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

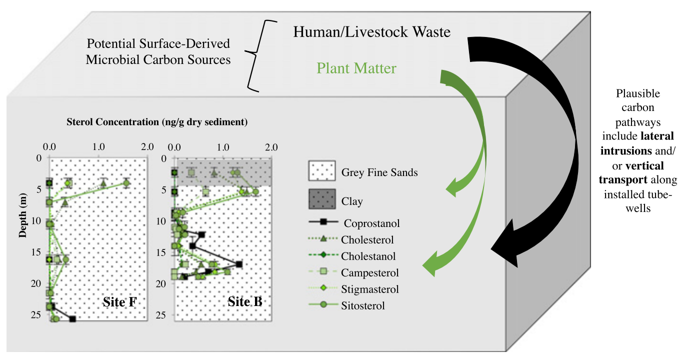
K.J. Whaley-Martin [a], B.J. Mailloux [b], A. van Geen [c], B.C. Bostick [c], K.M. Ahmed [d], I. Choudhury [d], G.F. Slater [a,*]

[a] School of Geography and Earth Sciences, McMaster University, ON, Canada
[b] Environmental Sciences Department, Barnard College, NY, NY 10027, USA
[c] Lamont-Doherty Earth Observatory, Columbia University, Palisides, NY 10964, USA
[d] Department of Geology, University of Dhaka, Dhaka 1000, Bangladesh

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.

* Corresponding author.
E-mail addresses: martikjw@mcmaster.ca (K.J. Whaley-Martin), bmaillou@barnard.edu (B.J. Mailloux), avangeen@ldeo.columbia.edu (A. van Geen), bostick@ldeo.columbia.edu (B.C. Bostick), kmahmed@du.ac.bd (K.M. Ahmed), gslater@mcmaster.ca (G.F. Slater).

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