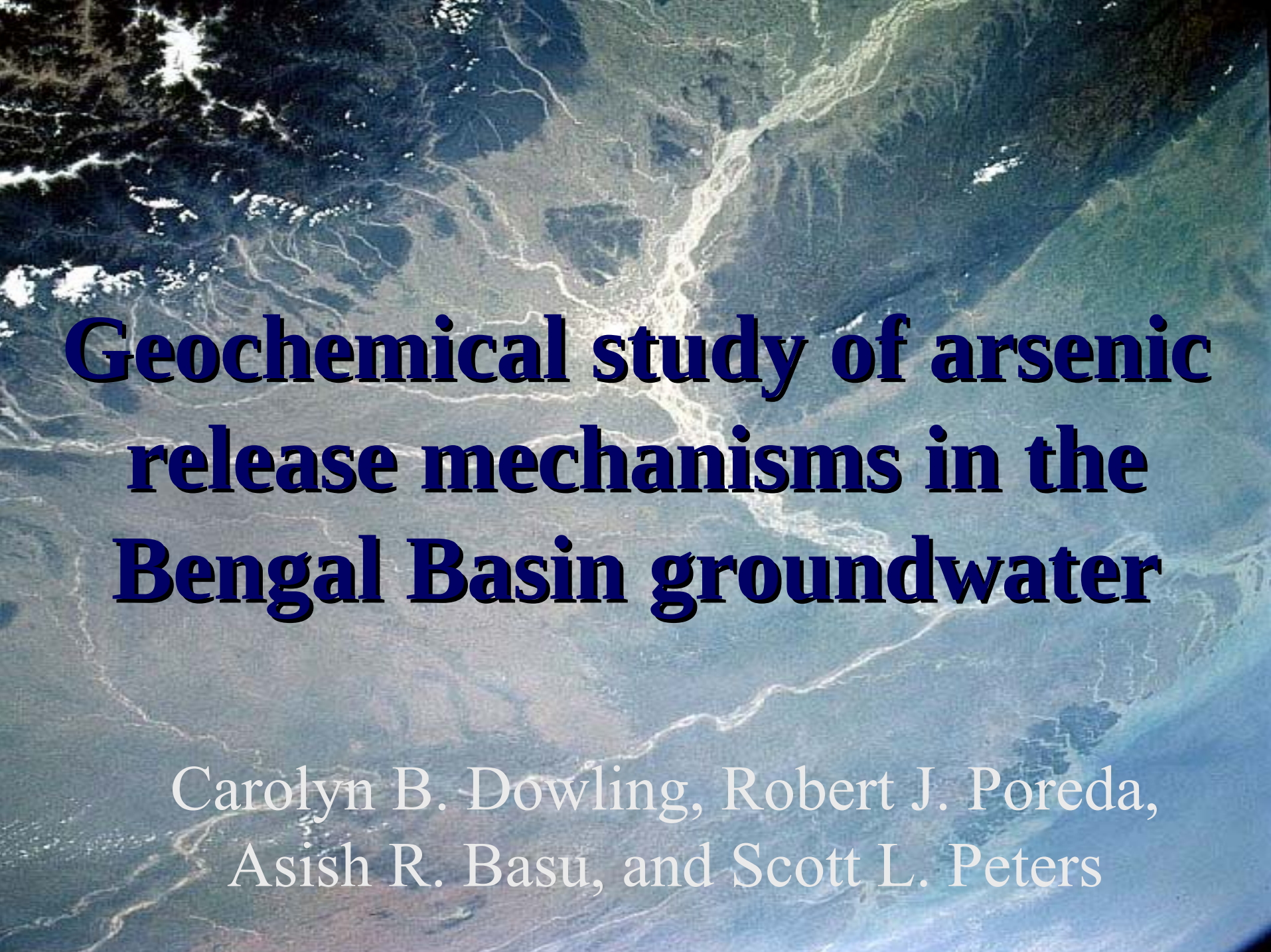


Geochemical study of arsenic release mechanisms in the Bengal Basin groundwater

Carolyn B. Dowling, Robert J. Poreda,
Asish R. Basu, and Scott L. Peters

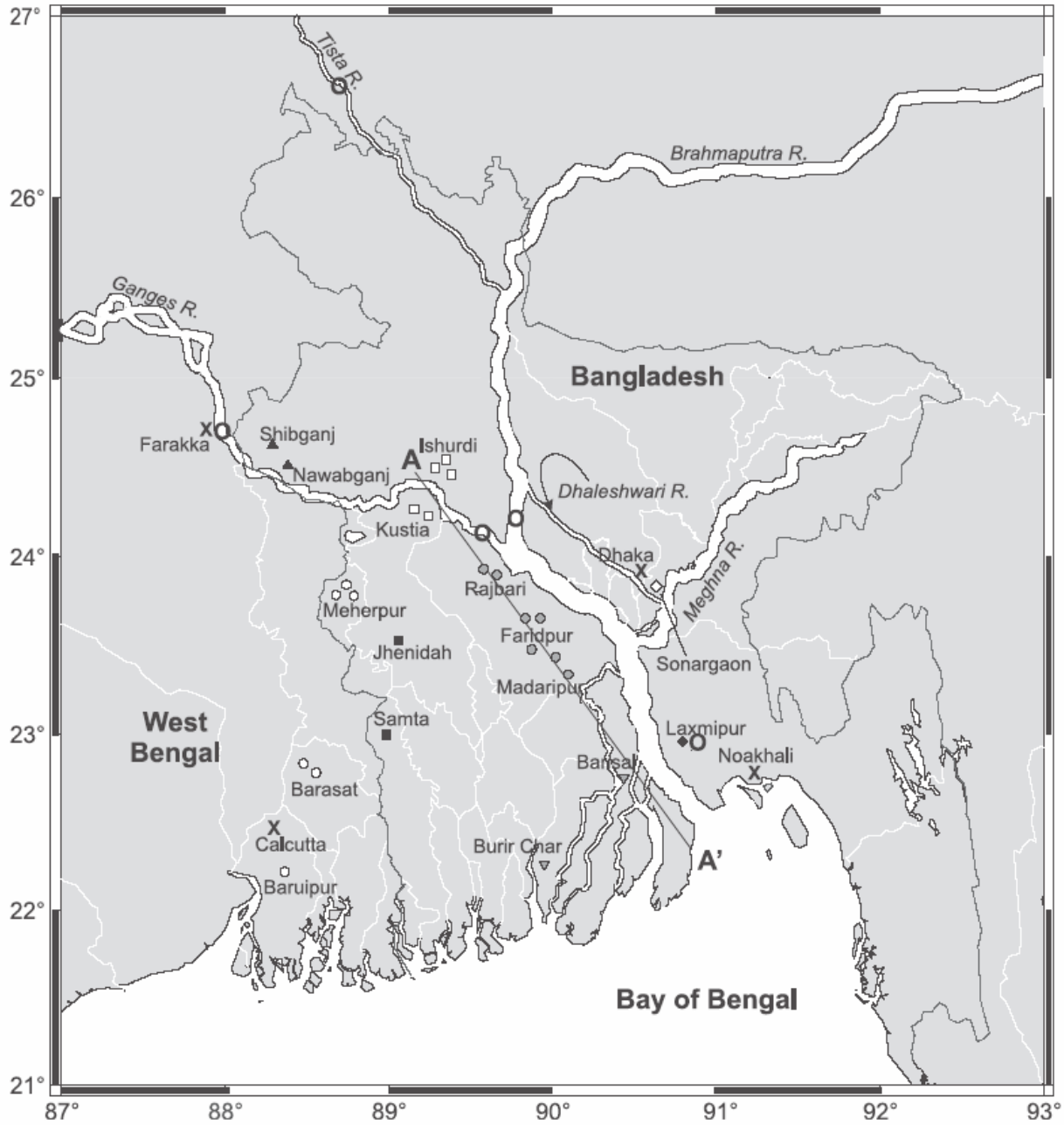


Figure 1. Bengal Basin groundwater and river sediment collection sites. This map shows the location of groundwater (variety of symbols) and river sediment (thick open cirlces) samples in Bangladesh. The sediment samples (thick open cirlces) are from Laxmipur and the northern and southern Ganges and Brahmaputra Rivers (collected by W. S. Moore and A. R. Basu). The crosses designate the larger towns.

Sampling

Sixty-eight groundwater samples

- **Bangladesh**
- **West Bengal (India)**
- **$^{3}He/^{3}H$ groundwater ages**
- **Major elements by Ion Chromatography**
- **Trace elements by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)**

Sediments from drill core

- **Trace elements by ICP-MS**

Compare adsorbed vs. dissolved trace element concentrations

Time Line

- World Health Organization (WHO)
