Redox trapping of groundwater arsenic through hyporheic zone in the Ganges-Brahmaputra-Meghna Delta

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Groundwater arsenic mobilization in GBMD

Mobilization mechanism

Reductive dissolution of Fe oxides containing arsenic

BGS & DPHE (2001)

Fendorf et al (2010, Science)
Redox trapping of groundwater As along Meghna river at regional scale

Bulk As concentrations of surface sediment averaged 16±7 mg/kg (n=9), while subsurface sediment (1-3 m depth) contained higher mean concentrations of As of 4,000 mg/kg (n=14), with > 100 mg/kg As measured at 8 sites and maximum 23,000 mg/kg As.
Hydrological processes in GBMD

Rainy season

- River
- Flood plain

Dry season

- River
- Flood plain

Oxic condition
Low Fe and As

Reducing condition
High Fe and As

BGS & DPHE (2001)
The Hyporheic Zone

A critical interface between groundwater and surface water environments: Because of mixing between groundwater and surface water, the chemical and biological character of the hyporheic zone may differ markedly from adjacent surface water and groundwater.

The hyporheic zone regulates sediment respiration rates, attenuate metals and nutrients, influence riparian vegetation regimes and ecological health.

Charette and Sholkovitz (2002, GRL)

USGS (1998)
Objectives

1. To investigate the coupled hydrological and geochemical processes controlling the redox trapping of groundwater As in the hyporheic zones of Meghna River of the GBMD.

2. To understand the hydrogeochemical processes regulating the groundwater discharge fluxes of As and other reactive elements.
Sampling locations for water and sediment cores

[Map showing sampling locations for water and sediment cores, with markers indicating different concentrations of arsenic (As) in groundwater (< 25 m, n=743).]

- **[As] in Ground water (< 25 m, n=743)**
  - Blue: <1 to <50 µg/L
  - Red: 50 to < 100 µg/L
  - Black: 100 to 1090 µg/L

Site S: RS-16, 17, 30, 31, 32, 33

Site J: RS-19, 20, 21, 34, 35

PZ5-PZ11

Seepage meters

[Monitoring Well (Mun002)]
Water Sampling

Sampling took place between Jan. 17 and Jan 25, 2006 and between Oct. 27 and Nov. 4, 2007. Four types of aqueous samples were collected: groundwater (n=22), riverbank pore water (very shallow groundwater, n=43), seepage water (n=5), and river water (n=9).

Groundwater: Groundwater samples were collected from shallow tube wells with depth ranging between 14 and 24 m in villages located within ~10 km and ~1 km from the riverbank sampling sites in Jan. 2006 (n=11) and Oct.-Nov. 2007 (n=11), respectively.

Riverbank sediment pore water: Pore water samples were collected at ~1-6 m depth using a “needle sampler” in Jan. 2006 and by a drive point piezometer system in Oct.-Nov. 2007.

Seepage water: Discharging groundwater (n=5) was collected in a thin-walled plastic bag attached to a seepage meter through a quick-connect fitting.

Sediment Cores Sampling

Between January 17 and 25 in 2006, a total of 13 riverbank sediments cores were obtained from the surface to 7 m depth at 5 locations. The cores were retrieved by a soil recovery probe (AMS Inc., USA) consisting of a probe (1.9 cm diameter and 30.5 cm length), extension rods (60 cm each section), and a slide hammer.
Hydrographs of groundwater table and river stage & groundwater discharge rate by seepage meter measurement

A

Well (MUN002)
River (SW275-5)

Water level (m)

12/10/02 6/28/03 1/14/04 8/1/04 2/17/05 9/5/05 3/24/06

B

Groundwater discharge rate (m/y)

N = 3
N = 5
N = 6
N = 5

Oct 31-2007
Nov 2-2007
Nov 3-2007
Nov 4-2007

USGS (1998)
## Average chemical composition of four types of water samples in Gazaria Upazila, Bangladesh

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<th>Sample type</th>
<th>Sampling</th>
<th>Number of</th>
<th>Depth</th>
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<th>DO</th>
<th>pH</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
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</table>
Depth profiles of chemical properties of Meghna Riverbank pore water
Depth profiles of sediment properties for the Meghna Riverbank sediment in Gazaria, Bangladesh

Site S

Site J

RS14 & RS15
Effect of surface layer grain size on groundwater As immobilization

A: Sandy riverbank

Meghna River

Rainy season

Reactive barrier

Dry season

Oxic-suboxic zone

Reducing zone

High groundwater discharge rate

B: Silt-clay riverbank

Meghna River

Rainy season

Dry season

No reactive barrier

Reducing zone (Silt-clay)

Reducing zone (sand)

Low groundwater discharge rate
Fe mineralogy and As speciation by X-ray absorption spectroscopy

Fe mineralogy of oxic-suboxic sediments shows the predominance of ferrihydrite or poorly crystalline goethite (49±8% of Fe minerals), as well as high quantity of Fe(II) mineral ((26±5%; fit as siderite) and iron silicates (22 ± 6%; fit as biotite), are also present in the samples.
The arsenic enrichment zone spans a length of 10-15 m horizontally from the river shore but is only 5-20 cm thick vertically.
Redox Oscillation of the Natural Reactive Barrier

![Graphs showing sedimentary iron (III) and arsenic concentrations at different depths (0-2 m, 2-5 m, 5-7 m) and different sites (Site S, Site J). The graphs illustrate the variation in dissolved iron and arsenic concentrations as a function of depth and site. The sedimentary iron (III) and arsenic concentrations are depicted with various markers, indicating different depth intervals and sites. The color bar indicates the redox conditions, with oxic or suboxic on the left and reducing or suboxic on the right.](image-url)
Concentrations of A, P, Mn, and SO$_4$ vs. that of Fe for the Meghna Riverbank pore waters
Chemical fluxes to the ocean via Meghna River by groundwater discharge

Table 6. Estimated groundwater flux of select trace metals from the Ganges-Brahmaputra river floodplain.

