing challenge globally (Kummerer, 2009) and a significant potential challenge in India (Mutiyar and Mittal, 2014).

Sulfanilamide is widely used as an antibacterial ingredient in creams and powders; it is also a transformation product of sulfamethoxazole (Jiang et al., 2014). Although its occurrence in groundwater has not been frequently reported in the literature, its persistence has been noted in contamination plumes from landfill sites with domestic waste (Baun et al., 2000; Holm et al., 1995). In this study, the absence of detectable sulphanilamide in surface waters and the presence of sulfamethoxazole suggest that the former could be the transformation product of sulfamethoxazole. Alternatively sulfanilamide may be rapidly removed in surface waters through a combination of microbial processing and natural UV breakdown (Kim and Tanaka,

2009). Recent laboratory-based studies have shown that microbial communities exposed to sulfanilamide degrade this compound much more rapidly than un-exposed cultures and that there is a strong temperature effect with enhanced degradation at 25 °C compared to 5 °C (Liao et al., 2016).

The ubiquitous detection of sub-microgram concentrations of sulfamethoxazole and sulfanilamide in groundwater, and the detection of sucralose at some sites, point to a sustained waste water input to surface waters at Varanasi and groundwater systems below Varanasi and Ramnagar – since all are common waste water tracers (Buerge et al., 2009; Dickenson et al., 2011; Richardson, 2009). The majority of urban households in India are not connected to the sewerage system (2011 Census). An estimated 650 metric tonnes of solid waste and 400 ML $d^{-1}$ of liquid waste is generated in Varanasi each day (Mondal et al., 2010). Several studies report elevated concentrations of $NO_3$ (up to 100 mg $L^{-1}$) in the shallow aquifer from waste water sources (Chaurasia et al., 2013; Raju et al., 2011). Nitrate concentrations vary substantially and low permeability horizons likely facilitate hot-spots of denitrification (Lawrence et al., 2000). The relatively recent use of sucralose in India (i.e. post 2000) and its persistence in groundwater (Robertson et al., 2016) together with the other EOC detections (Figures 2 and 3) strongly suggest that there is a significant component of modern (i.e. <20 $a^{-1}$) recharge to depth within the aquifer system.

Three polyfluoroalkyl substances (PFAS), including perfluorooctane sulfonate (PFOS n=6), perfluorononanoic acid (PFNA n=6) and perfluorodecanoic acid (PFDA n=1), were detected in groundwater (range <0.001-0.033 μg $L^{-1}$) and the River Ganges (range 0.003-0.025 μg $L^{-1}$), see Figure 2d. Maximum concentrations for PFOS were below the USEPA health advisory level for drinking water of 0.070 μg $L^{-1}$ for individual analytes (EPA, 2017) but many PFAS compounds, including PFOA are not included in the broad screening method employed in this study. It is thus possible that combined PFOS and PFOA concentrations may approach

371 the guideline value (also 0.07 μg $L^{-1}$) for combined PFAS. The sustained increase in PFAS
372 emissions over the last 20 years and presence of PFAS compounds is emerging a widespread
373 concern (Wang et al., 2014). Recent studies in USA (Hu et al., 2016) and India (Sharma et
374 al., 2016) show widespread occurrence of these compounds in surface and groundwater.
375 PFAS occurrence and emissions recently reported for Varanasi by Sharma et al. (2016)
376 showed much lower PFOS concentrations (<0.001 μg $L^{-1}$) compared to our study (0.003-
377 0.025 μg $L^{-1}$) for the River Ganges. However the trend of high PFOS emissions from
378 Varanasi (by comparing upstream and downstream concentrations, Figure 2d) is consistent,
379 with around an order of magnitude increase in PFOS from 0.003 μg $L^{-1}$ upstream of Varanasi
380 to 0.025 μg $L^{-1}$ downstream. There are many potential sources of PFAS including sewage
381 sludge (Milinovic et al., 2016), waste water (Houtz et al., 2016), discharge from fire
382 protection foams (Guelfo and Higgins, 2013; Houtz et al., 2013; Hu et al., 2016) and landfill
383 sites (Benskin et al., 2012).

384 PFOS was detected in all surface waters in this study (n=3) but in only 10% of groundwaters.
385 Highest concentrations were, however, detected in groundwater (0.033 μg $L^{-1}$ at site V03), a
386 deep municipal source in Varanasi (Figure 1). This site was also the only sample with
387 detectable PFNA and PFDA suggesting there is a local source of PFAS and a rapid pathway
388 to depth within the groundwater abstracted from this borehole. While it is the closest sample
389 to the Ganges (200 m), a comparison of the full EOC and pesticide detections with those
390 from surface waters suggest that this may not be the source of PFAS although cannot be ruled
391 out as this study was carried out in a single campaign and further temporal sampling in
392 surface waters would be required to confirm this. A combination of factors including the
393 negative charge of PFOS, competition for positively charged sorption sites from other
394 contaminants, neutral pH in groundwater and low TDS, when taken together, indicates PFOS

395 has the potential to be mobile in groundwater beneath Varanasi and less readily sorbed to
396 sediment surfaces (NGWA, 2017).