  - Until 1970s, population used polluted rivers
  - Drilled 2 million groundwater wells
- Most wells are contaminated with arsenic (As)
  - Levels are greater than WHO maximum contaminant level (MCL) of 0.01 ppm or 0.13 μM
  - Symptoms of Arsenic poisoning develop slowly
  - 30-60% of the population is affected

Groundwater Depth Profile of Dissolved As

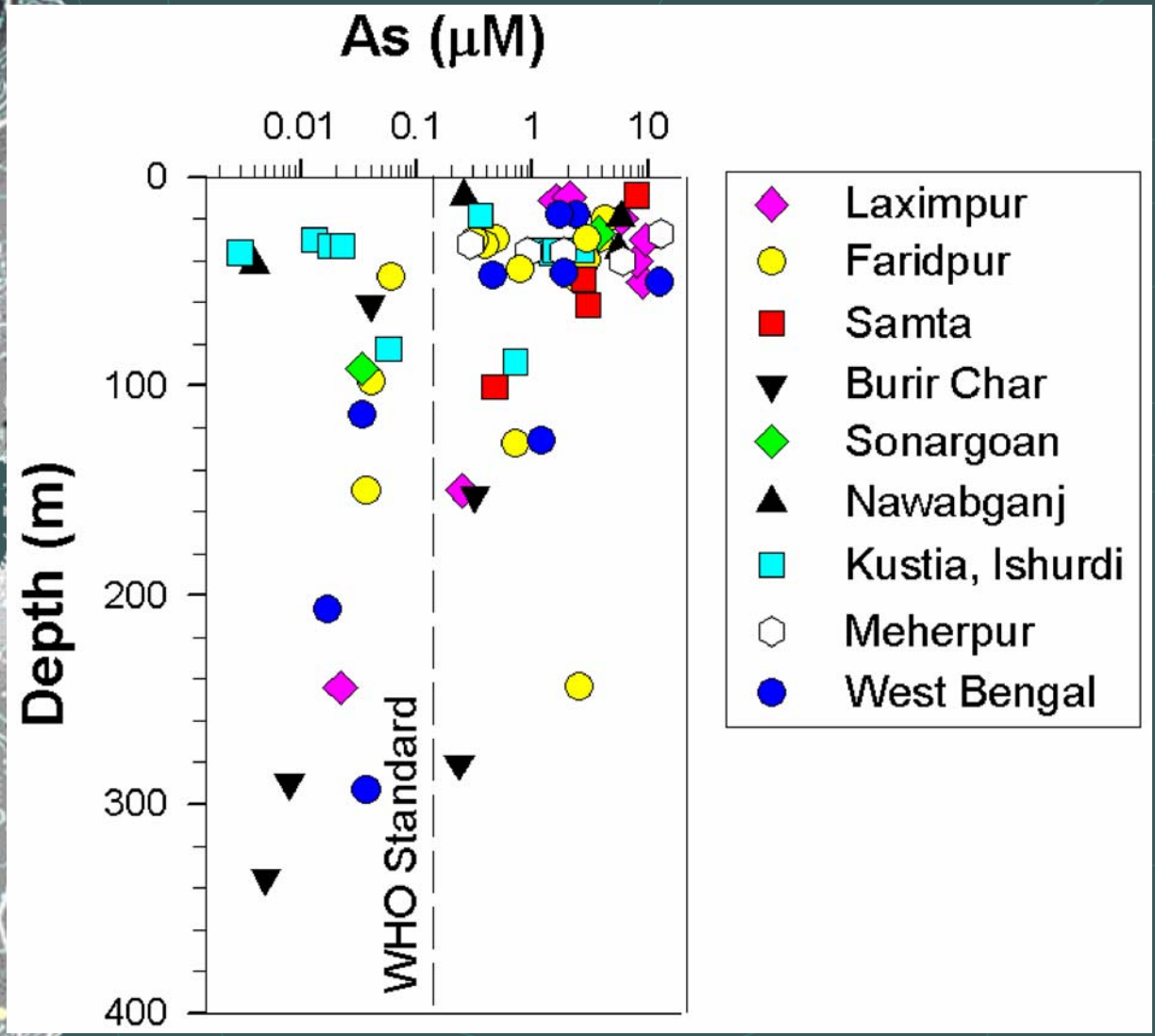


Figure 2. Depth profile of dissolved As. The groundwater arsenic concentrations above the WHO standard (0.01ppm; 0.13 μM) are concentrated in the shallow wells (<60m). The higher levels of As in the deeper wells (> 60m) are most likely from the wells screening both deep, As-free and shallow, As-rich groundwater.

Research Questions?

- Why do we care about Arsenic in groundwater?
- Is it a problem in the Bengal Basin?
- Which wells are contaminated by Arsenic?
  - Where are the wells located? What are their depths?
- Does As correlate with other elements?
- What are the sources of As?
  - Sediments? Industrial pollution? Agricultural pollution?
- Why is it a problem in the Bengal Basin?

