Science of the Total Environment 595 (2017) 63–71

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Human and livestock waste as a reduced carbon source contributing to the release of arsenic to shallow Bangladesh groundwater

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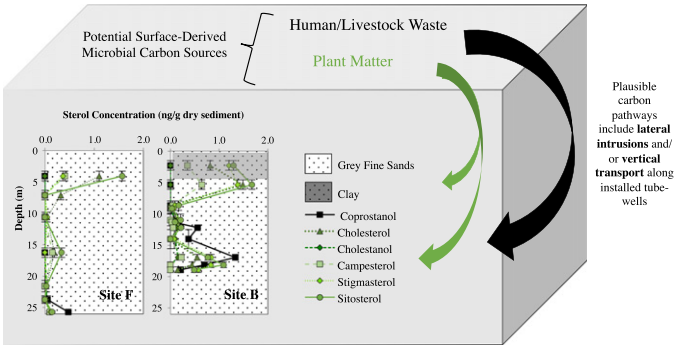
HIGHLIGHTS

- Carbon cycles in Bangladesh aquifers significantly affect microbial As release.
- Sterol biomarkers of human/livestock waste used to examine carbon source cycling.
- Sedimentary coprostanol found only at depth where $[Cl/Br]_{aq} > 1000$.
- Depths of human/livestock waste coincided with highest $[Fe]_{aq}$ and $[As]_{aq}$.
- Human/livestock waste DOC may be the young carbon source for microbial As release.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 January 2017
Received in revised form 20 March 2017
Accepted 25 March 2017
Available online 4 April 2017

Editor: D. Barcelo

Keywords:
Microbial carbon cycling
Bangladesh aquifers
Arsenic contamination
Contaminated groundwater
Human and livestock waste
Coprostanol

ABSTRACT

Recent studies have demonstrated that the supply of relatively young organic carbon stimulates the release of arsenic to groundwater in Bangladesh. This study explores the potential role of human and livestock waste as a significant source of this carbon in a densely populated rural area with limited sanitation. Profiles of aquifer sediment samples were analyzed for phytosterols and coprostanol to assess the relative contributions of plant-derived and human/livestock waste-derived organic carbon at two well-characterized sites in Araihazar. Coprostanol concentrations increased with depth from non-detection (<10 m at Site B and <23 m at Site F) to maxima of 1.3 and 0.5 ng/g in aquifer sands recovered from 17 m (Site B) and 26 m (Site F), respectively. The commonly used sewage contamination index ([5β-coprostanol]/([5α-cholestanol] + [5β-coprostanol])) exceeds 0.7 between 12 and 19 m at Site B and between 24 and 26 m at Site F, indicating input of human/livestock waste to these depths. Urine/fecal input within the same depth range is supported by groundwater Cl/Br mass ratios >1000 compared to Cl/Br <500 at depths >50 m. Installed tube wells in the area's study sites may act as a conduit for DOC and specifically human/livestock waste into the aquifer during flood events. The depth range of maximum input of human/livestock waste indicated by these independent markers coincides with the highest dissolved Fe (10–20 mg/L) and As (200–400 μg/L) concentrations in groundwater at both sites. The new findings suggest that the oxidation of human/livestock waste coupled to the reductive dissolution of iron-(oxy)-hydroxides and/or arsenate may enhance groundwater contamination with As.

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http://dx.doi.org/10.1016/j.scitotenv.2017.03.234
0048-9697/

1. Introduction

Chronic exposure to arsenic (As) contained in groundwater poses a considerable human health risk across rural Bangladesh and surrounding regions, where most villagers depend on shallow wells as their primary source of drinking water. The release of As from uncontaminated sediments into groundwater has been shown to be mediated through microbial mechanisms (Dhar et al., 2011; Harvey et al., 2002; Islam et al., 2004; Nickson et al., 1998, 2000, Postma et al., 2012, 2007; Swartz et al., 2004). Heterotrophic bacteria couple the reduction dissolution of iron (oxy)-hydroxide bearing particles (Cummings et al., 1999; Dhar et al., 2011; Dowling et al., 2002; Harvey et al., 2002; Islam et al., 2004; McArthur et al., 2001; Nickson et al., 1998, 2000, Postma et al., 2012, 2007; Swartz et al., 2004) or directly of As(V) (Ahmann et al., 1997; Postma et al., 2007) to the oxidation of organic carbon resulting in the release of adsorbed As from the sediment to groundwater. The supply and reactivity of the organic carbon driving this release is the ultimate thermodynamic driver of these processes. However, after more than a decade of research, the relative importance of advected carbon to sedimentary carbon, as well as the role of natural versus anthropogenic carbon sources, remains unclear. These distinctions are important because they have very different implications for the evolution of the distribution of As in Bangladesh aquifers under the influence of massive groundwater pumping (Burgess et al., 2010; Michael and Voss, 2008).

A number of potential sources of organic carbon including human waste (Harvey et al., 2002; McArthur et al., 2012), man-made constructed ponds (Lawson et al., 2013; Neumann et al., 2010), wetland/rice paddy environments (Meharg et al., 2006; Polizzotto et al., 2008; Stuckey et al., 2015), river-derived flows (van Geen et al., 2013), buried peat layers (Anawar et al., 2003; McArthur et al., 2004, 2001; Mladenov et al., 2010; Planer-Friedrich et al., 2012; Ravenscroft et al., 2001; Yamazaki et al., 2003) and organics deposited with sediments (Desbarats et al., 2014; Meharg et al., 2006; Nickson et al., 2000; Postma et al., 2012, 2007) have been proposed based on studies conducted at various sites. Recent evidence based on $\Delta^{14}C$ analysis of microbial lipids, DNA and biogenic methane from a few sites in Bangladesh has indicated that reductive dissolution of iron (Fe) oxides at depths <30 m may be driven primarily by relatively young surface-derived carbon sources as opposed to older sedimentary carbon (Harvey et al., 2002; Mailloux et al., 2013; Whaley-Martin et al., 2016). Determining which of the potential sources of surface derived reactive carbon, e.g. plant versus human/livestock waste, is a crucial next question as the implications to management and mitigation efforts of these two potential sources would be very different.

Potential sources of plant-derived carbon that have been proposed include ponds (Lawson et al., 2013; Neumann et al., 2014), local wetlands (Meharg et al., 2006) or rice-paddy crops (Polizzotto et al., 2008) which are all abundant in land coverage across Bangladesh (Islam and Rahman, 2010; Meharg and Rahman, 2003; Rahaman, 2012). In a recent field experiment, Stuckey et al. (2015) stimulated Fe reduction and As release from Cambodian sediments by adding large quantities of local grass as a microbial carbon source. In contrast, Neumann et al. (2014) found dissolved organic carbon (DOC) carried from rice-paddy fields (plant-derived) shows limited biological degradation under natural conditions and instead proposed DOC carried with recharge water from ponds as a predominant microbial carbon source at one site. While the origin of the DOC from ponds Neumann et al. (2014) referred to is unclear, many ponds in Bangladesh are extensively contaminated with latrine discharge and animal waste (Knappett et al., 2012a, b).

McArthur et al. (2012) suggested widespread contamination of shallow aquifers across the Bengal basin with human waste on the basis of Cl/Br ratios and Cl concentrations in groundwater (Davis et al., 1998; McArthur et al., 2012). However, the relationship between these indicators and fecal contamination or As concentrations in groundwater was unclear. Monitoring of a substantial number of shallow wells in Bangladesh has documented an inverse relationship between the fecal indicator *E. coli* and As concentrations (Leber et al., 2011; van Geen et al., 2011). This could be seen as an indication that human waste, if anything, inhibits the release of As to groundwater (McArthur et al., 2012). An alternate explanation supported by tritium-helium dating of groundwater is that enhanced recharge through more permeable surface soil favors the downwards transport of *E. coli* while at the same time diluting As released by aquifer sediments (Aziz et al., 2008; Stute et al., 2007).

Analysis of C_{29} sterols could potentially address this question as they can serve as biomarkers for complex pools of carbon that are travelling through the aquifer sediments (such as organic matter derived from plants versus human/livestock waste in sediments) (Biache and Philp, 2013; Chikaraishi et al., 2005; Furtula et al., 2012; Lee et al., 2011; Martins et al., 2011; Tolosa et al., 2013; Tse et al., 2014). The relative distributions of these biomarkers can provide an indication of how much input from each source has occurred.