397 ***Pesticides and their transformation products***

398 The three most frequently detected pesticide compounds and pesticide TPs were chlorpyrifos
399 (67%), phenoxyacetic acid (TP, 62%), and diuron (32%). There were only 9 detections of
400 pesticides or their TPs > 0.1 μg $L^{-1}$, of which the majority of these (60%) was detected in the
401 River Ganges. Atrazine and atrazine TPs follow a similar pattern of higher concentrations (up
402 to 50 time higher) and higher detection frequencies in the River Ganges, but with
403 concentrations all below 0.03 μg $L^{-1}$, considerably lower than was found for acid herbicides.
404 Chlorpyrifos and phenoxyacetic acid dominate herbicide detections in groundwaters.
405 Detections of chlorpyrifos in groundwater sources were frequent but concentrations were low
406 compared to other pesticides (median of 0.0024 μg $L^{-1}$ and range of 0.0006-0.004 μg $L^{-1}$)
407 compared to surface water concentrations (0.033-0.39 μg $L^{-1}$), which is consistent with other
408 pesticides in this study. This organophosphate is widely used in India as an insecticide for
409 food production as well as indoor use including for mosquito, ant and termite control.
410 Chlorpyrifos converts readily to chlorpyrifos-oxon (not screened for in this study) during
411 chlorine treatment, which is the main disinfection method currently used in Varanasi and
412 throughout India. Both compounds are of toxicological concern via dietary exposure (EPA,
413 2016). Chlorpyrifos is currently under an assessment for registration review by the US EPA
414 (EPA, 2016) and detections in raw drinking water sources in the USA are comparable with
415 the concentrations found in this study (Bradley et al., 2017). It is more persistent in soil and
416 water under anaerobic conditions, because aerobic aquatic metabolism is a key
417 transformation pathway in the environment (Chishti et al., 2013). The sustained
418 environmental input, and sub-oxic surface (Mishra et al., 2009) and groundwater conditions,

419 evidenced by high dissolved Fe concentrations beneath the city (Raju et al., 2011), may
420 explain the persistence of chlorpyrifos and other EOCs as well as the high frequency of
421 detection but low concentrations in groundwater.

422 Phenoxyacetic acid is a transformation product of a number of herbicides (McManus et al.,
423 2014) including 2-4 D, which was not detected in groundwater but was detected in all three
424 surface water samples (0.1± 0.1 μg $L^{-1}$). Two phenoxypropionic acid herbicides were also
425 detected but only in surface waters, including the TP of mecoprop-p (MCPP), 2-
426 phenoxypropionic acid and the herbicide 4-chlorophenoxyacetic acid. Both groups of acid
427 herbicides degrade in soil and through UV and electrochemical oxidation (Boye et al., 2002;
428 Muller and Buser, 1997; Willems et al., 1996), and both the parent compounds and TPs have
429 been shown to leach from soils and are widely detected in groundwater throughout the world
430 (Gibson and Suflita, 1986; Gustafson, 1989). Degradation of 2-4-D occurs under both aerobic
431 and anaerobic conditions in sewage sludge, while some studies have shown that MCPP is
432 more persistent under anaerobic conditions (Zipper et al., 1999a; Zipper et al., 1999b).

433 ***Geochemical controls***

434 A range of processes control EOC transport in the subsurface including sorption to organic
435 matter and clay minerals, surface charge and ion exchange and microbial degradation or
436 transformations. The fate of a contaminant is controlled by the physicochemical properties of
437 the subsurface environment (hydrochemistry, degree of confinement, redox conditions,
438 sediment chemistry, surface area etc) and the physicochemical properties of the
439 contaminants, i.e. solubility in water and Kow. The high organic carbon content and
440 argillaceous nature of the shallow aquifer system beneath Varanasi (Raju, 2012), which is
441 thicker on the Ramnagar side, will be important in controlling recharge and the transport of
442 micro-organic contaminants. Biodegradation of EOCs is known to be highly variable in

443 groundwater (Greskowiak et al., 2017) and redox conditions have been shown to play an
444 important role in the attenuation of some emerging contaminants in groundwater (Burke et
445 al., 2013; Massmann et al., 2006). For example while carbamazepine was found to be
446 persistent under both oxic and anoxic conditions (Massmann et al., 2006), para-
447 toluenesufonamide, a sulphonamide, was removed under oxic conditions and persisted under
448 anoxic conditions, while a range of mycin compounds were only removed under anoxic
449 conditions (Burke et al., 2013). The sub-oxic nature of the aquifer system beneath Varanasi
450 may therefore facilitate the persistence of sulphonamides and carbamazepine, which were
451 frequently detected in this study (Figure 2), and promote the selective degradation of others.
452 The pH for the aquifer system is c. 7± 0.4, and consistent with depth (Figure S1), and the
453 negative charged oxide surfaces may facilitate the movement of negatively charged EOCs,
454 such as diclofenac, which was frequently detected in this study.

455

456 **Groundwater residence times and recharge processes**

457 The downward hydraulic gradient from the shallow to the deeper aquifer system (Mohan et
458 al. 2011), is likely to be controlled by deep pumping, and provides a context for interpreting
459 the tracer results. There is some variation but generally consistent concentration depth
460 profiles for all three residence time tracers within the top 0-160 m (see Figure 5). Based on
461 $SF_6$ concentrations and lumped parameter model (LPM) estimates, distributions of residence
462 times found within the shallow private and deep municipal sources are consistent, and
463 typically between 30-70 years (Figure 5d). Mean residence time estimates are indicative of
464 rapid vertical flow and mixing of recently recharged groundwater with older deeper
465 groundwater. The presence of deep abstraction boreholes in Varanasi is the likely driver for
466 the rapid vertical flow of modern groundwater. In five sites where $SF_6$ was undetected,

467 throughout the depth profile (see Figure 5), suggests that the majority of groundwater at these
468 sites may have been recharged >50 years ago. These likely reflect shallow parts of the aquifer
469 system that are locally less well connected to shallow recharge sources and therefore have
470 less ingress of modern recharge overall. This observation could also be explained by
471 differences in pumping history at shallower sites, i.e. there has not been adequate pumping to
472 pull down modern recharge at these sites. For the deep municipal abstraction sites, one site in
473 Varanasi (V10) and two in Ramnagar (V14, V16) have no detectable $SF_6$. At two of these
474 sites, low concentrations of CFCs were detected, suggesting that there is a small component
475 of modern recharge (equivalent to between 2-8% using the BMM). The low detection
476 frequencies for micro-organics (sulfamethoxazole and sulfanilamide) at these sites supports
477 this interpretation.