Some Answers

- Arsenic contamination is a real issue
- Source is natural
- Bulk sediments supplies As to the groundwater
  - Microbial mediated reduction of iron oxy-hydroxides
  - a.k.a. the microbial breakdown of FeOOH

Dissolved As versus Fe, CH_4, and NH_4

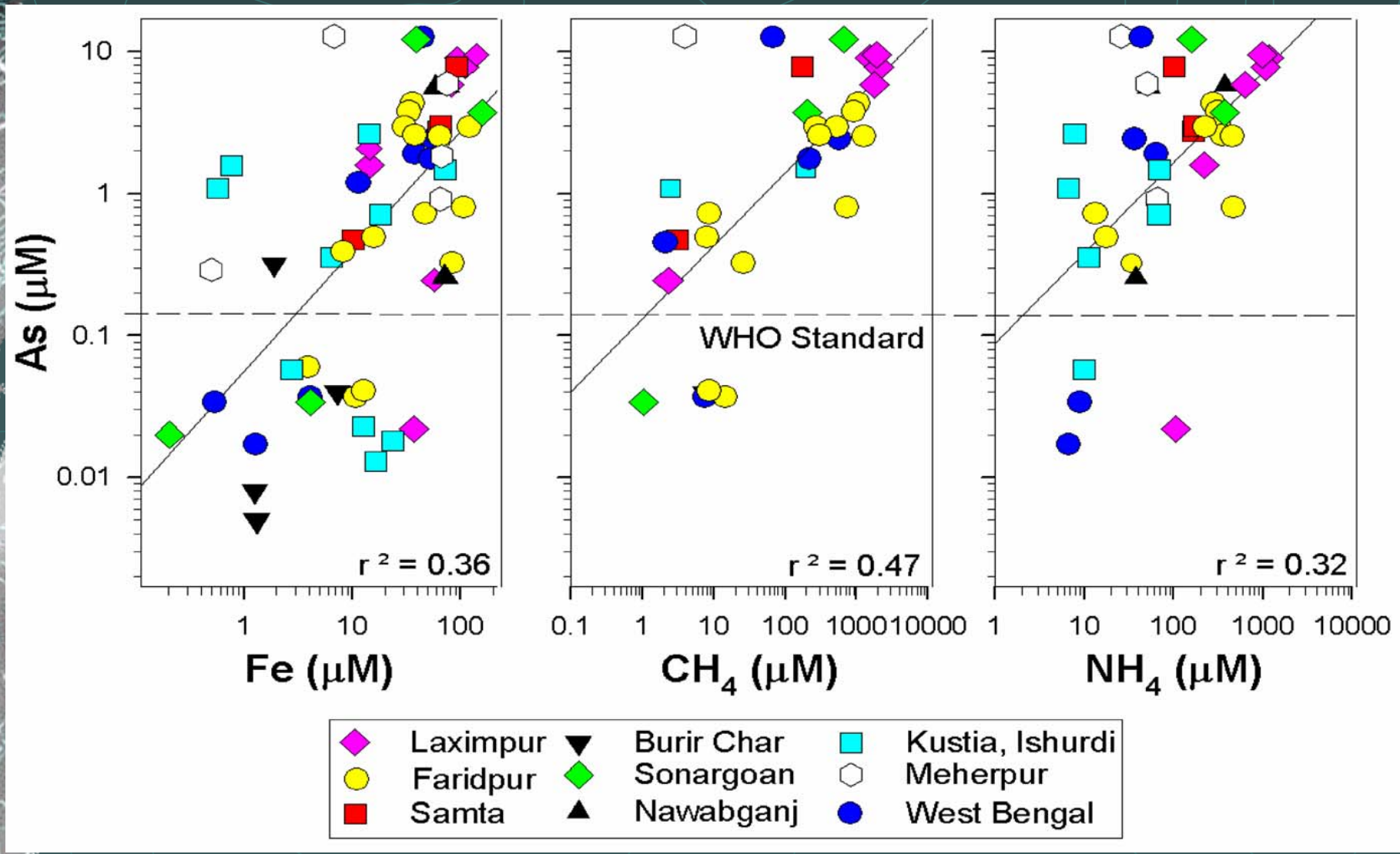


Figure 3. Dissolved As versus Fe, CH_4, and NH_4. Dissolved arsenic levels from all the wells in the Bengal Basin are plotted against iron, methane, and ammonia. There are only weak to modest correlations between arsenic and iron, methane, and ammonia.

Dissolved As versus CH_4, Fe, and NH_4 in Faridpur and Laxmipur

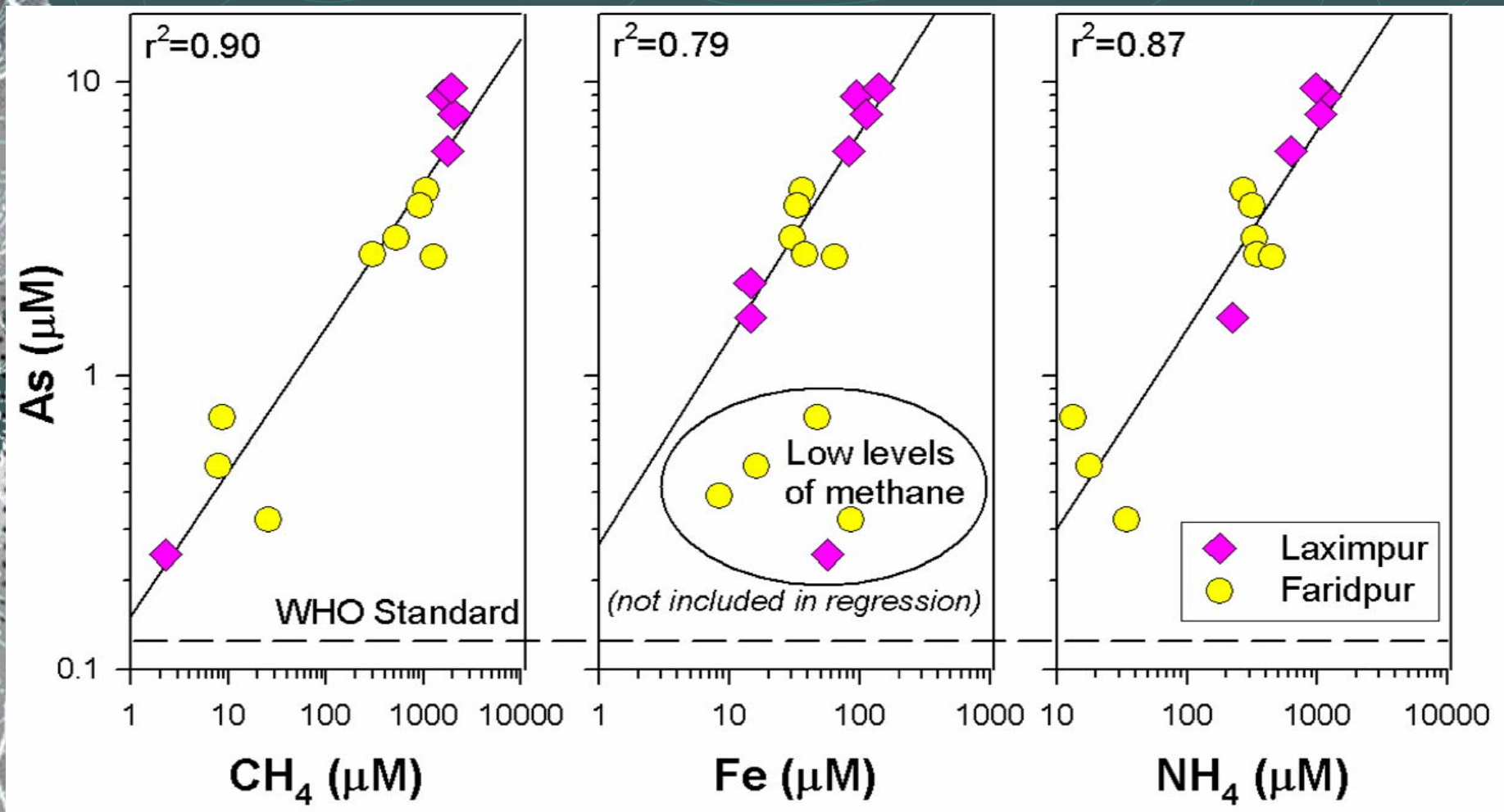
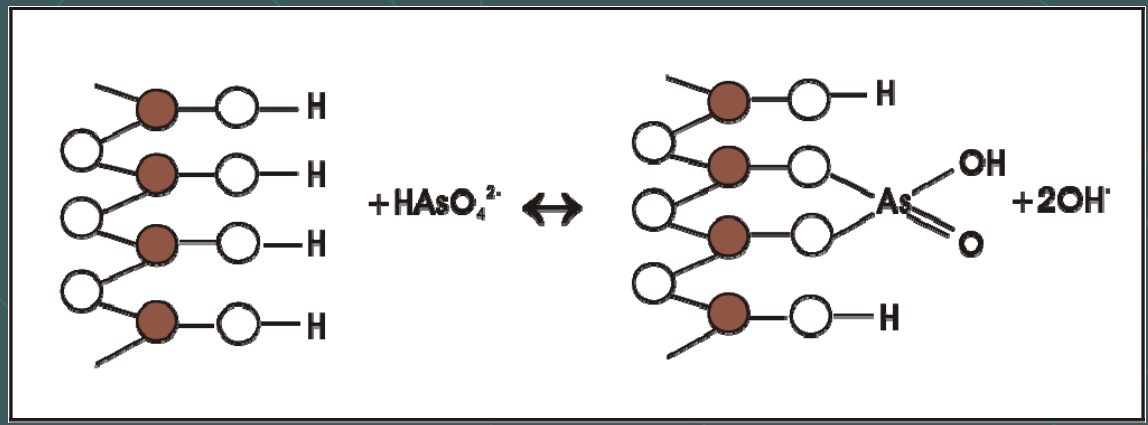