<table>
<thead>
<tr>
<th>Select trace metals</th>
<th>Mn</th>
<th>Ni</th>
<th>Zn</th>
<th>As</th>
<th>Ag</th>
<th>Pb</th>
<th>U</th>
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</thead>
<tbody>
<tr>
<td>Groundwater average (μmol/L)</td>
<td>10.546</td>
<td>0.033</td>
<td>3.531</td>
<td>2.239</td>
<td>0.004</td>
<td>0.011</td>
<td>0.005</td>
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<tr>
<td>Submarine discharge (mol/yr)</td>
<td>1.6 × 10⁹</td>
<td>5.0 × 10⁶</td>
<td>5.3 × 10⁸</td>
<td>3.4 × 10⁸</td>
<td>5.3 × 10⁵</td>
<td>1.7 × 10⁶</td>
<td>6.8 × 10⁵</td>
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<tr>
<td>Ocean average (mol)</td>
<td>7 × 10¹²</td>
<td>1.1 × 10¹³</td>
<td>8.4 × 10¹²</td>
<td>3.2 × 10¹³</td>
<td>3.5 × 10¹⁰</td>
<td>1.4 × 10¹⁰</td>
<td>1.8 × 10¹³</td>
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<tr>
<td>Present τ in the ocean (yr)</td>
<td>1.3 × 10³</td>
<td>8.2 × 10³</td>
<td>5.1 × 10²</td>
<td>3.9 × 10³</td>
<td>3.5 × 10²</td>
<td>8.1 × 10³</td>
<td>5 × 10³</td>
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<tr>
<td>Percentage of submarine flux (%)</td>
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<td>0.4</td>
<td>3.2</td>
<td>40.7</td>
<td>0.5</td>
<td>1.0</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Dowling et al (2003, GCA)

Dissolved Si as a conservative tracer
The reducing pore water (2-5 m depth) = 22.7 mg/L, River water = 3.9 mg/L, the oxic-suboxic pore water = 8.9 mg/L.
Mixing ratio = 73% river water + 27% reducing pore water

Total annual groundwater discharge of 7.8×10⁹ m³ y⁻¹ along the Meghna River was estimated based on the Meghna River’s base flow (~500 m³/s) during the dry season (BGS & DPHE, 2001)
Estimation of As trapping history

Assumption

Natural reactive barrier thickness: 10 cm; Groundwater flow rate: 10 m/y
Porosity: 25%; dry bulk mass density = 2.0 g/cm³

Velocity of the solute front
= groundwater flow velocity / [1+ dry bulk mass density/porosity)*Kd]

Kd (Partitioning coefficient) = Mass of adsorbate sorbed / Mass of adsorbate in solution

Kd of reducing Holocene aquifer = ~1-4 (van Geen et al., 2008; Jung et al., 2012)

Mobilization and immobilization processes of groundwater As have been occurring naturally before the system was highly modified by extensive groundwater pumping since 1970~80s.
Remobilization of As from Meghna riverbank sediment

Type I: nanopure water + kanamycin (50 mg/L); Type II: artificial groundwater + kanamycin (50 mg/L); Type III: artificial groundwater; Type IV: artificial groundwater + lactate (1 mM).

Jung et al (2012, EST)
Environmental Implications for arsenic recycling


USGS (1998)

Fendorf et al (2010)
Conclusions

1. Enrichment of sediment As up to ~700 mg/kg occurs along the sandy riverbank at about 0-2 m depth where a redox transition zone exists.

2. Depth profiles of riverbank pore water indicate that dissolved Fe (11.6±11.7 mg L⁻¹) and As (118±91 μg/L, mostly as arsenite) are elevated between 2-5 m depth where the reduction of Fe(III), Mn(IV) and sulfate prevails.

3. Dissolved Fe and As concentrations are low between 0-2 m depth (0.13±0.19 mg/L Fe, 1±1 μg/L As) and between 5-6 m depth (1.14±0.45 mg/L Fe, 28±17 μg/L As) where oxidation of sulfide, as well as denitrification or oxidation of ammonia occur.

4. Neither distinct redox transition zone nor As enrichment zone was identified from sediment depth profiles (n=2) with silt-clay surface layer where hydrological mixing between groundwater and river water is limited.

5. The time scale required to form As-enriched sediments along the Meghna Riverbank is estimated to be approximately 350 to 1300 years. This suggests that groundwater As has been naturally elevated prior to anthropogenic perturbation of GBMD aquifer by extensive well pumping.

6. Coupled hydrological and geochemical processes in the redox transition zone of GBMD not only diminish groundwater As discharge and retains As in the riverbank sediment to allow a source of “recycled” arsenic to aquifer on a centennial to millennial time scale, but also attenuate chemical fluxes of reactive elements discharged to the river or the ocean.