478 Figure 6 shows a cross-plot of CFC-12 vs $SF_6$ and mixing lines for the following flow
479 models: piston flow model (PFM), exponential mixing model (EMM), exponential flow
480 model (EFM) and binary mixing model (BMM). Only one sample showed potential evidence
481 of contamination (i.e. concentrations in excess of modern fractions accounting for analytical
482 error) for CFC-12. There is no evidence of geogenic contamination from $SF_6$. A number of
483 groundwaters that fall close to the BMM line, with between 1-15% modern recharge, are
484 likely to represent within borehole short-circuit vertical leakage or bypass flow and mixing
485 between modern shallow groundwater and $SF_6$ 'dead' (i.e. >70 years) waters. For this group
486 of sites the ingress of a small component of modern recharge within the borehole could be
487 due to either defective casing and or borehole seals, which could also deteriorate with age.
488 The other samples fall closer to the EFM, EMM or PFM and can be interpreted as evidence
489 for hydraulic gradient controlled flow in the case and vertical drawdown and mixing either
490 within the aquifer or within the borehole due to the large screened interval. There are eight
491 samples, mostly from deep sites, which fall on the left of the BMM line and are indicative of

CFC-12 degradation - consistent with other studies in comparable sedimentary settings in the Indo-Gangetic Basin (Figure 6) (Horneman et al., 2008; Lapworth et al., 2015). Groundwater residence tracer profiles match the depth trends observed for the EOCs and other micro-organic contaminants and strongly suggest a significant component of younger groundwater at depth, even at sites which are cased out below 100 m and are completed at depths of 200 m.

**Deep groundwater vulnerability beneath urban centres**

Higher concentrations of EOCs were found in deeper municipal wells compared to intermediate depth private sources (Figure 3). This can be explained due to the combination of much higher pumping rates at the municipal sites, and the enhanced vertical migration of contaminants within the local aquifer system influenced by the borehole pumping. This suggests that the aquifer system is vulnerable to vertical contaminant migration within the aquifer and that aquifer anisotropy ratio (horizontal *K* /vertical *K*) is low. For the deep municipal abstraction sites (>100 m), more frequent detections and higher concentrations for all tracers were found at sites beneath Varanasi compared to Ramnagar even though the boreholes are deeper beneath Varanasi and the screen depths are consistent (see figure 3). There are three likely hypotheses to explain this: i) there are higher waste water inputs to the subsurface beneath Varanasi; ii) the deeper groundwater on the Varanasi side is less protected by low permeability horizons compared to the Ramnagar side; and iii) there is a longer history of deep pumping beneath Varanasi. The first hypothesis can be rejected based on a consistent EOC and residence time tracer results obtained in the shallow groundwater from both areas (Figure 3). There has been deep pumping on both sides for over 30 years so it is unlikely that the pumping history can explain this tracer evidence. It is clear from the

516 lithology (Figure 1) that there are thicker clay layers on the Ramnagar side of the R. Ganges
517 where the deep municipal sites are located and the deeper groundwater is likely to be more
518 confined. Additional evidence of high Fe (up to 7 mg $L^{-1}$), lower concentrations of nitrate
519 (Raju et al., 2011) and higher arsenic contamination (up to 80 mg $L^{-1}$) (Nandimandalam,
520 2012) beneath Ramnagar also indicates reducing conditions which are consistent with
521 confined groundwater.

522 Depth profiles of residence-time tracers, EOC and pesticides collectively provide compelling
523 evidence that modern recharge at depth within the groundwater systems beneath both
524 Varanasi and Ramnagar are controlled by local geological conditions. The fact that waste
525 water and recharge tracers do not systematically decrease with depth suggests that there is a
526 significant component of younger contaminated groundwater from the shallow aquifers
527 where long-term intensive pumping has taken place. The comparable residence time tracer
528 concentrations within deep municipal sites and intermediate sites beneath Varanasi (Figure 5)
529 also suggest that there may be a pumping influence controlling ingress of modern recharge.
530 The difference in depth profiles between specific organic contaminant groups, including the
531 residence time tracers, can be partly explained by the fact that the former are controlled by
532 local, sometimes different, sources and the residence time tracers are a more diffuse recharge
533 input to the aquifer system. The use of multiple tracers supports the assertion of vertical
534 migration of modern groundwater (0-30 years). In addition, similar SEC and dissolved
535 organic matter fluorescence profiles found in this study (see Supporting Information), and
536 high detections of arsenic and nitrate found at depth (within Pleistocene aquifers) in previous
537 studies also support this hypothesis (Nandimandalam, 2012; Raju, 2012; Raju et al., 2011).
538 Where only very low concentrations of residence time tracers and EOCs are detected at
539 depth, either greater local confinement or a reduced contribution of modern groundwater via
540 short-circuit vertical ingress due to inadequate borehole seals are possible explanations for

541 the tracer results (Jasechko et al., 2017). Modelling studies have shown that a hydraulic
542 barrier from shallower pumping may potentially protect the deeper groundwater system
543 (Burgess et al., 2010; Michael and Voss, 2008; Michael and Voss, 2009a, b). However the
544 intensity of abstraction from depth in this setting appears to overcome this potentially
545 protective mechanism. Indeed, modelling studies have recently demonstrated the rapid
546 migration of contaminants >150 m beneath Dhaka, which also has a long legacy of pumping
547 from deep municipal sources (Khan et al., 2016).