Figure 4 . Dissolved As versus CH_4, Fe, and NH_4 in Faridpur and Laxmipur. Dissolved arsenic levels from wells located in Faridpur and Laxmipur are plotted against methane, iron, and ammonia. There are reasonable correlation (r^2 = 0.8-0.9) between arsenic and methane, iron, and ammonia. The As- CH_4 and As-NH_4, correlations indicate that there are active microbes in the anoxic groundwater. The As, CH_4, and NH_4 associations combined with the Fe data support bacterial reduction of FeOOH as the main release mechanism of As into the groundwater. The samples experiencing low levels of microbial activity (based on CH_4 levels) are excluded from the As-Fe correlation.

Arsenic Geochemistry

- Species
  - As(V), Arsenate, AsO_4^{3-}
  - As(III), Arsenite, $As_2O_4^{2-}$
    - 30-60X toxic and 5-10X mobile
- As strongly adsorbs onto iron oxy-hydroxides (FeOOH)



- As-laden FeOOH are deposited in estuaries and wetlands

Sampling

- Where is the Arsenic located?
  - Groundwater chemistry
- Is the Arsenic coming from the sediments?
  - Sediment chemistry
- What is the watershed hydrology?
  - Groundwater flow

Existing Theories of As Release

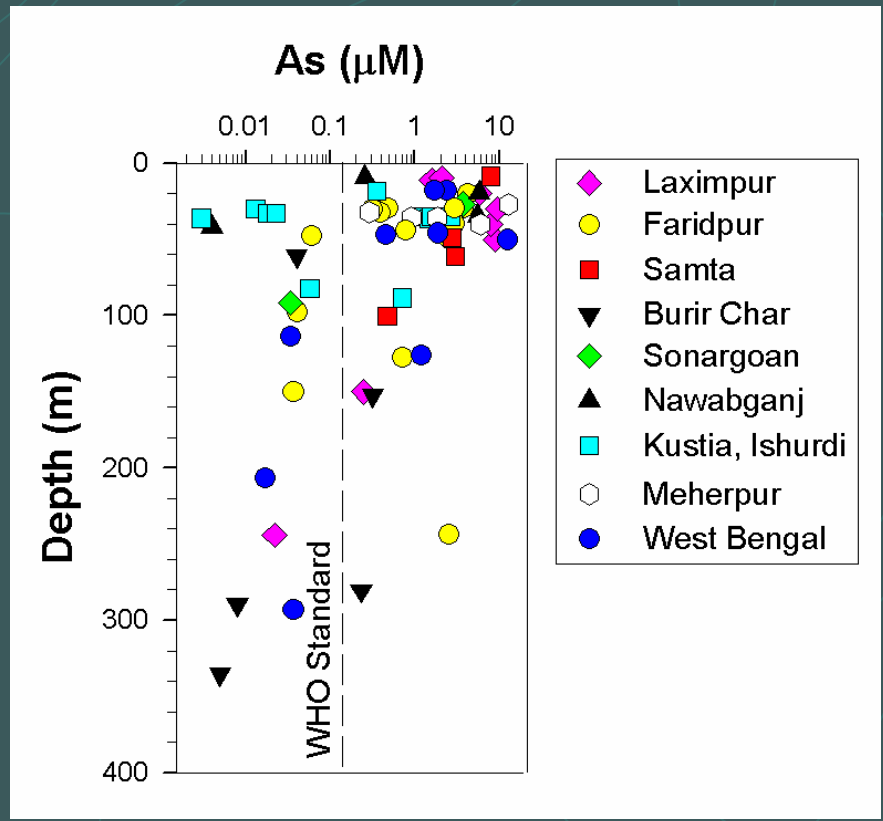
- Oxidation of pyrite *(Rarely used anymore)*
  - Requires oxic water
- Competitive exchange with phosphorus
  - Phosphate (PO_4^{3-})
  - Dissolved As and P exchange for one another
- Dissolution of iron oxy-hydroxides (FeOOH)
  - FeOOH strongly adsorb As
  - Correlation between Fe and As
  - Anaerobic microbes

Sampling

- Sixty-eight groundwater samples
  - Bangladesh
  - West Bengal (India)
- Sediment
  - Drill core
  - River