The octanol-water partitioning coefficients of these hydrophobic compounds are high, indicating that they are likely to sorb strongly onto aquifer sediments and will be retarded relative to the movement of groundwater (Froehner and Sánez, 2013). Phytosterols (i.e. β-sitosterol, stigmasterol and campesterol) are reliable biomarkers of plant matter in sediments. In contrast, coprostanol (5β-cholestan-3β-ol, $\log K_{OW} \approx 8.2$) is biosynthesized from cholesterol exclusively within the mammalian gut and comprises 25 to 90% of total steroids in feces (Leeming et al., 1996). It is therefore a widely accepted biomarker for sewage/fecal matter of human or animal origin (Chou and Liu, 2004; Furtula et al., 2012; Hussain et al., 2010; Lee et al., 2011; Martins et al., 2011). Under aerobic conditions in sandy sediments, Pratt et al. (2008) observed that coprostanol degrades more slowly than fecal bacterial indicators. Under anaerobic conditions, coprostanol can persist in sediments for years to centuries (Bartlett, 1987; Nishimura and Koyama, 1977; Reeves and Patton, 2005; Tse et al., 2014).

This study documents the vertical distribution of C_{29} sterols at two well-characterized sites in Araihazar Upazila, Bangladesh (Dhar et al., 2008; Stute et al., 2007) that are impacted by high levels of As in groundwater. The sterol distributions are compared with other indicators of unsewered wastes (Cl/Br mass ratios), as well as As and Fe concentrations. The organic extracts used for the present study are the same that were previously used for $\Delta^{14}C$ analysis of bacterial lipids (Whaley-Martin et al., 2016) and showed that young carbon was driving microbial metabolisms.

2. Methods

2.1. Field sites

The area surrounding the first of the two sites, Site B in Baylakandi Village (23.7800 N 90.6400 E), is very densely populated and groundwater in most wells contains >50 μg/L As (Fig. 1b). In contrast, the area around Site F in Lashkardi Village (23.774 N 90.606 E) is less densely populated and groundwater from most surrounding wells contains <50 μg/L, and in many cases <10 μg/L, which is the World Health Organization guideline for As in drinking water (Fig. 1a). At Site B, a 7-m thick clay/silt layer caps the sandy aquifer whereas the sandy formation extends essentially to the surface at Site F (Dhar et al., 2008). As described in detail in Whaley-Martin et al. (2016), sediments were collected in January 2013 by gravity coring, sectioned directly into whirlpacks, immediately frozen, shipped on ice and frozen until future analyses. Data for groundwater samples collected between 2002 and 2015 from pre-existing well nests at the two sites (Dhar et al., 2008) using a battery operated downhole pump (Groundwater Essentials©) is also presented. Wells were purged until the

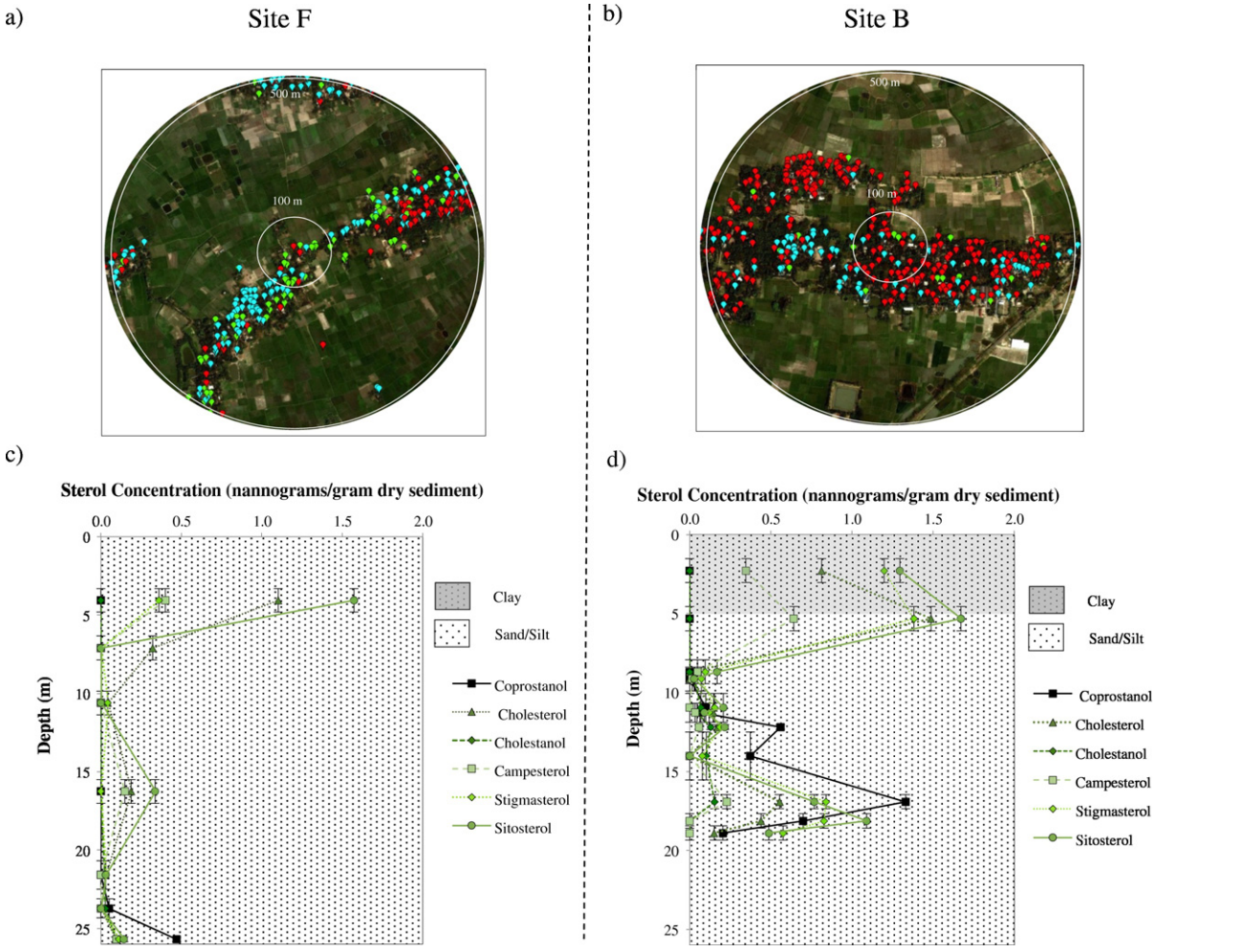

Fig. 1. Local well distributions and groundwater arsenic concentrations from a 2012–13 survey within 100 m (inner white circle) and 500 m (outer white circle) from Site F (a) and Site B (b) where [As] in groundwater are indicated by blue circles <10 μg/L, green circles 10 to 50 μg/L and red circles >50 μg/L. Depth profiles of phytosterols (green symbols: cholesterol, cholestanol, campesterol, stigmasterol and sitosterol) and sewage biomarker coprostanol (black symbols) in shallow aquifer sediments (ng/g sediment) of the Araihazar Upazila, Bangladesh of (c) Site F and (d) Site B.

conductivity stabilizes before groundwater was collected in two scintillation vials, without filtration.

2.2. Sterol lipid extraction, separation and derivatization

Prior to extractions, all sediments were freeze-dried for 48–72 h. A detailed description of the organic compound extraction and separation is provided in Whaley-Martin et al. (2016). Sediment samples (~300 g to 1 kg) were extracted twice overnight using a modified Bligh and Dyer extraction and the organic phase was removed after phase separation in separatory funnels. A three-fraction (Fraction$_1$ = dichloromethane (DCM), Fraction$_2$ = acetone, Fraction$_3$ = methanol) silica gel chromatographic elution was carried out. Methanol fractions were utilized for phospholipid fatty acid analyses reported in a previous study (Whaley-Martin et al., 2016). Preliminary tests revealed elution of sterols occurred in both the Fraction$_{1\&2}$ in agreement with a recent study (Birk et al., 2012) showing high recoveries using elution with DCM and acetone. The DCM and acetone fractions containing the sterols were blow down to dryness under N_2 and underwent a BSTFA (*N,O*-bis-(trimethylsilyl)-trifluoroacetamide, Sigma-Aldrich) derivatization using pyridine as a catalyst for 30 min at 65 °C to create trimethylsilyl (TMS)-derivatives of the original sterols. TMS-derivatives were found to be better resolved through the chromatographic separation than the original steroid precursors, as seen in previous studies (Marcos and Pozo, 2015).

