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Geochemistry and speciation of solid and aqueous phase arsenic in the Bengal Delta Plain aquifers

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Occurrences of arsenic (As) in groundwater

- ❖ Arsenic in groundwater is a major environmental problem globally

- South-east Asian countries like India, Bangladesh, Nepal, Pakistan, China, Taiwan, Vietnam and Thailand
- North America and Canada
- South America (Argentina and Chile)
- Europe (Hungary, Greece, Romania, Finland, Sweden)
- Africa (Ghana, Tanzania)

- ❖ The source of arsenic in groundwater is mostly geogenic
- ❖ Mining related incidences, geothermal sources etc. are also reported
- ❖ Arsenic concentrations are generally above 10 $\mu g\ L^{-1}$

Distribution of documented world problems with As in groundwater

Source: Smedley and Kinniburgh, Applied Geochemistry, 17, 259-284, 2002

Status of As in groundwater (India and Bangladesh)

- > 0.5 – 3200 µg L^{-1} recorded

- Indian/Bangladeshi legal limit 50 µg L^{-1}
- WHO/EU limit 10 µg L^{-1}

- Estimated population exposed to waters containing As > 50 µg L^{-1}

- Bangladesh up to 40 million
- West Bengal up to 10 million

- Chronic exposure can lead to:

- Skin pigmentation changes and keratosis
- Skin cancer and other internal cancers

Study area and sampling

❖ Chakdaha block, Nadia district

- high As concentrations previously recorded (Nath et al., 2005; Charlet et al., 2007)

❖ Eh, pH, temp measured in the field

❖ Samples for major and trace elements acidified with HNO_3

Source: http://www.soesju.org/arsenic/wb.htm

Composition of groundwater sampled from the study area

	Mean	Median	Min - Max
Depth /m	30	24	9 – 73
As /µg L^{-1}	243	239	1.13 – 475
pH	7.32	7.32	7 – 7.7
Eh /mV	-201	-208	-241 – -142
Ca /mg L^{-1}	125	115	95 – 187
Mg /mg L^{-1}	36	33	22 – 61
Na /mg L^{-1}	32	26	15 – 86
K /mg L^{-1}	5	4	1.6 – 28
Mn /µg L^{-1}	593	402	177 – 1589
Fe /mg L^{-1}	7.55	7.29	0.09 – 14.7
HCO_3 /mg L^{-1}	585	551	447 – 786
Cl /mg L^{-1}	29	22	1.6 – 13.8
SO_4 /mg L^{-1}	2	0.39	0.01 – 14
NH_4 /mg L^{-1}	4	3.9	0.01 – 14.7

- **Circumneutral groundwater**
- **Ca-HCO_3 dominated**
- **High dissolved As, Fe and Mn**
- **Reducing groundwater**