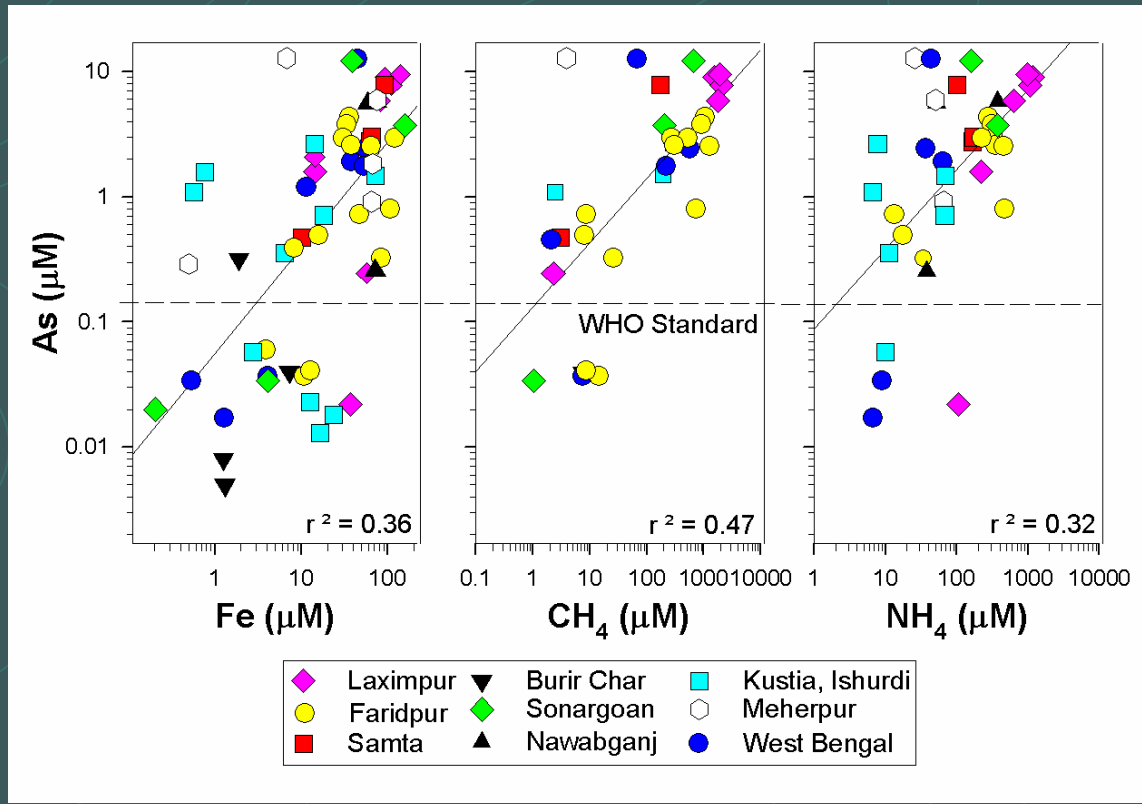
Groundwater Depth Profile

- Is As a problem?
  - More than 60% of samples above 0.13 μM
- Where are the wells?
  - Throughout the country
- What are the depths?
  - Highest levels of As at shallow depths (< 60 m)



Does As correlate with others?

- Iron (Fe)
  - Previous studies link As and Fe
  - Weak correlation between As and Fe (r^2=0.37)
- Methane (CH_4) & Ammonia (NH_4)
  - Microbial activity
  - Weak to modest correlation (r^2: 0.39-0.55)

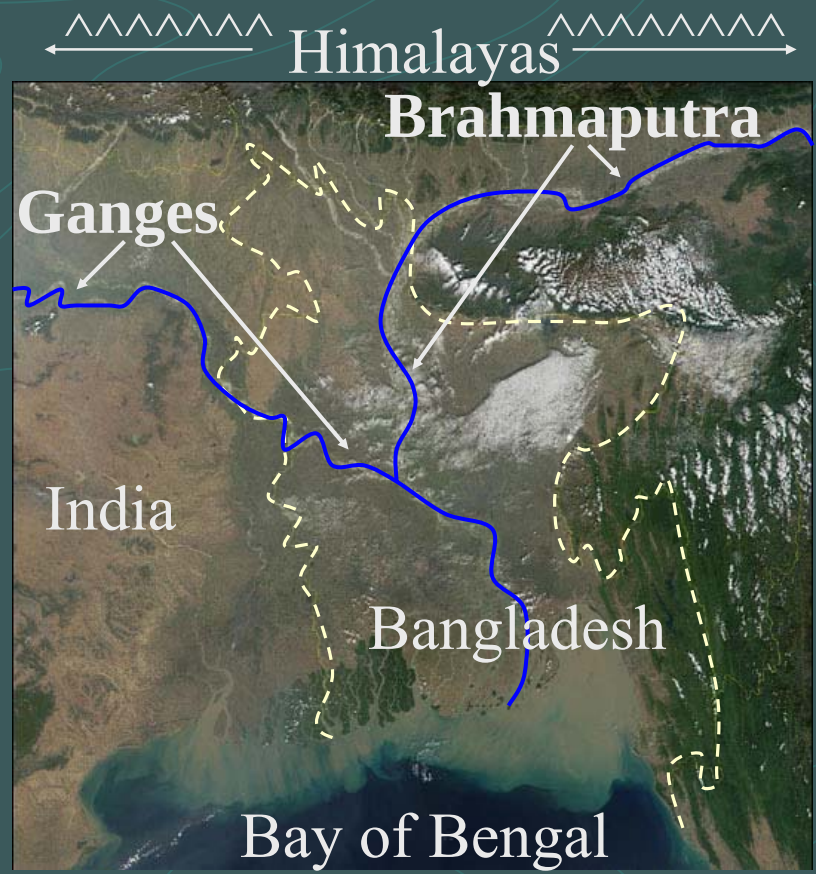


Are microbes involved?

- As-CH_4 and As-NH_4 correlations
  - As microbes are oxidizing organic matter, they are breaking down FeOOH
  - Microbes converting As(V) to As(III)
  - Microbes
    - *Shewanella alga* BrY
    - MIT-13
    - *Geospirillum barnesii SES-3*

Background

- Bangladesh and West Bengal State, India
- Quaternary deposits
  - Ganges-Brahmaputra
  - Himalayas
- Sea level changes and river migration
  - Complex stratigraphy of coarse and fine-grained sediment.



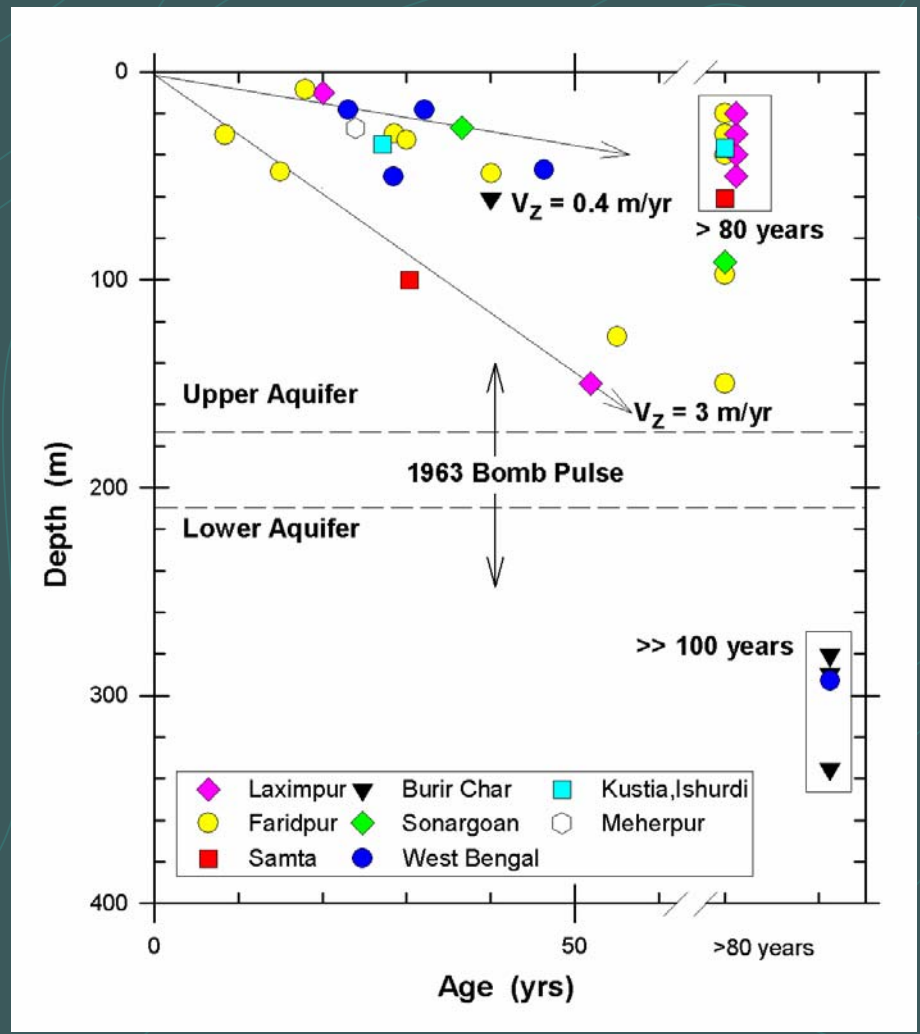
(Modified from http://www.geoexplorer.co.uk)