548 **Conclusions**

549 The results from this study demonstrate the diverse array of both regulated contaminants,
550 such as pesticides, and EOCs such as antimicrobial compounds in groundwater and surface
551 water in urban settings of India. The highest risks in terms of ecosystem health and human
552 health from drinking water are associated with inadequate waste management and surface
553 water pollution and shallow groundwater pollution. EOCs will continue to pose a potential
554 risk to urban drinking water supplies given the need for conjunctive use and continued
555 dependence on surface water in many urban centres in India, combined with the limited
556 treatment options for removing many of these EOCs. Lower concentrations and numbers of
557 EOCs and legacy contaminants (e.g. pesticides and PFAS) in some deep groundwater sources
558 highlight the potential for attenuation and dilution within the aquifer system, particularly
559 where thick confining low permeability horizons are present. However, the occurrence of
560 modern recharge and contaminants within the deep aquifer system beneath urban centres
561 shows that deep groundwater is potentially vulnerable to contaminant migration both within
562 the aquifer system and also due to inadequate borehole construction. Further water quality
563 monitoring at pumped sites and dedicated monitoring boreholes is required to assess the
564 future security of deep (>100 m) drinking water sources beneath growing urban centres.

565 The widespread occurrence of antimicrobials even at low concentrations in the subsurface
566 raises concerns about the development of antimicrobial resistance (AMR) in the environment
567 (Sharma et al., 2017) and their impact on natural microbiological processes in the subsurface
568 and microbiological diversity (Waldron et al., 2009). The widespread occurrence of
569 antimicrobials in groundwater has potential implications for understanding how pollutants are
570 transported in the subsurface. This study highlights the benefits of using multiple tracers to
571 constrain recharge and groundwater flow processes and demonstrates the utility of EOCs as
572 tracers in urban centres for assessing deep groundwater vulnerability.

573 **Acknowledgements**

574 The views expressed do not necessarily reflect the UK Government's or the Indian
575 Government's official policies. This paper is published with the permission of the Executive
576 Director of the British Geological Survey (NERC). We acknowledge the assistance from the
577 municipal water company of Varanasi (JAL KAL Varanasi) for access to sites and assistance
578 in planning and undertaking the study including assistance in the field by Engineers A. Singh,
579 K.C Yadav and C.V Yadav. We also thank the private borehole owners who allowed us to
580 sample their borehole as part of this study. We acknowledge the assistance of Shahid Jamal
581 (MSc student at IIT-Kharagpur) during the fieldwork. This work was jointly funded by the
582 UK Government (BEIS) and the Government of India (MHRD) through the joint British
583 Geological Survey - Indian Institute of Technology Kharagpur project SANDHI, as well as
584 direct funding from the British Geological Survey (NERC).

585

586 **Supporting Information**

587 This includes further details on the groundwater sampling protocol, the EOC analytical
588 methodology and QA and the excitation-emission fluorescence analysis.

## References


Ahmed, S., 1994. The Rhetoric of Participation Re-examined: The State, NGOs and Water Users at Varanasi, Uttar Pradesh, India. The Environmentalist 14(1), 3-16.

Anumol, T., Vijayanandan, A., Park, M., Philip, L., Snyder, S.A., 2016. Occurrence and fate of emerging trace organic chemicals in wastewater plants in Chennai, India. Environment International 92-93, 33-42.

Ascott, M.J., Lapworth, D.J., Gooddy, D.C., Sage, R.C., Karapanos, I., 2016. Impacts of extreme flooding on riverbank filtration water quality. Science of the Total Environment 554-555, 89-101.

Baun, A., Jensen, S.D., Bjerg, P.L., Christensen, T.H., Nyholm, N., 2000. Toxicity of Organic Chemical Pollution in Groundwater Downgradient of a Landfill (Grindsted, Denmark). Environmental Science & Technology 34, 1647-1652.

Benskin, J.P., Li, B., Ikonomou, M.G., Grace, J.R., Li, L.Y., 2012. Per- and Polyfluoroalkyl Substances in Landfill Leachate: Patterns, Time Trends, and Sources. Environmenal Science & Technology 46, 11532-11540.

Bhanumathi, R., Sabeena, F., Isac, S.R., Shukla, B.N., Singh, D.V., 2003. Molecular Characterization of Vibrio cholerae O139 Bengal Isolated from Water and the Aquatic Plant Eichhornia crassipes in the River Ganga, Varanasi, India. Applied and Environmental Microbiology 69, 2389-2394.

Bonsor, H.C., MacDonald, A.M., Ahmed, K.M., Burgess, W.G., Basharat, M., Calow, R.C., Dixit, A., Foster, S.S.D., Gopal, K., Lapworth, D.J., Moench, M., Mukherjee, A., Rao, M.S., Shamsudduha, M., Smith, L., Taylor, R.G., Tucker, J., van Steenbergen, F., Yadav, S.K., Zahid, A., 2017. Hydrogeological typologies of the Indo-Gangetic basin alluvial aquifer, South Asia. Hydrogeology Journal, 1-30.

Boye, B., Dieng, M.M., Brillas, E., 2002. Degradation of Herbicide 4-Chlorophenoxyacetic Acid by Advanced Electrochemical Oxidation Methods. Environmental Science & Technology 36, 3030-3035.

Bradley, P.M., Journey, C.A., Romanok, K.M., Barber, L.B., Buxton, H.T., Foreman, W.T., Furlong, E.T., Glassmeyer, S.T., Hladik, M.L., Iwanowicz, L.R., Jones, D.K., Kolpin, D.W., Kuivila, K.M., Loftin, K.A., Mills, M.A., Meyer, M.T., Orlando, J.L., Reilly, T.J., Smalling, K.L., Villeneuve, D.L., 2017. Expanded Target-Chemical Analysis Reveals Extensive Mixed-Organic-Contaminant Exposure in U.S. Streams. Environmental Science & Technology 51, 4792-4802.