2.3. Sterol analysis through gas chromatography-mass spectrometry (GC–MS)

Sterol standards used for identification and quantification with GC–MS were cholestanol (5-α-cholestan-3β-ol, ≥95%, Sigma Aldrich), cholesterol (cholet-5-en-3β-ol, ~94%, Sigma Aldrich), stigmasterol (24-ethylcholesta-5,22E-dien-3β-ol, ~95%, Sigma Aldrich), campesterol (24-α-methyl-5-cholesten-3β-ol, ~65%, Sigma Aldrich), sitosterol (24-ethylcholest-5-en-3-β-ol, ≥97%, Sigma Aldrich) and coprostanol (5β-cholestan-3β-ol, ≥98%, Santa Cruz Biotechnology). All standards underwent the BSTFA derivatization at the same time as samples and their TMS-derivatives were used to compare to sample extracts (Table A1). Concentrated samples (run in 30 μL of BSTFA + 10 μL of pyridine) were run with 1 μL injections on an Agilent Technologies 6890N GC with an Agilent DB5-MS capillary column (30 m × 0.32 μm, 0.25 μm film thickness) coupled to a 5973 quadrupole mass spectrometer scanning for masses from 50 to 500 *m/z*. Operating GC–MS conditions included a temperature program with an initial hold for 1 min at 40 °C ramped to 300 °C at 4 °C/min and held at 300 °C for 24 min (Biache and Philp, 2013). The limit of quantification (0.5 μg/mL) was determined based on linearity of the sterol calibration curves. Final sterol LOQ's for each particular sample (ng/g of sediment) was dependent on the total mass of sediment weight extracted (Table A2).

2.4. Inorganic groundwater analysis

Cl, Br and other anion concentrations were determined using a DIONEX-500 ion chromatograph system equipped with an IonPac® AS18 anion-exchange column using standard EPA methods. QA/QC included duplicates (<1% RPD), blanks, lab standards and Certified Reference Materials to ensure that recoveries and analytical accuracy and precision were within 5%. Concentrations of As and Fe were determined using high resolution-inductively coupled plasma mass spectrometry (HR-ICP-MS) using previously described methods (Cheng et al., 2004). Reference materials NIST1640A and 1643A and internal consistency standards are included with each run. The long-run reproducibility of this method is on the order of 5% and the detection limit <0.1 μg/L.

3. Results

3.1. Profiles of phytosterols and coprostanol in the sediment

Concentrations of the phytosterol plant biomarkers in the two sediment profiles extending to 19 m depth at Site B (n = 11) and to 26 m at Site F (n = 7) ranged from <2 ng/g to <LODs (Table A2). Concentrations of phytosterols are the highest at ≤5 m depth at both sites, decline to non-detectable levels at intermediate depths, and return to values that are almost as high at 17–19 m depth at Site B and 24–26 m at Site F (Fig. 1c–d). In contrast, concentrations of the sewage biomarker coprostanol remained below detection to a depth of 10 m at Site B and to 24 m at Site F, respectively. Coprostanol concentrations of 0.5 ng/g or higher were measured in four intervals between 12 and 18 m depth at Site B, and at 26 m at Site F.

The sewage index ([5β-coprostanol]/([5α-cholestanol] + [5β-coprostanol]) is a commonly used measure to determine the presence, extent and distribution of fecal/sewage contamination (Bull et al., 2002; Martins et al., 2011; Reeves and Patton, 2005; Vane et al., 2010). At 12–19 m depth at Site B and 24–26 m depth at Site F, this ratio is >0.7 and provides a clear indication of human/livestock waste input to the sediment (Bull et al., 2002; Martins et al., 2011; Vane et al., 2010).

3.2. Profiles of Cl and Br in groundwater

At depths >50 m, concentrations of Cl in groundwater at Site F are about twenty times higher than at Site B. However ratios of Cl/Br (278 ± 40) in groundwater from these deeper well depths are comparable at both sites. In contrast, Cl concentrations in the shallow aquifer are up to an order of magnitude higher than at depth at Site B (Fig. 2). The higher Cl concentrations are paired with particularly high Cl/Br ratios (1528 ± 719, n = 157). There were several outliers at Site B between April and October 2005 (n = 6) indicating input from an unidentified dilute bromide source at 11.6 m depth. This temporarily increased the Cl/Br mass ratio to ~97,300 (Fig. A4a and A4b). Considered an anomaly, they were excluded from average concentrations reported above for Site B. At Site F, Cl concentrations in the shallow aquifer are lower than in the shallow aquifer at Site B but Cl/Br ratios (726 ± 636, n = 249) are still elevated compared to deeper groundwater. Binary mixing relationships for Cl/Br as a function of Cl that consider various end members reported in previous studies suggest a significant contribution of human/livestock urine and/or waste throughout the shallow aquifer at Site B and primarily within the 20–25 m depth range at Site F (Fig. 2).

3.3. Profiles of iron and arsenic in groundwater

Consistent profiles of dissolved Fe and As have been monitored for over a decade at Sites B and F (Dhar et al., 2008; Stute et al., 2007). Below the thick clay layer that caps the shallow aquifer at Site B, concentrations of Fe and As in groundwater rapidly increase to maximum values of about 25 mg/L and 500 μg/L in the 15–20 m depth range (Fig. 3). At Site F, where the sandy aquifer extends almost to the surface, concentrations of Fe and As increase with depth as well, but much more gradually and only to 7 mg/L and 200 μg/L, respectively.

The contrast between the two profiles explains the marked difference in the As content of water pumped from private wells, most of which are <50 m deep (Fig. 1). Below 20 m at Site B, the aquifer is interspersed with several relatively thin clay layers and concentrations of Fe and As decline gradually. Even at 55 m depth, however, groundwater As concentrations are still >50 μg/L. At Site F instead, groundwater from the aquifer below the thick layer contains As concentrations <10 μg/L, even if groundwater Fe concentrations remain high at 20 mg/L.

4. Discussion

4.1. Pathways for plant sterols and human/livestock waste

Plant-derived sterols are produced primarily above ground and it is therefore not surprising that their highest concentrations were measured within the upper 5 m of sediment at both sites (Fig. 1c,d) in agreement with the observations of Al Lawati et al. (2013) at a study site in Vietnam. Concentrations of plant-derived sterols were not markedly different in shallow silt/clay at Site B compared to the shallow sandy sediment collected at Site F. At a depth of about 10 m, concentrations of the sterols declined by at least an order of magnitude at both sites. This is not inconsistent with the relatively recalcitrant nature of these

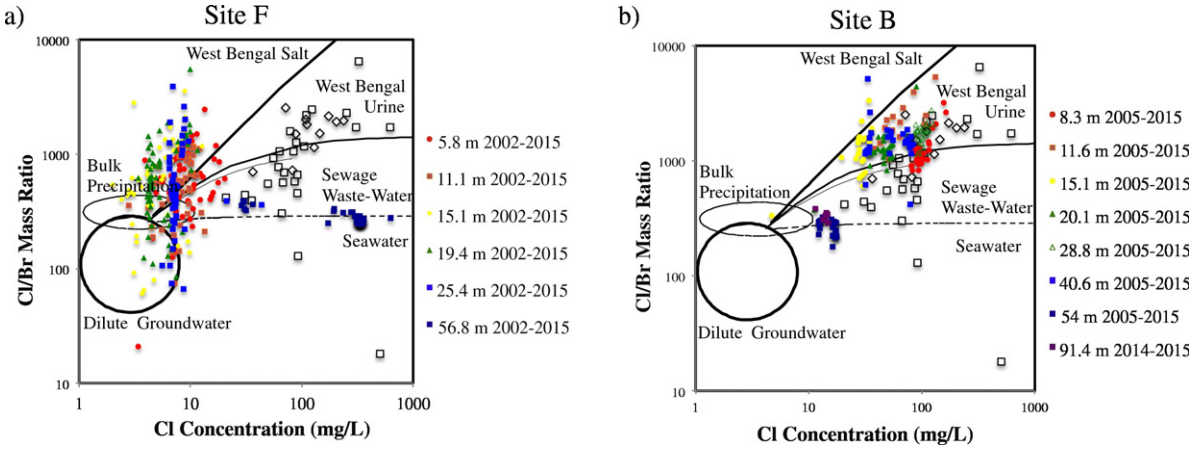

Fig. 2. Groundwater Cl/Br mass ratios and Cl concentrations (mg/L) at (a) Site F: 5.8 to 56.8 m depth in 2002–2015 b) Site B: 8.3 to 91 m depth 2005–2015. Open white square markers are derived from USA septic leachate samples (Panno et al. 2005, 2006), open white diamond markers are septic tank outfall samples measured in the West Bengal, Bangladesh (McArthur et al., 2012). Graphs are modified from Katz et al. (2011) and McArthur et al. (2012) basing binary mixing lines with Cl/Br and Cl concentrations using end members based on literature values for dilute groundwater, bulk precipitation, West Bengal salt, West Bengal urine, sewage waste-water and seawater.