Groundwater Age Dating

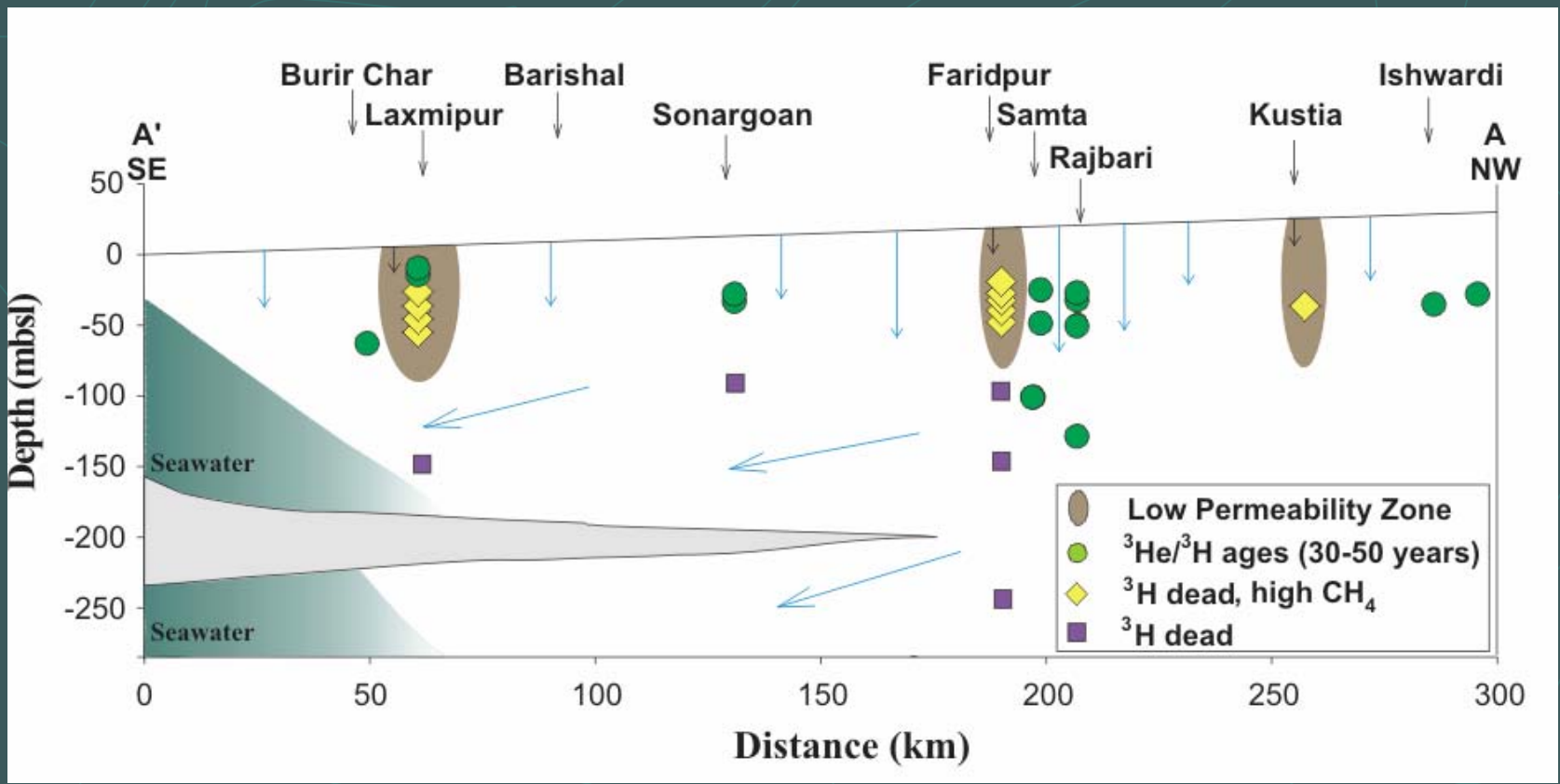
- $^{3}H/^{3}He$ Age Dating Technique
- Tritium (^{3}H) is formed
  - Above ground nuclear testing
  - Cosmogenic reactions ($^{14}N + n = {}^{3}H + {}^{12}C$)
- Component of water molecule ($^{3}H_2O$)
- ^{3}H decays to ^{3}He
  - $t_{1/2}$=12.4 yrs
- Groundwater residence time:
  - $t=(1/\lambda)\ln\{1+(^{3}He^{*}/^{3}H)\}$

Groundwater Age Dating

- Variations in ground-water velocities
  - ~0.4 m/yr
  - ~3 m/yr
- Complicated stratigraphy
- Complex distribution of As