Buerge, I., Buser, H.-R., Kahle, M., Muller, M.D., Poiger, T., 2009. Ubiquitous Occurrence of the Artificial Sweetener Acesulfame in the Aquatic Environment: An Ideal Chemical Marker of Domestic Wastewater in Groundwater. Environmental Science & Technology 43(12), 4381-4385.

Burgess, W.G., Hoque, M.A., Michael, H.A., Voss, C.I., Breit, G.N., Ahmed, K.M., 2010. Vulnerability of deep groundwater in the Bengal Aquifer System to contamination by arsenic. Nature Geoscience 3, 83-87.

Burke, V., Richter, D., Hass, U., Duennbier, U., Greskowiak, J., Massmann, G., 2013. Redox-dependent removal of 27 organic trace pollutants: compilation of results from tank aeration experiments. Environmental Earth Sciences 71, 3685-3695.

Busenberg, E., Plummer, L.N., 2000. Dating young groundwater with sulfur hexafluoride: Natural and anthropogenic sources of sulfur hexafluoride. Water Resources Research 36, 3011-3030.

Chakraborti, D., Das, B., Murrill, M.T., 2011. Examining India's Groundwater Quality Management. Environmental Science & Technology 45, 27-33.

Chaurasia, J., Rai, P.K., Singh, A.K., 2013. Physico-chemical status of groundwater near Varuna river in Varanasi city, India. International Journal of Environmental Science 3.

Chishti, Z., Hussain, S., Arshad, K.R., Khalid, A., Arshad, M., 2013. Microbial degradation of chlorpyrifos in liquid media and soil. Journal of Environmental Management 114, 372-380.

Cook, P. and Böhlke, J.-K., 2000. Environmental Tracers in Subsurface Hydrology. Cook, In: Cook, P. and Herczeg, A. (Eds), pp. 1-30, Kluwer Academic Publishers, Boston, pp. 526

Darling, W.G., Gooddy, D.C., MacDonald, A.M., Morris, B.L., 2012. The practicalities of using CFCs and SF6 for groundwater dating and tracing. Applied Geochemistry 27, 1688-1697.

639 Dickenson, E.R., Snyder, S.A., Sedlak, D.L., Drewes, J.E., 2011. Indicator compounds for assessment of
640 wastewater effluent contributions to flow and water quality. Water Research 45, 1199-1212.
641 EPA (2016) Chlorpyrifos Refined Drinking Water Assessment for Registration Review, pp. 125, US
642 Environment Protection Agency.
643 EPA (2017) Drinking Water Health Advisories for PFOA and PFOS, US EPA. Available:
644 https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-
645 and-pfos. Accessed June 2017.
646 Farooqi, A., Masuda, H., Firdous, N., 2007. Toxic fluoride and arsenic contaminated groundwater in the
647 Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources. Environmental
648 Pollution 145, 839-849.
649 Focazio, M.J., Kolpin, D.W., Barnes, K.K., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Barber, L.B., Thurman,
650 M.E., 2008. A national reconnaissance for pharmaceuticals and other organic wastewater
651 contaminants in the United States - II) Untreated drinking water sources. Science of the Total
652 Environment 402, 201-216.
653 Gibson, S.A., Suflita, J.M., 1986. Extrapolation of Biodegradation Results to Groundwater Aquifers:
654 Reductive Dehalogenation of Aromatic Compounds. Applied and Environmental Microbiology 52,
655 681-688.
656 Gleeson, T., Befus, K.M., Jasechko, S., Luijendijk, E., Cardenas, M.B., 2015. The global volume and
657 distribution of modern groundwater. Nature Geoscience 9, 161-167.
658 Gooddy, D.C., Darling, W.G., Abesser, C., Lapworth, D.J., 2006. Using chlorofluorocarbons (CFCs) and
659 sulphur hexafluoride (SF6) to characterise groundwater movement and residence time in a
660 lowland Chalk catchment. Journal of Hydrology 330, 44-52.
661 Greskowiak, J., Hamann, E., Burke, V., Massmann, G., 2017. The uncertainty of biodegradation rate
662 constants of emerging organic compounds in soil and groundwater - A compilation of literature
663 values for 82 substances. Water Research 126, 122-133.
664 Guelfo, J.L., Higgins, C.P., 2013. Subsurface Transport Potential of Perfluoroalkyl Acids at Aqueous Film-
665 Forming Foam (AFFF)-Impacted Sites. Environ Sci Technol 47, 4164-4171.
666 Gustafson, D.I., 1989. Groundwater ubiquity score: A simple method for assessing pesticide leachability.
667 Environmental Toxicology and Chemistry 8, 339-357.
668 Haack, S.K., Metge, D.W., Fogarty, L.R., Meyer, M.T., Barber, L.B., Harvey, R.W., Leblanc, D.R., Kolpin,
669 D.W., 2012. Effects on groundwater microbial communities of an engineered 30-day in situ
670 exposure to the antibiotic sulfamethoxazole. Environmental Science & Technology 46, 7478-7486.
671 Hamner, S., Tripathi, A., Mishra, R.K., Bouskill, N., Broadaway, S.C., Pyle, B.H., Ford, T.E., 2006. The role
672 of water use patterns and sewage pollution in incidence of water-borne/enteric diseases along
673 the Ganges river in Varanasi, India. International Journal of Environmental Health Research 16,
674 113-132.
675 Holm, J.V., Rugge, K., Bjerg, P.L., Christensen, T.H., 1995. Occurrence and Distribution of Pharmaceutical
676 Organic Compounds in the Groundwater Downgradient of a Landfill (Grindsted, Denmark).
677 Environmental Science & Technology 29, 1418-1420.
678 Hoque, M.A., McArthur, J.M., Sikdar, P.K., Ball, J.D. and Molla, T.N., 2014. Tracing recharge to aquifers
679 beneath an Asian megacity with Cl/Br and stable isotopes: the example of Dhaka, Bangladesh.
680 Hydrogeology journal, 22(7), pp.1549-1560.
681 Horneman, A., Stute, M., Schlosser, P., Smethie, W., Jr., Santella, N., Ho, D.T., Mailloux, B., Gorman, E.,
682 Zheng, Y., van Geen, A., 2008. Degradation rates of CFC-11, CFC-12 and CFC-113 in anoxic shallow
683 aquifers of Araihazar, Bangladesh. Journal of Contaminant Hydrology 97, 27-41.
684 Houtz, E.F., Higgins, C.P., Field, J.A., Sedlak, D.L., 2013. Persistence of Perfluoroalkyl Acid Precursors in
685 AFFF-Impacted Groundwater and Soil. Environmental Science & Technology 47, 8187-8195.
686 Houtz, E.F., Sutton, R., Park, J.S., Sedlak, M., 2016. Poly- and perfluoroalkyl substances in wastewater:
687 Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. Water
688 Research 95, 142-149.