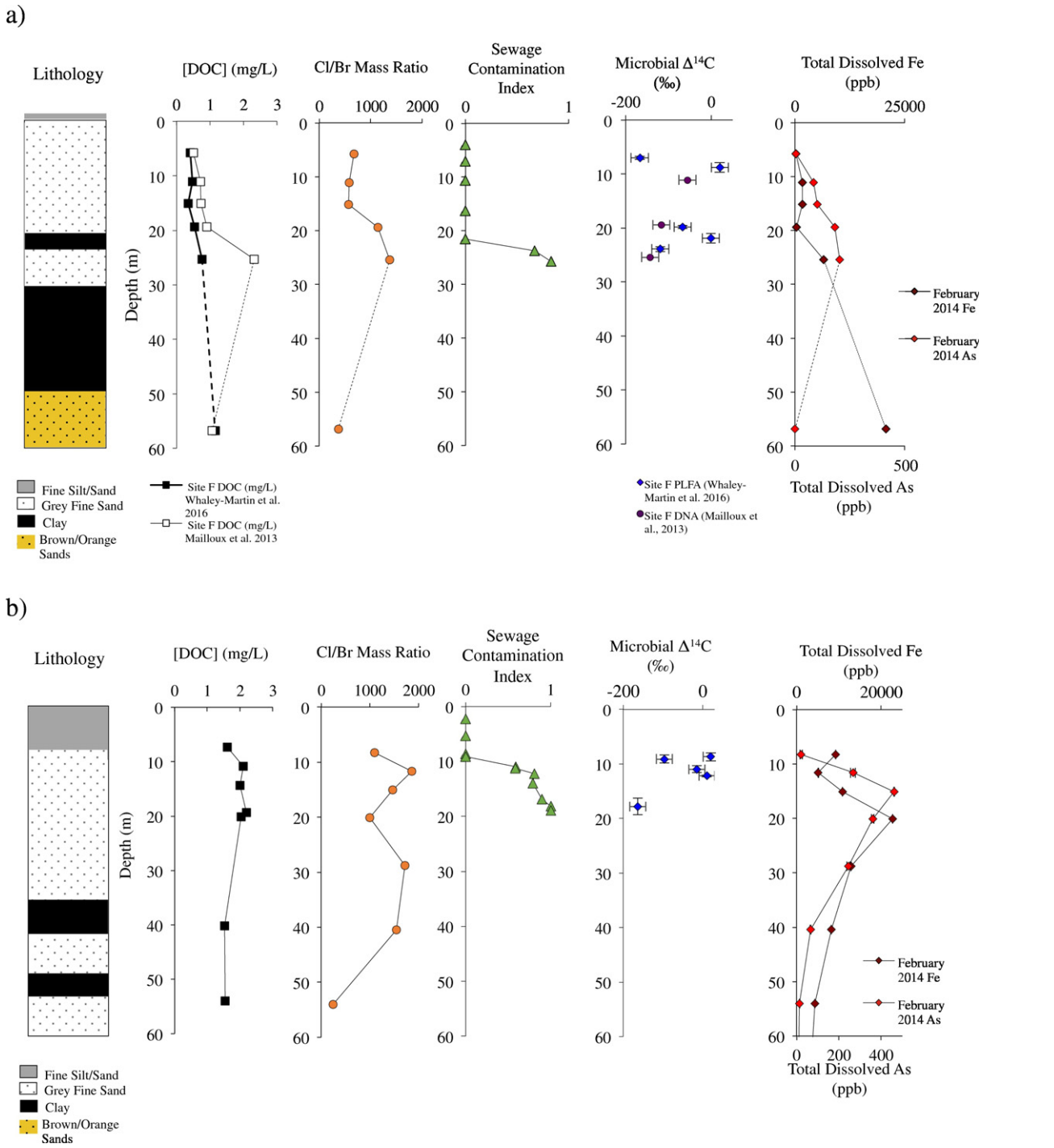

Fig. 3. Biogeochemical depth profiles from 0 to 60 m of a) Site F and b) Site B from available 2013/2014 data for lithology (Dhar et al., 2008), DOC concentrations, Cl/Br mass ratios, sewage contamination indexes, PLFA $\Delta^{14}C$ and total dissolved Fe and As (January to February 2014) in groundwater.

biomarkers, given that radiocarbon dating shows that the sediment at this depth is several thousand years old (Mailloux et al., 2013; Zheng et al., 2005). Perhaps more surprising is a return to higher concentrations of plant-derived sterols below 17 m depth at Site B and below 14 m at Site F. There is no obvious change in the nature of these deposits that could support a sedimentological explanation for a return to higher plant-derived sterol concentrations at depth.

Although coprostanol is also produced by humans and livestock above-ground, it was not detected down to a depth of 11 m at Site B and 22 m at Site F (Fig. 1c,d). This is unexpected given the continued practice of open defecation in South Asia, the very basic nature of the pit latrines, and the abundance of cattle in the study area. The imprint of human activities may be restricted to the very top layer of soil at these sites, which was not sampled. In addition, the shallowest samples were of the lowest mass and therefore had higher limits of detection than deeper samples (Table A2). However, these limits of detection did not prevent successful detection of the phytosterols. Therefore, coprostanol and phytosterols can be assumed to not be co-occurring in similar abundances within the shallowest sediments. Differences in the degradation rates of coprostanol versus the phytosterols (Pratt et al., 2008) could explain the absence of coprostanol in shallower sediments, although this seems unlikely given the similarities in structure

of the sterols. The strikingly higher coprostanol concentrations within the same deeper intervals that contain plant-derived sterols at Sites B and F suggest a common input mechanism to these depths.

There are several possible scenarios that could explain how these sterols are supplied to aquifer sediments in the 10–25 m depth range while bypassing shallower intervals. The first is depositional and invokes surface input by vegetation and the local population and livestock several thousand years ago, followed by the rapid deposition of sediment that was relatively free of plant material and human/livestock waste. This cannot be ruled out given that the Bengal basin has long supported a high population density and is a highly dynamic depositional environment. A large branch of the Brahmaputra River, for instance, is believed to have passed through the area as little as a few hundred years ago (Weinman et al., 2008). Its avulsion undoubtedly perturbed previous sediment erosion and deposition patterns. Under this scenario, the elevated Cl/Br mass ratios in groundwater from 2002 to 2015 at these sites (strongly at Site B), an independent indication of recent input of human/livestock waste to the same depth intervals, would be coincidental.

Another possible explanation is lateral inflow from a shallower area where both plant-derived sterols and human/livestock waste entered the recharge water and were subsequently advected to greater depth. The correlation observed in the underlying sediments between phytosterol and coprostanol distributions would be expected from sewage-derived carbon from animals with omnivorous or herbivorous diets that have both sterol groups within their fecal components (Bull et al., 2002; Leeming et al., 1996) or from plant and sewage matter travelling along similar flow paths. There are several difficulties with this explanation, however. Any migration of the sterols through groundwater movement would be slowed considerably by adsorption. The K_{OW}'s of the sterols in combination with the range of total organic carbon contents estimated in the sediments (Legg et al., 2012) results in calculated soil/solution distribution coefficients ranging from 10^4 to 10^7.These values imply retardation factors of 10^5 to 10^8 relative to conservative constituents of groundwater such as Cl and Br. Tritium-helium dating has shown the groundwater to be 20 and 5 years old relative to the time of recharge at Sites B and F, respectively (Stute et al., 2007). According to this scenario, the accumulation of sterols observed between 10 and 25 m depth would therefore have to reflect an input hundreds of thousands of years ago, which is well before the formation was deposited. However, faster lateral transport rates from potential colloidal flow through the sand units may be occurring since organic phases of sewage discharges have been associated with colloidal transport during heavy rainfall (Eganhouse and Sherblom, 2001). A much shorter flow path through zones of high horizontal conductivity, possibly enhanced by irrigation pumping, cannot be excluded although it would have to be minor fraction of the flow given the gradual increase in groundwater age with depth (Stute et al., 2007).