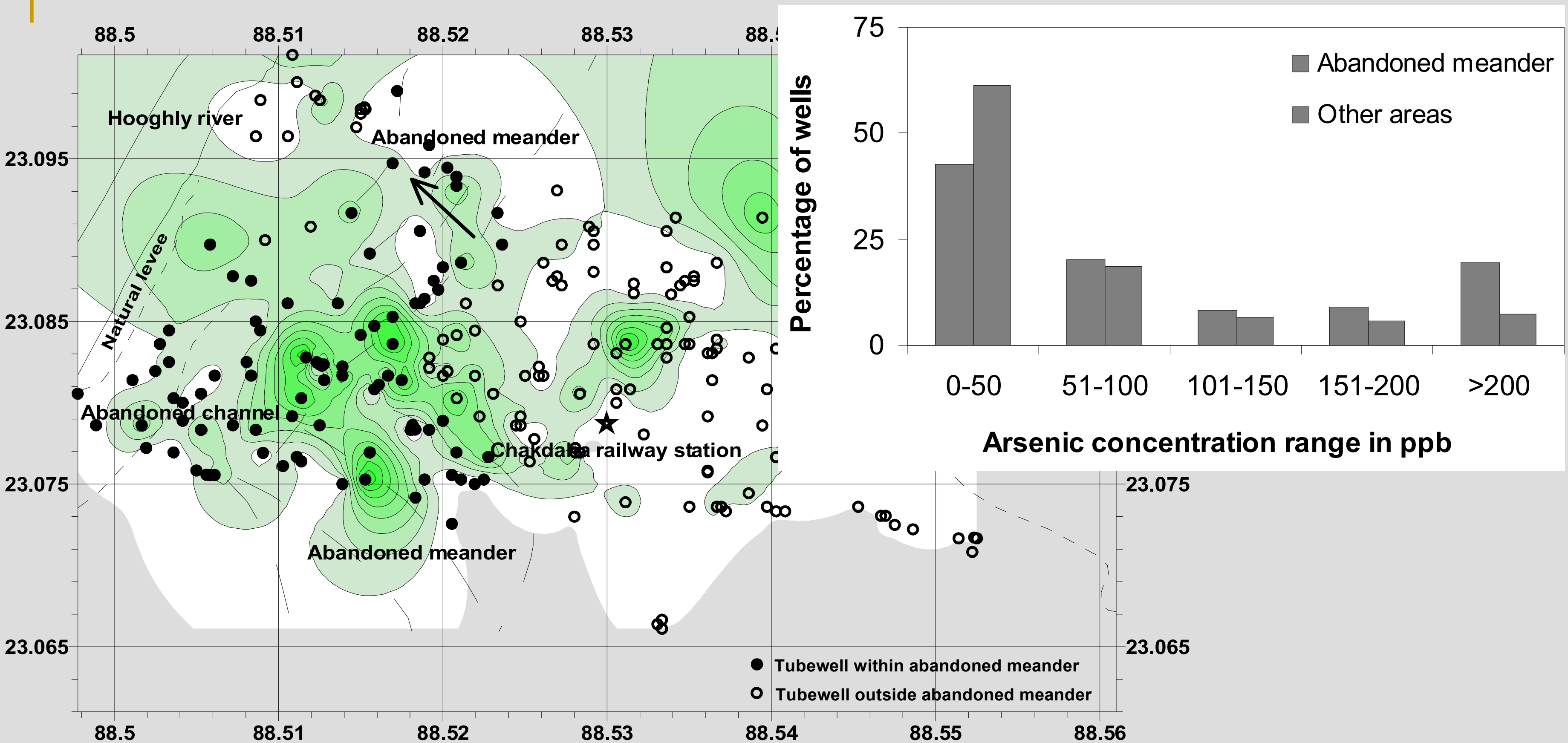
As species in tubewell waters

	Mean ± standard error	Median	Min - Max
ΣAs / μgL^{-1}	155 ± 61	75	1 - 476
As(V) / μgL^{-1}	25 ± 9	7	0.6 - 165
As(III) / μgL^{-1}	145 ± 52	71	0.5 - 395
MMAA / μgL^{-1}	0.07 ± 0.04	0	0 - 1.0
DMAA / μgL^{-1}	0.7 ± 0.2	0.3	0 - 4.9

❖ **High values of inorganic arsenic concentrations**

- **As(III) is the dominant species in groundwater**
- **methylated arsenic species also detected in groundwater**