689 Hu, X.D.C., Andrews, D.Q., Lindstrom, A.B., Bruton, T.A., Schaider, L.A., Grandjean, P., Lohmann, R.,
690 Carignan, C.C., Blum, A., Balan, S.A., Higgins, C.P., Sunderland, E.M., 2016. Detection of Poly- and
691 Perfluoroalkyl Substances (PFASs) in US Drinking Water Linked to Industrial Sites, Military Fire
692 Training Areas, and Wastewater Treatment Plants. Environmental Science & Technology Letters 3,
693 344-350.
694 Jal-Kal, 2016. Drillers logs for municipal abstration sites for Ramingar and Varanasi accessed at the Jal Kal
695 offices in Varanasi in 2016. Jal-Kal, Varanasi, India.
696 Jasechko, S., Perrone, D., Befus, K.M., Bayani Cardenas, M., Ferguson, G., Gleeson, T., Luijendijk, E.,
697 McDonnell, Jeffrey J., Taylor, R.G., Wada, Y., Kirchner, J.W., 2017. Global aquifers dominated by
698 fossil groundwaters but wells vulnerable to modern contamination. Nature Geoscience 10, 425-
699 429.
700 Jiang, B., Li, A., Cui, D., Cai, R., Ma, F., Wang, Y., 2014. Biodegradation and metabolic pathway of
701 sulfamethoxazole by Pseudomonas psychrophila HA-4, a newly isolated cold-adapted
702 sulfamethoxazole-degrading bacterium. Applied Microbiology and Biotechnology 98, 4671-4681.
703 Khan, M.R., Koneshloo, M., Knappett, P.S., Ahmed, K.M., Bostick, B.C., Mailloux, B.J., Mozumder, R.H.,
704 Zahid, A., Harvey, C.F., van Geen, A., Michael, H.A., 2016. Megacity pumping and preferential flow
705 threaten groundwater quality. Nature Communications 7, 12833.
706 Kim, I., Tanaka, H., 2009. Photodegradation characteristics of PPCPs in water with UV treatment.
707 Environment International 35, 793-802.
708 Kumar, R., Tiwari, A.K., Yadav, G.S., Singh, N.P., 2014. Geohydrological investigation using vertical
709 electrical sounding at Banaras Hindu Univeristy campus, Varanasi, U.P, India. International Journal
710 of Engineering Sciences & Research Technology 3, 252-256.
711 Kummerer, K., 2009. Antibiotics in the aquatic environment--a review--part II. Chemosphere 75, 435-
712 441.
713 Kurunthachalam, S.K., 2012. Pharmaceutical Substances in India are a Point of Great Concern?
714 Hydrology: Current Research 3, 3-5.
715 Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S., 2012. Emerging organic contaminants in
716 groundwater: A review of sources, fate and occurrence. Environmental Pollution 163, 287-303.
717 Lapworth, D.J., MacDonald, A.M., Krishan, G., Rao, M.S., Gooddy, D.C., Darling, W.G., 2015.
718 Groundwater recharge and age-depth profiles of intensively exploited groundwater resources in
719 northwest India. Geophysical Research Letters 42, 7554-7562.
720 Lapworth, D.J., Krishan, G., MacDonald, A.M., Rao, M.S., 2017. Groundwater quality in the alluvial
721 aquifer system of northwest India: New evidence of the extent of anthropogenic and geogenic
722 contamination. Science of the Total Environment 599-600, 1433-1444.
723 Lawrence, A.R., Gooddy, D.C., Kanatharana, P., Meeslip, W., Ramnarong, V., 2000. Groundwater
724 evolution beneath Hat Yai, a rapidly developing city in Thailand. Hydrogeology Journal 8, 564-575.
725 Liao, X., Li, B., Zou, R., Xie, S., Yuan, B., 2016. Antibiotic sulfanilamide biodegradation by acclimated
726 microbial populations. Applied Microbiology and Biotechnology 100, 2439-2447.
727 MacDonald, A.M., Bonsor, H.C., Ahmed, K.M., Burgess, W.G., Basharat, M., Calow, R.C., Dixit, A., Foster,
728 S.S.D., Gopal, K., Lapworth, D.J., Lark, R.M., Moench, M., Mukherjee, A., Rao, M.S., Shamsudduha,
729 M., Smith, L., Taylor, R.G., Tucker, J., van Steenbergen, F., Yadav, S.K., 2016. Groundwater quality
730 and depletion in the Indo-Gangetic Basin mapped from in situ observations. Nature Geoscience 9,
731 762-766.
732 Maloszewski, P. and Zuber, A. (1996) Lumped parameter models for the interpretation of environmental
733 tracer data. IAEA Report No. IAEA-TECDOC-910, pp 207. Available at:
734 http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/28/020/28020904.pdf.
735 Massmann, G., Greskowiak, J., Dünnbier, U., Zuehlke, S., Knappe, A., Pekdeger, A., 2006. The impact of
736 variable temperatures on the redox conditions and the behaviour of pharmaceutical residues
737 during artificial recharge. Journal of Hydrology 328, 141-156.
738 McManus, S.L., Moloney, M., Richards, K.G., Coxon, C.E., Danaher, M., 2014. Determination and
739 Occurrence of Phenoxyacetic Acid Herbicides and Their Transformation Products in Groundwater