The third explanation requires a preferential path that leads directly from the surface to the 10–25 m depth intervals where plant and human/livestock sterols have accumulated in the sediment. The large number of tubewells installed in the area may provide such a conduit. A total of 337 wells constructed of PVC pipe, without the use of any grout, were installed within a radius of 500 m of Site B when the most recent survey was conducted in 2012–13 (Fig. 1a,b). The screened intervals of most of these wells span the 10–25 m depth range (Fig. 4). On the basis of the high rate and replacement of household wells (Van Geen et al., 2014), at least a comparable number were previously installed by the same households within the area and abandoned without taking any measures to seal them. Given that the fields surrounding the village are flooded every monsoon and that the village itself is flooded roughly once a decade, transport of plant-derived sterols and human/livestock waste down these wells, or along their annulus, and into the sediment is conceivable. Knappett et al. (2012a, b) also invoked transport along a well's annulus to explain the higher frequency of *E. coli* in groundwater pumped from unsealed wells compared to wells that had been grouted. However, transport of human/livestock waste along a well's annulus would not explain the absence and reappearance of coprostanol at depth. Therefore, organic matter input through the well's screen during flooding may be a more dominant pathway. According to these scenarios, the lower population and well density could possibly explain the generally lower concentrations of sterols at Site F compared to Site B. Generally lower Cl/Br ratios in shallow groundwater at Site F compared to Site B and a broad resemblance to vertical profiles of the sewage contamination index may suggest that the input of a non-adsorbing indicator of human waste such as Cl also occurs predominantly in flooded wells through screens or year-round along a well's annulus.

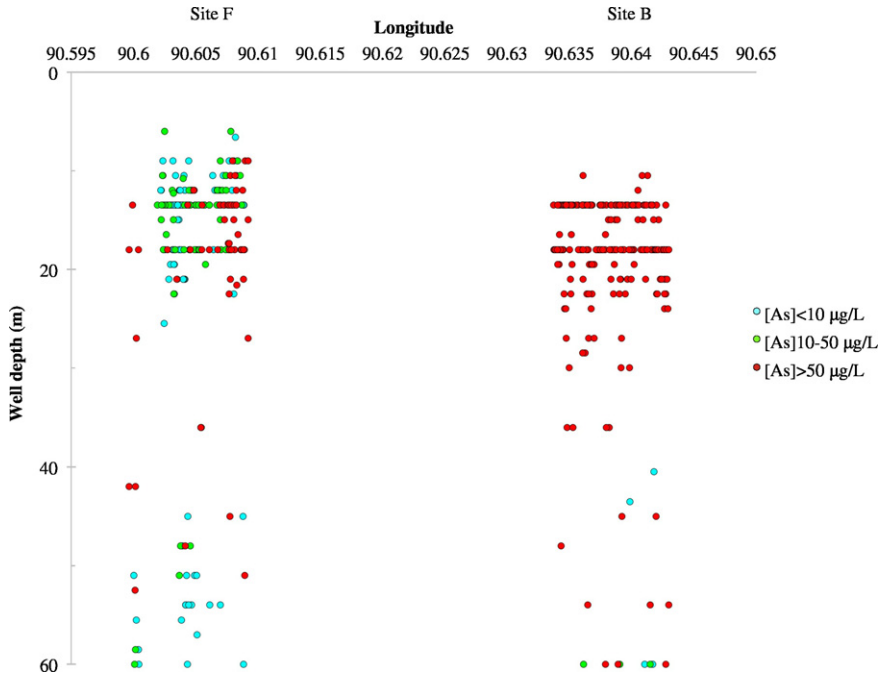

Fig. 4. Longitude, latitude and depths (m) of screening wells and associated groundwater total arsenic concentrations within 500 m of Site F and Site B.

Table 1
Calculated sewage contamination indexes ([5β-coprostanol]/([5α-cholestanol] + [5β-coprostanol])) for each sediment depth at Site B and Site F. Bold values indicate the sewage contamination index was >0.7.

Site B				Site F			
Depth (m)	Sewage contamination index [5β-coprostanol]/([5α-cholestanol] + [5β-coprostanol])	$[As]_{aq}$[a] (μg/L)	$[Fe]_{aq}$[a] (mg/L)	Depth (m)	Sewage contamination index [5β-coprostanol]/([5α-cholestanol] + [5β-coprostanol])	$[As]_{aq}$[a] (μg/L)	$[Fe]_{aq}$[a] (mg/L)
2.3	<LOD	N/A	N/A	4.1	<LOD	N/A	N/A
5.3	<LOD	N/A	N/A	7.1	<LOD	20	0.6
8.7	<LOD	25	8	10.6	<LOD	72	1.4
9.1	<LOD	90	7	16.3	<LOD	130	1.4
11	0.6	245	5	21.6	<LOD	190	2.6
11.3	0.6	255	5	23.7	**0.7**	200	4
12.2	**0.8**	370	6	25.7	**0.8**	205	6.5
14	**0.8**	430	8	–	–	–	–
16.9	**0.9**	420	18	–	–	–	–
18.1	**1**	410	20	–	–	–	–
18.9	**1**	380	21	–	–	–	–

[a] Arsenic and iron concentrations were estimated for each particular sediment depth based on the groundwater depth profiles measured in the 2014–2015 groundwater samples.

4.2. Reactivity of plant and human/livestock waste organic matter

Profiles of the sterol-based sewage contamination index bear a remarkable resemblance to dissolved Fe and As profiles in groundwater at the two study sites, including more pronounced features at Site B compared to Site F (Table 1; Fig. 3). The strong correlations found between the sewage contamination and arsenic concentrations (Fig. A2) support that human/livestock waste may provide the carbon source driving microbially mediated arsenic release at these sites. In addition, the installation of large numbers of tubewells, by providing a pathway for plant- and human/livestock-derived sterols and other organic matter, might enhance the release of As to groundwater in already grey (reduced) Holocene sands. This would create a pathway that appears to shunt sterols including coprostanol (plant and/or sewage), from the surface to aquifers sediments in the 10–25 m depth range. The transport of these sterols and associated DOC components present in the water may enhance the reductive dissolution of Fe oxides and the release of As to groundwater at these depths.

Understanding how the organic nature of human/livestock waste may enhance microbial Fe reduction in Bangladesh aquifers is important to determine whether this mechanism is plausible in these systems. Bangladesh aquifer sediments are oligotrophic containing low carbon and inputs of labile carbon sources has been shown experimentally (Dhar et al., 2011; Islam et al., 2004; Stuckey et al., 2015) to stimulate the in situ sedimentary bacterial communities and ultimately arsenic release. Islam et al. (2004) detected a major shift in the sediment associated community with iron-reducing (*Geobacter*) bacteria increases when a small amounts of carbon (acetate) was added to Bangladesh sediments in a microcosm experiment. Sewage waste-water contains higher proportions of organic compounds (i.e. short-chained fatty acids such as acetate, propionate, and butyrate) (Wong et al., 2006) produced through fermentation in the animal gut that are readily degraded by anaerobic reducing microbial communities (Smith et al., 2008) compared to other sources (i.e. unfermented plant material and recalcitrant sedimentary organic carbon). In agreement with this notion, in a sewage-contaminated aquifer with similar geochemical characteristics to Site F and Site B, ($Fe(OH_3)$ coated mineral grains, circum-neutral pH and anoxic groundwater), Lee and Bennett (1998) reported enhanced reductive dissolution and mobilization of Fe at depth where anaerobic indigenous bacterial communities were utilizing sewage-derived organics as their carbon sources.

Previous work conducted at our two study sites has shown that the microbial community, including presumably the ubiquitous Fe and As reducers, is fueled in large part by relatively young advected carbon (Mailloux et al., 2013; Whaley-Martin et al., 2016). Unlike the microbial radiocarbon ages which show no systematic different between the two sites, the radiocarbon age of DOC in these shallow aquifers is considerably younger at Site B ($\Delta^{14}C_{DOC}$ - 151 ± 25‰) compared to Site F ($\Delta^{14}C_{DOC}$ - 353 ± 40‰) (Whaley-Martin et al., 2016), possibly because of larger contributions of relatively young organic matter. In addition, DOC concentrations are 1.5 times higher and coprostanol concentrations almost 3 times higher at Site B compared to Site F. These observations, while not definitive, suggest that whatever the pathway that shunts sterols, including coprostanol, from the surface to aquifers sediments in the 10–25 m depth range may have implications for As in shallow aquifers and deserves further study.