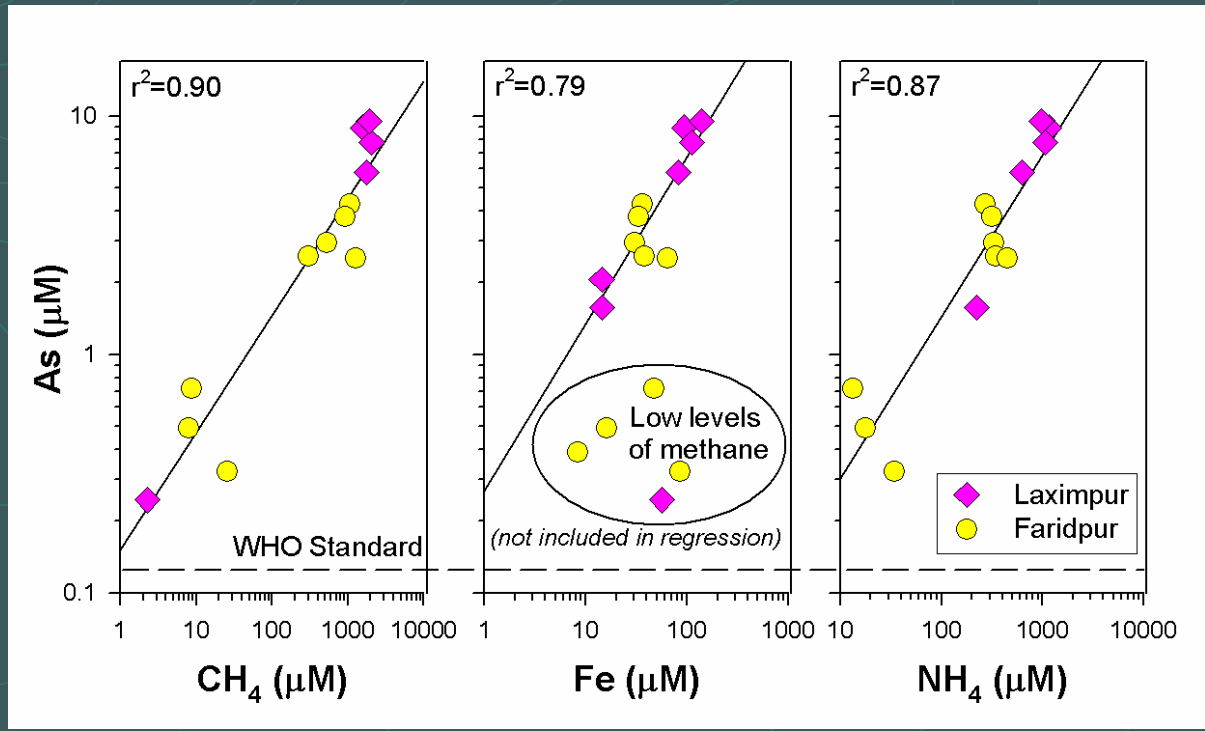
Watershed Hydrology



Correlations with Arsenic

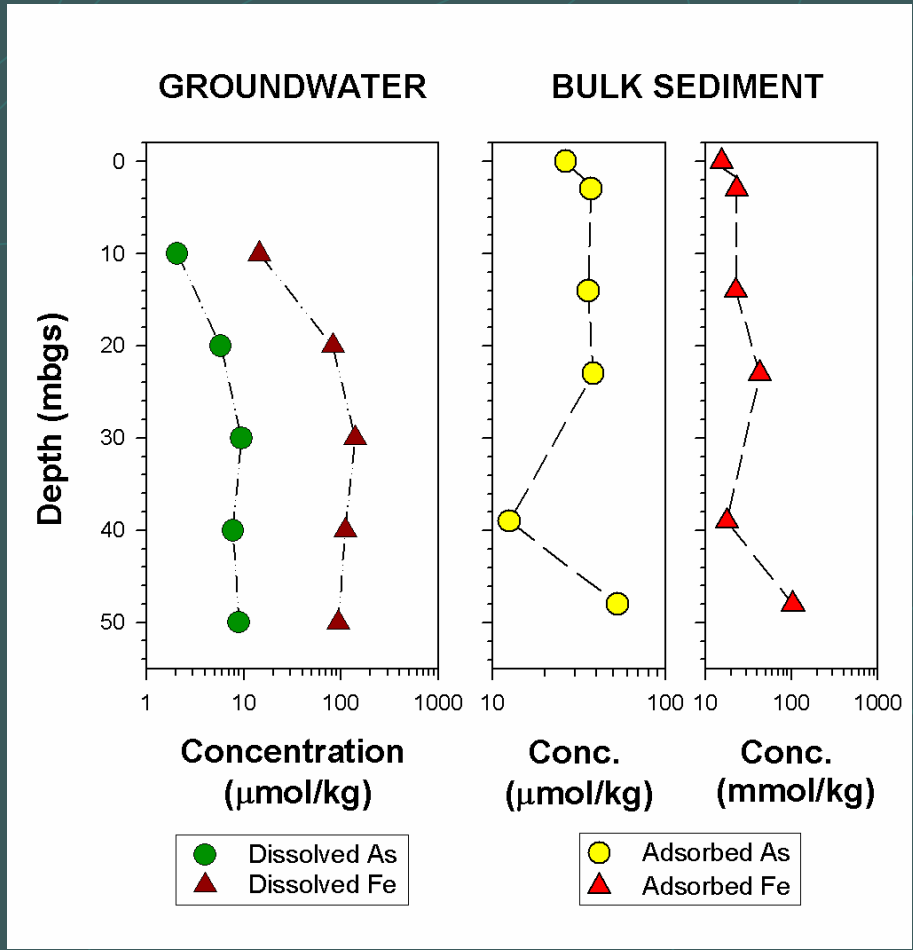
Faridpur and Laxmipur

- As-rich areas
  - Faridpur
  - Laxmipur
- Strong correlations with CH_4, Fe, & NH_4 (r^2: 0.8-0.9)



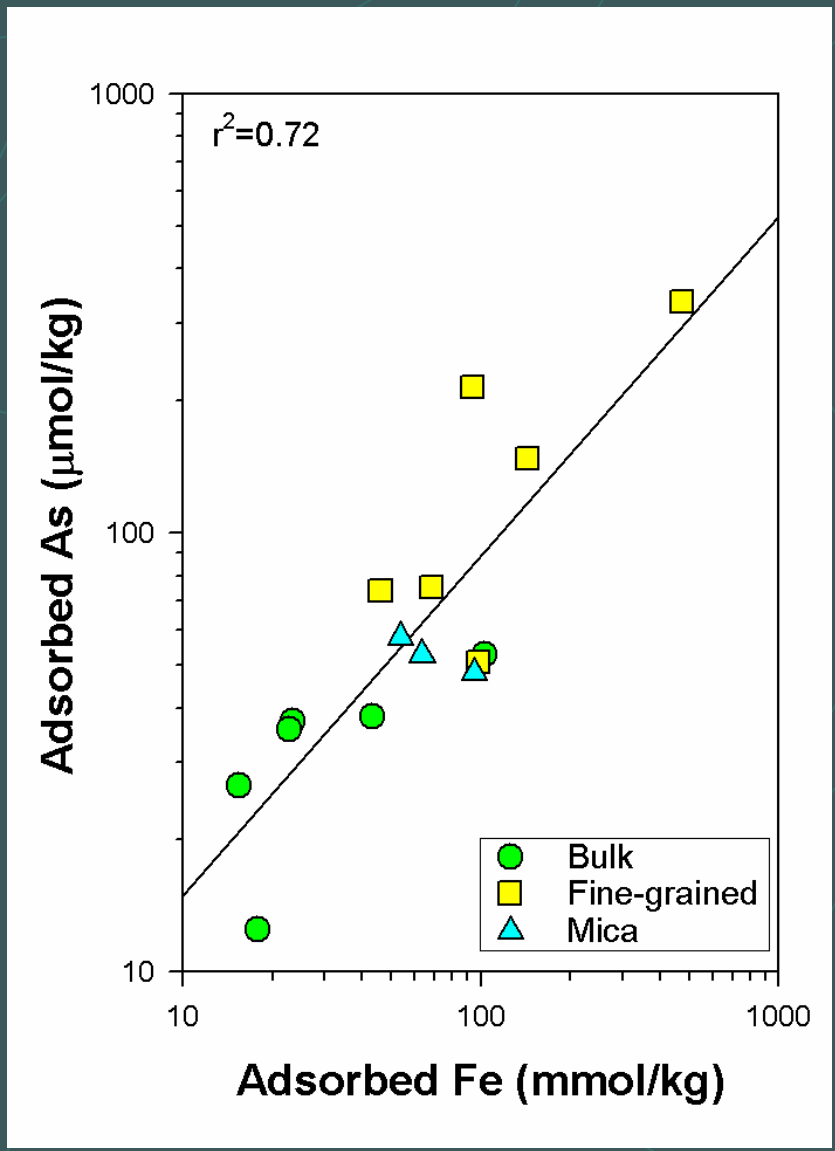
What is the source of As?