Using Ultra High Performance Liquid Chromatography Coupled to Tandem Mass Spectrometry. Molecules 19, 20627-20649.
Michael, H.A., Voss, C.I., 2008. Evaluation of the sustainability of deep groundwater as an arsenic-safe resource in the Bengal Basin. Procedings of the National Acadamy of Science U S A 105, 8531-8536.
Michael, H.A., Voss, C.I., 2009a. Controls on groundwater flow in the Bengal Basin of India and Bangladesh: regional modeling analysis. Hydrogeology Journal 17, 1561-1577.
Michael, H.A., Voss, C.I., 2009b. Estimation of regional-scale groundwater flow properties in the Bengal Basin of India and Bangladesh. Hydrogeology Journal 17, 1329-1346.
Milinovic, J., Lacorte, S., Rigol, A., Vidal, M., 2016. Sorption of perfluoroalkyl substances in sewage sludge. Environmental Science and Pollution Research 23, 8339-8348.
Mishra, A., Mukhejee, A., Tripathi, B.D., 2009. Seasonal and Temporal Variations in Physico-chemical and Bacteriological Characteristics of River Ganga in Varanasi. International Journal of Environmental Research 3, 395-402.
Mishra, V., 2005. The Ganga at Varanasi and a travail to stop her abuse. Current Science 89, 755-763.
Mohan, K., Srivastava, A., Rai, P., 2011. Ground Water in the City of Varanasi, India: present status and prospects. Quaestiones Geographicae 30(3), 47-60.
Mondal, M.K., Rashmi, Dasgupta, B.V., 2010. EIA of municipal solid waste disposal site in Varanasi using RIAM analysis. Resources, Conservation and Recycling 54, 541-546.
Morris, B.L., Darling, W.G., Gooddy, D.C., Litvak, R.G., Neumann, I., Nemaltseva, E.J., Poddubnaia, I., 2006. Assessing the extent of induced leakage to an urban aquifer using environmental tracers: an example from Bishkek, capital of Kyrgyzstan, Central Asia. Hydrogeology Journal 14(1-2).
Mukherjee, A., Fryar, A.E., Scanlon, B.R., Bhattacharya, P., Bhattacharya, A., 2011. Elevated arsenic in deeper groundwater of the western Bengal basin, India: Extent and controls from regional to local scale. Applied Geochemistry 26, 600-613.
Muller, M.D., Buser, H.-R., 1997. Conversion Reactions of Various Phenoxyalkanoic Acid Herbicides in Soil. 1. Enantiomerization and Enantioselective Degradation of the Chiral 2-Phenoxypropionic Acid Herbicides. Environmental Science & Technology 31, 1953-1959.
Mutiyar, P.K., Mittal, A.K., 2014. Risk assessment of antibiotic residues in different water matrices in India: key issues and challenges. Environmental Science and Pollution Research 21, 7723-7736.
Nandimandalam, J.R., 2012. Evaluation of hydrogeochemical processes in the Pleistocene aquifers of Middle Ganga Plain, Uttar Pradesh, India. Environmental Earth Sciences 65, 1291-1308.
NGWA, 2017. Groundwater and PFAS: State of Knowledge and Practice - Draft for consultation. NGWA, http://comments.ngwa.org/.
Pal, A., Gin, K.Y., Lin, A.Y., Reinhard, M., 2010. Impacts of emerging organic contaminants on freshwater resources: review of recent occurrences, sources, fate and effects. Science of the Total Environment 408, 6062-6069.
Petrie, B., Barden, R., Kasprzyk-Hordern, B., 2015. A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Research 72, 3-27.
Petrovic, M., Gonzalez, S., Barcelo´, D., 2003. Analysis and removal of emerging contaminants in wastewater and drinking water. Trends in Analytical Chemistry 22, 685-696.
Planning Commission, G.o.I., 2014. Uttar Pradesh Development Report, Chapters 10 (Urban Water) & 11 (Water Resources: Management and Development), pp. 267-333.
Raju, N.J., 2012. Arsenic Exposure through Groundwater in the Middle Ganga Plain in the Varanasi Environs, India: A Future Threat. Journal of the Geological Society of India 79, 302-314.
Raju, N.J., Ram, P., Dey, S., 2009. Groundwater Quality in the Lower Varuna River Basin, Varanasi District, Uttar Pradesh. Journal of the Geological Society of India 73, 178-192.
Raju, N.J., Ram, P., Gossel, W., 2014. Evaluation of groundwater vulnerability in the lower Varuna catchment area, Uttar Pradesh, India using AVI concept. Journal of the Geological Society of India 83, 273-278.