5. Conclusion

Our new observations from two well-characterized sites in Bangladesh document the supply of plant- and human/livestock-derived organic matter to the depth range where both Fe and As are released to groundwater. The presence of coprostanol, in particular, which can be uniquely traced to the gut of higher animals, suggest the supply of a reactive carbon pool that could potentially stimulate the release of As from aquifers sediments. There is no evidence at the regional scale that such input has led to widespread Fe oxide reduction and As release in similarly populated areas where shallow aquifers are composed of orange Pleistocene sands. This does not mean a supply of reactive carbon associated with human and livestock waste could not potentially enhance the release of As from grey Holocene sediments. Given the indication of the potential role of human/livestock waste, resolving the mechanisms of transport of these sources to depth is a crucial next step.

Acknowledgements

The authors thank M. Rajib Mozumber for providing drill cuttings for sterol analysis. This work was supported by a National Sciences and Engineering Research Council (NSERC) doctoral award to KJW-M, an NSERC Discovery grant to GFS and NIEHS Superfund Research Program grant P42 ES010349. We gratefully acknowledged the helpful insight from three anonymous reviewers. This is a Lamont-Doherty Earth observatory contribution 8103.

Appendix A. Supplementary data

Included in the appendix are aerial photographs of the study sites, the correlational relationship between the sewage contamination index and As concentrations, tables of sedimentary sterol concentrations and groundwater total [As] and [Fe] concentrations. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.scitotenv.2017.03.234.

References

Ahmann, D., Krumholz, L.R., Hemond, H.F., Lovley, D.R., Morel, F.M.M., 1997. Microbial mobilization of arsenic from sediments of the Aberjona watershed. Environ. Sci. Technol. 31:2923–2930. http://dx.doi.org/10.1021/es970124k.

Al Lawati, W.M., Jean, J.S., Kulp, T.R., Lee, M.K., Polya, D.A., Liu, C.C., Van Dongen, B.E., 2013. Characterisation of organic matter associated with groundwater arsenic in reducing aquifers of southwestern Taiwan. J. Hazard. Mater. 262:970–979. http://dx.doi.org/10.1016/j.jhazmat.2012.08.007.

Anawar, H.M., Akai, J., Komaki, K., Terao, H., Yoshioka, T., Ishizuka, T., Safiullah, S., Kato, K., 2003. Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes. J. Geochem. Explor. 77:109–131. http://dx.doi.org/10.1016/S0375-6742(02)00273-X.

Aziz, Z., van Geen, A., Stute, M., Versteeg, R., Horneman, A., Zheng, Y., Goodbred, S., Steckler, M., Weinman, B., Gavrieli, I., Hoque, M.A., Shamsudduha, M., Ahmed, K.M., 2008. Impact of local recharge on arsenic concentrations in shallow aquifers inferred from the electromagnetic conductivity of soils in Araihazar, Bangladesh. Water Resour. Res. 44:1–15. http://dx.doi.org/10.1029/2007WR006000.

Bartlett, P.D., 1987. Degradation of coprostanol in an experimental system. Mar. Pollut. Bull. 18:27–29. http://dx.doi.org/10.1016/0025-326X(87)90653-9.

Biache, C., Philp, R.P., 2013. The use of sterol distributions combined with compound specific isotope analyses as a tool to identify the origin of fecal contamination in rivers. Water Res. 47:1201–1208. http://dx.doi.org/10.1016/j.watres.2012.11.037.

Birk, J.J., Dippold, M., Wiesenberg, G.L.B., Glaser, B., 2012. Combined quantification of faecal sterols, stanols, stanones and bile acids in soils and terrestrial sediments by gas chromatography–mass spectrometry. J. Chromatogr. A 1242:1–10. http://dx.doi.org/10.1016/j.chroma.2012.04.027.

Bull, I.D., Lockheart, M.J., Elhmmali, M.M., Roberts, D.J., Evershed, R.P., 2002. The origin of faeces by means of biomarker detection. Environ. Int. 27:647–654. http://dx.doi.org/10.1016/S0160-4120(01)00124-6.

Burgess, W., Hoque, M., Michael, H., Voss, C., Breit, G., Ahmed, K., 2010. Vulnerability of deep groundwater in the Bengal Aquifer System to contamination by arsenic. Nat. Geosci. 3:83–87. http://dx.doi.org/10.1038/ngeo750.

Cheng, Z., Zheng, Y., Mortlock, R., van Geen, A., 2004. Rapid multi-element analysis of groundwater by high-resolution inductively coupled plasma mass spectrometry. Anal. Bioanal. Chem. 379:512–518. http://dx.doi.org/10.1007/s00216-004-2618-x.

Chikaraishi, Y., Yusuke, Y., Naraoka, H., 2005. Carbon and hydrogen isotopic compositions of sterols from riverine and marine sediments. Limnol. Oceanogr. 50, 1763–1770.

Chou, C.-C., Liu, Y.-P., 2004. Determination of fecal sterols in the sediments of different wastewater outputs by GC–MS. Int. J. Environ. Anal. Chem. 84:379–388. http://dx.doi.org/10.1080/03067310410001680019.

Cummings, D.E., Caccavo, F., Fendorf, S., Rosenzweig, R.F., 1999. Arsenic mobilization by the dissimilatory Fe(III)-reducing bacterium *Shewanella* alga BrY. Environ. Sci. Technol. 33:723–729. http://dx.doi.org/10.1021/es980541c.

Davis, S., Whittemore, D.O., Fabryka-Martin, J., 1998. Uses of chloride/bromide ratios in potable ground water in the United States. Ground Water 36, 338–350.

Desbarats, A.J., Koenig, C.E.M., Pal, T., Mukherjee, P.K., Beckie, R.D., 2014. Groundwater flow dynamics and arsenic source characterization in an aquifer system of West Bengal, India. Water Resour. Res.:4974–5002 http://dx.doi.org/10.1002/2013WR014034. Received.

Dhar, R.K., Zheng, Y., Stute, M., van Geen, A., Cheng, Z., Shanewaz, M., Shamsudduha, M., Hoque, M.A., Rahman, M.W., Ahmed, K.M., 2008. Temporal variability of groundwater chemistry in shallow and deep aquifers of Araihazar, Bangladesh. J. Contam. Hydrol. 99:97–111. http://dx.doi.org/10.1016/j.jconhyd.2008.03.007.

Dhar, R.K., Zheng, Y., Saltikov, C.W., Radloff, K.A., Mailloux, B.J., Ahmed, K.M., van Geen, A., 2011. Microbes enhance mobility of arsenic in Pleistocene aquifer sand from Bangladesh. Environ. Sci. Technol. 45:2648–2654. http://dx.doi.org/10.1021/es1022015.

Dowling, C.B., Poreda, R.J., Basu, A.R., Peters, S.L., Aggarwal, P.K., 2002. Geochemical study of arsenic release mechanisms in the Bengal Basin groundwater. Water Resour. Res. 38:1173. http://dx.doi.org/10.1029/2001WR000968.

Eganhouse, R.P., Sherblom, P.M., 2001. Anthropogenic organic contaminants in the effluent of a combined sewer overflow: impact on boston harbor. Mar. Environ. Res. 51.

Froehner, S., Sánez, J., 2013. Evaluation of potential sewage contamination by fecal sterol biomarkers adsorbed in natural biofilms. Environ. Sci. Process. Impacts 15:2080–2086. http://dx.doi.org/10.1039/c3em00025g.

Furtula, V., Jackson, C.R., Osman, R., Chambers, P.A., 2012. Use of *Enterococcus*, BST and sterols for poultry pollution source tracking in surface and groundwater sterols for poultry pollution source tracking in surface and groundwater. Environmental Health: Emerging Issues and Practice, pp. 57–78.

van Geen, A., Ahmed, K.M., Akita, Y., Alam, M.J., Culligan, P.J., Emch, M., Escamilla, V., Feighery, J., Ferguson, A.S., Knappett, P., Layton, A.C., Mailloux, B.J., McKay, L.D., Mey, J.L., Serre, M.L., Streatfield, P.K., Wu, J., Yunus, M., 2011. Fecal contamination of shallow tubewells in Bangladesh inversely related to arsenic. Environ. Sci. Technol. 45:1199–1205. http://dx.doi.org/10.1021/es103192b.

van Geen, A., Bostick, B.C., Thi, K.T., Lan, V.M., Mai, N.-N., Manh, P.D., Viet, P.H., Radloff, K., Aziz, Z., Mey, J.L., Stahl, M.O., Harvey, C.F., Oates, P., Weinman, B., Stengel, C., Frei, F., Kipfer, R., Berg, M., 2013. Retardation of arsenic transport through a Pleistocene aquifer. Nature 501, 204–207.