- Sediments influence groundwater
  - Mineralogy
  - Grain size
  - Adsorption/desorption
- Dissolved As and Fe have similar patterns
- Adsorbed As and Fe have comparable patterns
- Bulk capable of supplying As to groundwater



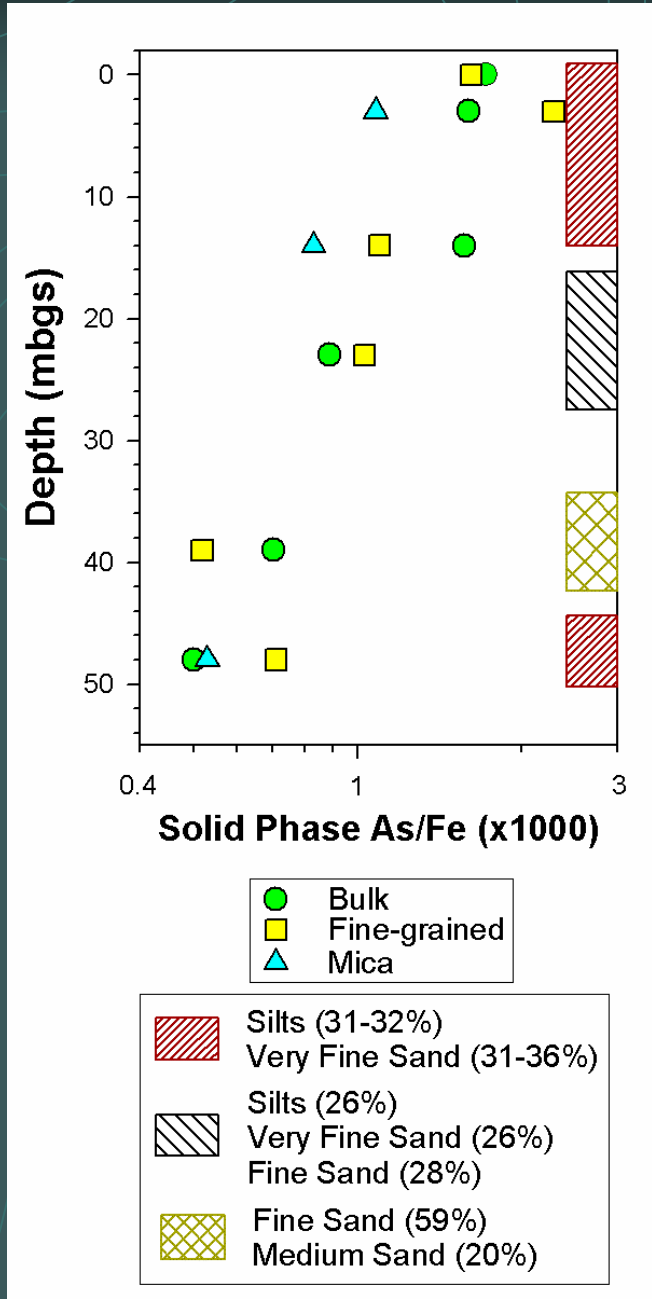
Sediment As-Fe

- Modest correlation at any depth
  - r^2=0.7
- Sources of As and Fe in all solid phases may be the same
  - Microbial dissolution of FeOOH
- Grain size plays an important role

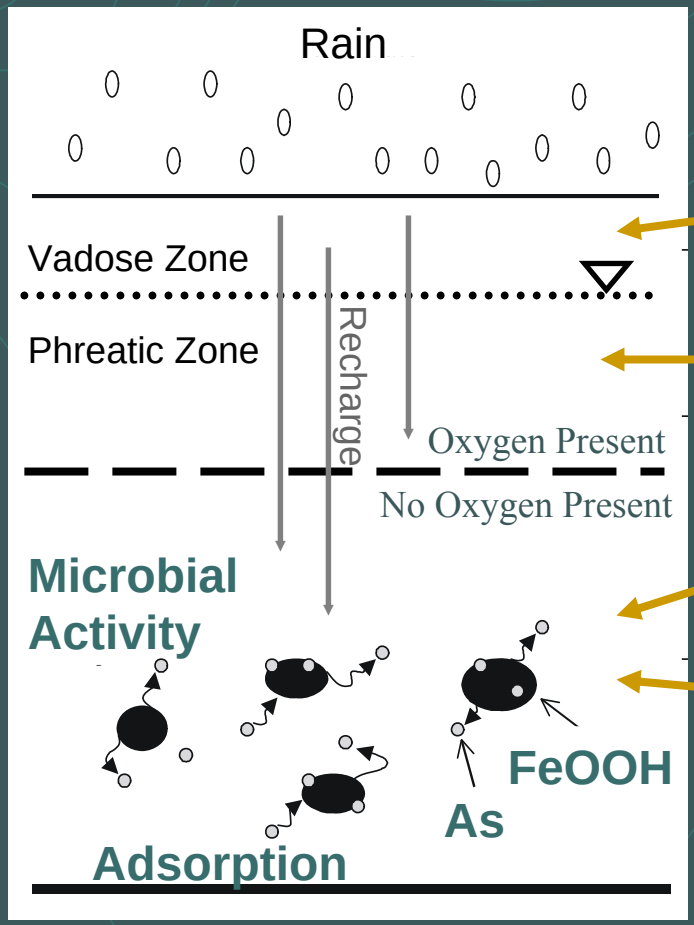


As/Fe Ratios with Depth

- As-Fe ratios decrease with depth
- More groundwater has flowed through the deeper sediments
- Removed As from deeper aquifer system



Overview of As Release



- Vadose Zone (unsaturated)
- Phreatic Zone (saturated)
  - Aerobic organisms consume O_2
  - Anaerobic microbes reduce FeOOH
    - Releases Fe and As
  - Dissolved As levels
    - Biological activity
    - Adsorption reactions

Summary

- As in groundwater
  - 30-60% population is affected
  - 60% of the samples above WHO MCL (0.13 μM)
  - Depth less than 60 m
  - Anoxic groundwater greater than 60 yrs
- Complicated distribution of As in groundwater

Summary

- Source of As
  - The As-laden sediments
  - Released from the sediments through microbes
  - Bulk sediments are capable of supplying all of the arsenic to the groundwater

Present

- The Bad News
  - Groundwater will have high arsenic levels for a very long period of time.
- The Good News
  - The drinking supply wells can be drilled to deeper depths.

Future Research?

(Modified from http://www.central.k12.ca.us)

- Universal Problem??
  - Rapid accumulation of sediments from Himalayas
    - Yangtze River
    - Irrawaddy River
    - Mekong River
  - Sea level changes and river migration
  - Mekong Delta, Vietnam
    - Dong The Nguyen
    - Feb. 2004 AAAS travel proposal
    - Future NSF proposal