Raju, N.J., Shukla, U.K., Ram, P., 2011. Hydrogeochemistry for the assessment of groundwater quality in Varanasi: a fast-urbanizing center in Uttar Pradesh, India. Environmental Monitoring and Assessment 173, 279-300.
Reuters, 2017. India's Ganges clean-up in shambles, Modi intervenes. Accessed June 2017: https://uk.reuters.com/article/india-ganges/exclusive-indias-ganges-clean-up-in-a-shambles-modi-intervenes-idUKKBN1780ZC
Richardson, S.D., 2009. Water Analysis: Emerging Contaminants and Current Issues. Analytical Chemistry 81, 4645-4677.
Robertson, W.D., Van Stempvoort, D.R., Spoelstra, J., Brown, S.J., Schiff, S.L., 2016. Degradation of sucralose in groundwater and implications for age dating contaminated groundwater. Water Research 88, 653-660.
Selvaraj, K.K., Shanmugam, G., Sampath, S., Larsson, D.G., Ramaswamy, B.R., 2014. GC-MS determination of bisphenol A and alkylphenol ethoxylates in river water from India and their ecotoxicological risk assessment. Ecotoxicology and Environmental Safety 99, 13-20.
Sharma, B., Parul, Verma, A.K., Jain, U., Yadav, J.K., Singh, R., Mishra, R., 2017. Occurrence of multidrug resistant Escherichia coli in groundwater of Brij region (Uttar Pradesh) and its public health implications. Veterinary World 10, 293-301.
Sharma, B.M., Bharat, G.K., Tayal, S., Larssen, T., Becanova, J., Karaskova, P., Whitehead, P.G., Futter, M.N., Butterfield, D., Nizzetto, L., 2016. Perfluoroalkyl substances (PFAS) in river and ground/drinking water of the Ganges River basin: Emissions and implications for human exposure. Environmental Pollution 208, 704-713.
Soni, D.K., Singh, R.K., Singh, D.V., Dubey, S.K., 2013. Characterization of Listeria monocytogenes isolated from Ganges water, human clinical and milk samples at Varanasi, India. Infection Genetics and Evolution 14, 83-91.
Sorensen, J.P., Lapworth, D.J., Nkhuwa, D.C., Stuart, M.E., Gooddy, D.C., Bell, R.A., Chirwa, M., Kabika, J., Liemisa, M., Chibesa, M., Pedley, S., 2015. Emerging contaminants in urban groundwater sources in Africa. Water Research 72, 51-63.
Stuart, M., Lapworth, D., Crane, E., Hart, A., 2012. Review of risk from potential emerging contaminants in UK groundwater. Science of the Total Environment 416, 1-21.
Stuart, M.E., Lapworth, D.J., Thomas, J., Edwards, L., 2014. Fingerprinting groundwater pollution in catchments with contrasting contaminant sources using microorganic compounds. Science of the Total Environment 468, 564-577.
Underwood, J.C., Harvey, R.W., Metge, D.W., Repert, D.A., Baumgartner, L.K., Smith, R.L., Roane, T.M., Barber, L.B., 2011. Effects of the antimicrobial sulfamethoxazole on groundwater bacterial enrichment. Environ Sci Technol 45, 3096-3101.
Van Donk, E., Peacor, S., Grosser, K., De Senerpont Domis, L.N., Lurling, M., 2016. Pharmaceuticals May Disrupt Natural Chemical Information Flows and Species Interactions in Aquatic Systems: Ideas and Perspectives on a Hidden Global Change. Rev Environ Contam Toxicol 238, 91-105.
Waldron, P.J., Wu, L.Y., Van Nostrand, J.D., Schadt, C.W., He, Z.L., Watson, D.B., Jardine, P.M., Palumbo, A.V., Hazen, T.C., Zhou, J.Z., 2009. Functional Gene Array-Based Analysis of Microbial Community Structure in Groundwaters with a Gradient of Contaminant Levels. Environmental Science & Technology 43, 3529-3534.
Wang, Z.Y., Cousins, I.T., Scheringer, M., Buck, R.C., Hungerbuhler, K., 2014. Global emission inventories for C-4-C-14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. Environment International 70, 62-75.
White, D., Lapworth, J., Stuart, M.E., Williams, P.J., 2016. Hydrochemical profiles in urban groundwater systems: New insights into contaminant sources and pathways in the subsurface from legacy and emerging contaminants. Science of the Total Environment 562, 962-973.
White, D., Williams, P.J., Civil, W., Lapworth, D.J., 2017. A field based method for preconcentration of micro organics using solid phase extraction. British Geological Survey Open Report, p. 21.

841 Willems, H.P.L., Lewis, K.J., Dyson, J.S., Lewis, F.J., 1996. Mineralization of 2,4-D and Atrazine in the
842 unsaturated zone of a sandy loam soil. Soil Biology & Biochemistry 28, 989-996.
843 Yeung, L.W., Yamashita, N., Taniyasu, S., Lam, P.K., Sinha, R.K., Borole, D.V., Kannan, K., 2009. A survey
844 of perfluorinated compounds in surface water and biota including dolphins from the Ganges River
845 and in other waterbodies in India. Chemosphere 76, 55-62.
846 Zipper, C., Bolliger, C., Fleischmann, T., Suter, M.J.F., Angst, W., Muller, M.D., Kohler, H.P.E., 1999a. Fate
847 of the herbicides mecoprop, dichlorprop, and 2,4-D in aerobic and anaerobic sewage sludge as
848 determined by laboratory batch studies and enantiomer-specific analysis. Biodegradation 10, 271-
849 278.
850 Zipper, C., Fleischmann, T., Kohler, H.P.E., 1999b. Aerobic biodegradation of chiral phenoxyalkanoic acid
851 derivatives during incubations with activated sludge. Fems Microbiology Ecology 29, 197-204.
852 Zuber, A. (1986) Mathematical models for the interpretation of environmental radioisotopes in
853 groundwater systems pp. 1–59. In: Fritz, P. and Fontes, J.C. (Eds). Handbook of Environmental
854 Geochemistry, The Terrestrial Environment. Elsevier, Amsterdam, Netherlands.