Harvey, C.F., Swartz, C.H., Badruzzaman, A.B.M., Keon-Blute, N., Yu, W., Ali, M.A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P.M., Ashfaque, K.N., Islam, S., Hemond, H.F., Ahmed, M.F., 2002. Arsenic mobility and groundwater extraction in Bangladesh. Science (80-.) 298:1602–1606. http://dx.doi.org/10.1126/science.1076978.

Hussain, M.A., Ford, R., Hill, J., 2010. Determination of fecal contamination indicator sterols in an Australian water supply system. Environ. Monit. Assess. 165:147–157. http://dx.doi.org/10.1007/s10661-009-0934-5.

Islam, M., Rahman, M., 2010. Changes in wetlands in Dhaka City: trends and physico-environmental consequences. J. Life Earth Sci. 5, 37–42.

Islam, F.S., Gault, A.G., Boothman, C., Polya, D.A., Charnock, J.M., Chatterjee, D., Lloyd, J.R., 2004. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. Nature 430, 68–71.

Katz, B.G., Eberts, S.M., Kauffman, L.J., 2011. 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. J. Hydrol. 397:151–166. http://dx.doi.org/10.1016/j.jhydrol.2010.11.017.

Knappett, P.S.K., Mckay, L.D., Layton, A., Williams, D.E., Alam, J., Huq, R., Mey, J., Feighery, J.E., Culligan, P.J., Mailloux, B.J., Escamilla, V., Emch, M., Perfect, E., Sayler, G.S., Ahmed, M., Geen, A.Van, 2012a. Implications of fecal bacteria input from latrine-polluted ponds for wells in Sandy aquifers. Environ. Sci. 46:1361–1370. http://dx.doi.org/10.1021/es202773w.

Knappett, P., Escamilla, V., Layton, A., McKay, L., Emch, M., Williams, D.E., Huq, R., Alam, J., Farhana, L., Mailloux, B., Ferguson, A., Sayler, G.S., Ahmed, K.M., van Geen, A., 2012b. Impact of population and latrines on fecal contamination of ponds in rural Bangladesh. Science of the Total Environment 409:3174–3182. http://dx.doi.org/10.1016/j.scitotenv.2011.04.043.

Lawson, M., Ichael, Polya, D.A., Boyce, A.J., Bryant, C., Mondal, D., Shantz, A., Ballentine, C.J., 2013. Pond-derived organic carbon driving changes in arsenic hazard found in Asian groundwaters. Environ. Sci. Technol. 47:7085–7094. http://dx.doi.org/10.1021/es400114q.

Leber, J., Rahman, M., Ahmed, K.M., Mailloux, B., van Geen, A., 2011. Contrasting influence of geology on *E. coli* and arsenic in aquifers of Bangladesh. Ground Water 49:111–123. http://dx.doi.org/10.1111/j.1745-6584.2010.00689.x.

Lee, Roger W., Bennett, P., 1998. Reductive dissolution and reactive solute transport in a sewage-contaminated glacial outwash aquifer. Ground Water 36, 583–595.

Lee, H.J., Hong, S.H., Kim, M., Ha, S.Y., An, S.M., Shim, W.J., 2011. Tracing origins of sewage and organic matter using dissolved sterols in Masan and Haengam Bay, Korea. Ocean Sci. J. 46:95–103. http://dx.doi.org/10.1007/s12601-011-0009-8.

Leeming, R., Ball, A., Ashbolt, N., Nichols, P., 1996. Using faecal sterols from humans and animals to distinguish faecal pollution in receiving waters. Water Res. 30:2893–2900. http://dx.doi.org/10.1016/S0043-1354(96)00011-5.

Legg, T.M., Zheng, Y., Simone, B., Radloff, K.A., Mladenov, N., Gonzalez, A., Knights, D., Siu, H.C., Rahman, M.M., Ahmed, K.M., McKnight, D.M., Nemergut, D.R., 2012. Carbon, metals, and grain size correlate with bacterial community structure in sediments of a high arsenic aquifer. Front. Microbiol. 3:82. http://dx.doi.org/10.3389/fmicb.2012.00082.

Mailloux, B.J., Trembath-Reichert, E., Cheung, J., Watson, M., Stute, M., Freyer, G.A., Ferguson, A.S., Ahmed, K.M., Alam, M.J., Buchholz, B.A., Thomas, J., Layton, A.C., Zheng, Y., Bostick, B.C., van Geen, A., 2013. Advection of surface-derived organic carbon fuels microbial reduction in Bangladesh groundwater. Proc. Natl. Acad. Sci. U. S. A. 110:5331–5335. http://dx.doi.org/10.1073/pnas.1213141110.

Marcos, J., Pozo, O.J., 2015. Derivatization of steroids in biological samples for GC–MS and LC–MS analyses. Bioanalysis 7, 2515–2536.

Martins, C.C., Seyffert, B.H., Braun, J.A.F., Fillmann, G., 2011. Input of organic matter in a large South American tropical estuary (Paranaguá estuarine system, Brazil) indicated by sedimentary sterols and multivariate statistical approach. J. Braz. Chem. Soc. 22:1585–1594. http://dx.doi.org/10.1590/S0103-50532011000800023.

McArthur, J.M., Ravenscroft, P., Safiulla, S., Thirlwall, M.F., 2001. Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh. Water Resour. Res. 37:109–117. http://dx.doi.org/10.1029/2000WR900270.

McArthur, J.M., Banerjee, D.M., Hudson-Edwards, K.A., Mishra, R., Purohit, R., Ravenscroft, P., Cronin, A., Howarth, R.J., Chatterjee, A., Talukder, T., Lowry, D., Houghton, S., Chadha, D.K., 2004. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. Appl. Geochem. 19:1255–1293. http://dx.doi.org/10.1016/j.apgeochem.2004.02.001.

McArthur, J.M., Sikdar, P.K., Hoque, M.A., Ghosal, U., 2012. 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. 437:390–402. http://dx.doi.org/10.1016/j.scitotenv.2012.07.068.

Meharg, A.A., Rahman, M., 2003. Arsenic contamination of Bangladesh paddy field soils: implications for rice contribution to arsenic consumption. Environ. Sci. Technol. 37:229–234. http://dx.doi.org/10.1021/es0259842.

Meharg, A.a., Scrimgeour, C., Hossain, S.A., Fuller, K., Cruickshank, K., Williams, P.N., Kinniburgh, D.G., 2006. Codeposition of organic carbon and arsenic in Bengal Delta aquifers. Environ. Sci. Technol. 40:4928–4935. http://dx.doi.org/10.1021/es060722b.

Michael, H.A., Voss, C.I., 2008. Evaluation of the sustainability of deep groundwater as an arsenic-safe resource in the Bengal Basin. Proc. Natl. Acad. Sci. U. S. A. 105:8531–8536. http://dx.doi.org/10.1073/pnas.0710477105.

Mladenov, N., Zheng, Y., Miller, M.P., Nemergut, D.R., Legg, T., Simone, B., Hageman, C., Rahman, M.M., Ahmed, K.M., Mcknight, D.M., 2010. Dissolved organic matter sources and consequences for iron and arsenic mobilization in Bangladesh aquifers. Environ. Sci. Technol. 44:123–128. http://dx.doi.org/10.1021/es901472g.

Neumann, R.B., Ashfaque, K.N., Badruzzaman, A.B.M., Ashraf Ali, M., Shoemaker, J.K., Harvey, C.F., 2010. Anthropogenic influences on groundwater arsenic concentrations in Bangladesh. Nat. Geosci. 3:46–52. http://dx.doi.org/10.1038/ngeo685.

Neumann, R.B., Pracht, L.E., Polizzotto, M.L., Badruzzaman, A.B., Ali, M.A., 2014. Biodegradable organic carbon in sediments of an arsenic-contaminated aquifer in Bangladesh. Environ. Sci. Technol. Lett. 1:221–225. http://dx.doi.org/10.1021/ez5000644.

Nickson, R., McArthur, J., Burgess, W., Ahmed, K.M., Ravenscroft, P., Rahmann, M., 1998. Arsenic poisoning of Bangladesh groundwater. Nature 395, 338.

Nickson, R.T., McArthur, J.M., Ravenscroft, P., Burgess, W.G., Ahmed, K.M., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Appl. Geochem. 15:403–413. http://dx.doi.org.libaccess.lib.mcmaster.ca/10.1016/S0883-2927(99)00086-4.

Nishimura, M., Koyama, T., 1977. The occurrence of stanols in various living organisms and the behavior of sterols in contemporary sediments. Geochim. Cosmochim. Acta 41:379–385. http://dx.doi.org/10.1016/0016-7037(77)90265-4.

Panno, S., Hackley, K., Hwang, H., Greenberg, S., Krapac, I., Landsberger, S., 2005. Database for the characterization and identification of sources of sodium and chloride in natural waters of Illinois. Open File Ser. 1, 15.

Panno, S.V., Hackley, K.C., Hwang, H.H., Greenberg, S.E., Krapac, I.G., Landsberger, S., O'Kelly, 2006. Characterization and identification of na-cl sources in ground water. Ground Water 44:176–187. http://dx.doi.org/10.1111/j.1745-6584.2005.00127.x.

Planer-Friedrich, B., Härtig, C., Lissner, H., Steinborn, J., Süß, E., Qumrul Hassan, M., Zahid, A., Alam, M., Merkel, B., 2012. Organic carbon mobilization in a Bangladesh aquifer explained by seasonal monsoon-driven storativity changes. Appl. Geochem. 27: 2324–2334. http://dx.doi.org/10.1016/j.apgeochem.2012.08.005.

Polizzotto, M.L., Kocar, B.D., Benner, S.G., Sampson, M., Fendorf, S., 2008. Near-surface wetland sediments as a source of arsenic release to ground water in Asia. Nature 454:505–508. http://dx.doi.org/10.1038/nature07093.

Postma, D., Larsen, F., Minh Hue, N.T., Duc, M.T., Viet, P.H., Nhan, P.Q., Jessen, S., 2007. Arsenic in groundwater of the Red River floodplain, Vietnam: controlling geochemical processes and reactive transport modeling. Geochim. Cosmochim. Acta 71, 5054–5071.

Postma, D., Larsen, F., Thai, N.T., Trang, P.T.K., Jakobsen, R., Nhan, P.Q., Long, T.V., Viet, P.H., Murray, A.S., 2012. Groundwater arsenic concentrations in Vietnam controlled by sediment age. Nat. Geosci. 5, 656–661.

Pratt, C., Warnken, J., Leeming, R., Arthur, M.J., Grice, D.I., 2008. Degradation and responses of coprostanol and selected sterol biomarkers in sediments to a simulated major sewage pollution event: a microcosm experiment under sub-tropical estuarine conditions. Org. Geochem. 39:353–369. http://dx.doi.org/10.1016/j.orggeochem.2007.06.009.

Rahaman, U., 2012. GIS Based Mapping and Environmental Impact of Wetlands Changes in a Riverine District of Bangladesh. 3 pp. 321–338.

Ravenscroft, P., McArthur, J., Hoque, B., 2001. Geochemical and palaeohydrological controls on pollution of groundwater by arsenic. In: Chappell, W.R., Abernathy, C.O., Calderon, R. (Eds.), Arsenic Exposure and Health Effects IV, pp. 1–20.

Reeves, A., Patton, D., 2005. Faecal sterols as indicators of sewage contamination in estuarine sediments of the Tay Estuary, Scotland: an extended baseline survey. Hydrol. Earth Syst. Sci. 9:81–94. http://dx.doi.org/10.5194/hess-9-81-2005.

Smith, M.T.E., Smernik, R.J., Merrington, G., Tibbett, M., 2008. Changes in sewage sludge carbon forms along a treatment stream. Chemosphere 72:981–985. http://dx.doi.org/10.1016/j.chemosphere.2008.02.062.

Stuckey, J.W., Schaefer, M.V., Kocar, B.D., Benner, S.G., Fendorf, S., 2015. Arsenic release metabolically limited to permanently water-saturated soil in Mekong Delta. Nat. Geosci. 8:1–9. http://dx.doi.org/10.1038/NGEO2589.

Stute, M., Zheng, Y., Schlosser, P., Horneman, A., Dhar, R.K., Datta, S., Hoque, M.A., Seddique, A.A., Shamsudduha, M., Ahmed, K.M., van Geen, A., 2007. Hydrological control of As concentrations in Bangladesh groundwater. Water Resour. Res. 43, W09417. http://dx.doi.org/10.1029/2005WR004499.

Swartz, C.H., Blute, N.K., Badruzzman, B., Ali, A., Brabander, D., Jay, J., Besancon, J., Islam, S., Hemond, H.F., Harvey, C.F., 2004. Mobility of arsenic in a Bangladesh aquifer: inferences from geochemical profiles, leaching data, and mineralogical characterization. Geochim. Cosmochim. Acta 68:4539–4557. http://dx.doi.org/10.1016/j.gca.2004.04.020.

Tolosa, I., Fiorini, S., Gasser, B., Martín, J., Miquel, J.C., 2013. Carbon sources in suspended particles and surface sediments from the Beaufort Sea revealed by molecular lipid biomarkers and compound-specific isotope analysis. Biogeosciences 10:2061–2087. http://dx.doi.org/10.5194/bg-10-2061-2013.

Tse, T.J., Codling, G., Jones, P.D., Thoms, K., Liber, K., Giesy, J.P., Wheater, H., Doig, L.E., 2014. Reconstructing long-term trends in municipal sewage discharge into a small lake in northern Manitoba, Canada. Chemosphere 103:299–305. http://dx.doi.org/10.1016/j.chemosphere.2013.12.019.

Van Geen, A., Ahmed, E.B., Pitcher, L., Mey, J.L., Ahsan, H., Graziano, J.H., Ahmed, K.M., 2014. Comparison of two blanket surveys of arsenic in tubewells conducted 12 years apart in a 25 km^2 area of Bangladesh. Sci. Total Environ. 488–489: 484–492. http://dx.doi.org/10.1016/j.scitotenv.2013.12.049.

Vane, C.H., Kim, A.W., McGowan, S., Leng, M.J., Heaton, T.H.E., Kendrick, C.P., Coombs, P., Yang, H., Swann, G.E.A., 2010. Sedimentary records of sewage pollution using faecal markers in contrasting peri-urban shallow lakes. Sci. Total Environ. 409:345–356. http://dx.doi.org/10.1016/j.scitotenv.2010.09.033.

Weinman, B., Goodbred, S.L., Zheng, Y., Aziz, Z., Steckler, M., van Geen, A., Singhvi, Ashok K., Nagar, Y.C., 2008. Contributions of floodplain stratigraphy and evolution to the spatial patterns of groundwater arsenic in Araihazar, Bangladesh. Bull. Geol. Soc. Am. 120:1567–1580. http://dx.doi.org/10.1130/B26209.1.

Whaley-Martin, K.J., Mailloux, B., van Geen, A., Bostick, B.C., Silvern, R.F., Kim, C., Ahmed, K.M., Choudhury, I., Slater, G.F., 2016. Stimulation of microbially-mediated arsenic release in Bangladesh aquifers by young carbon indicated by radiocarbon analysis of bacterial lipids. Environ. Sci. Technol. 50, 7353–7363.

Wong, J.M., de Souza, R., Kendall, C.W., Emam, A., Jenkins, D.J., 2006. Colonic health: fermentation and short chain fatty acids. J. Clin. Gastroenterol. 40, 235–243 (doi: 00004836-200603000-00015 [pii]).

Yamazaki, C., Ishiga, H., Ahmed, F., Itoh, K., Suyama, K., Yamamoto, H., 2003. Vertical distribution of arsenic in ganges delta sediments in Deuli Village, Bangladesh. Soil Sci. Plant Nutr. 49:567–574. http://dx.doi.org/10.1080/00380768.2003.10410046.

Zheng, Y., van Geen, A., Stute, M., Dhar, R., Mo, Z., Cheng, Z., Horneman, A., Gavrieli, I., Simpson, H.J., Versteeg, R., Steckler, M., Grazioli-Venier, A., Goodbred, S., Shahnewaz, M., Shamsudduha, M., Hoque, M.A., Ahmed, K.M., 2005. Geochemical and hydrogeological contrasts between shallow and deeper aquifers in two villages of Araihazar, Bangladesh: implications for deeper aquifers as drinking water sources. Geochim. Cosmochim. Acta 69:5203–5218. http://dx.doi.org/10.1016/j.gca.2005.06.001.