Distribution of As in relation to Geomorphology

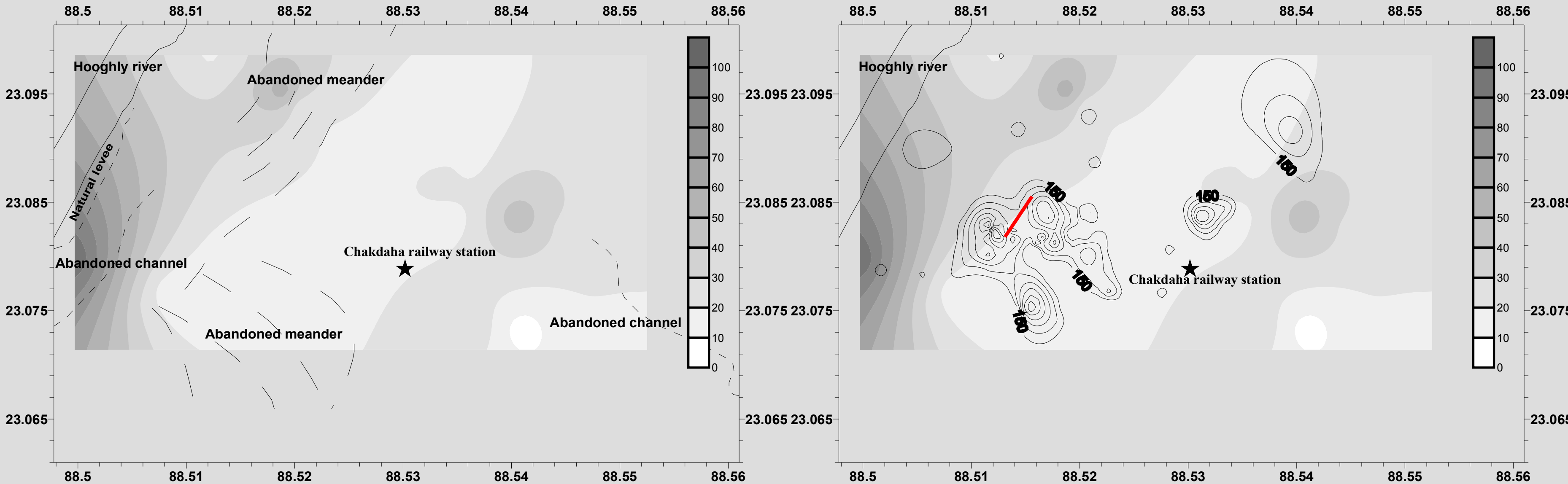


- High As areas is associated with geomorphological features like abandoned meander and channels.

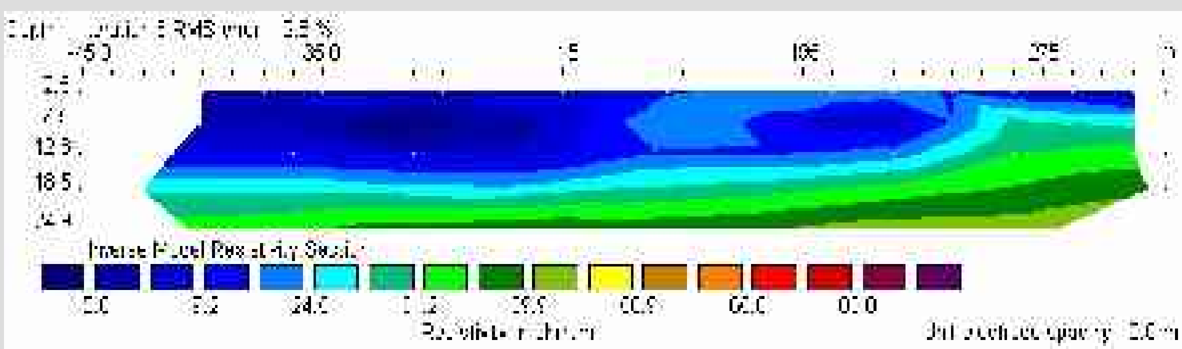
- Histogram validated the close coincidence with more 50% of the wells contains As above 50 μgL^{-1} in the zone of abandoned meander and channels.

Nath et al. (2005) *Mineralogical Magazine*, **69**, 841-853

Surface geology, lithology, groundwater recharge and As distribution

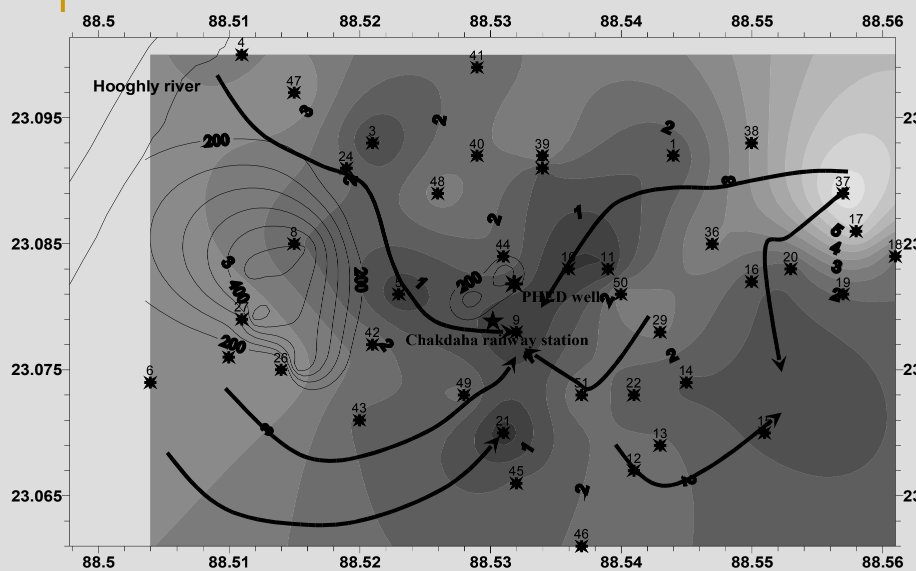


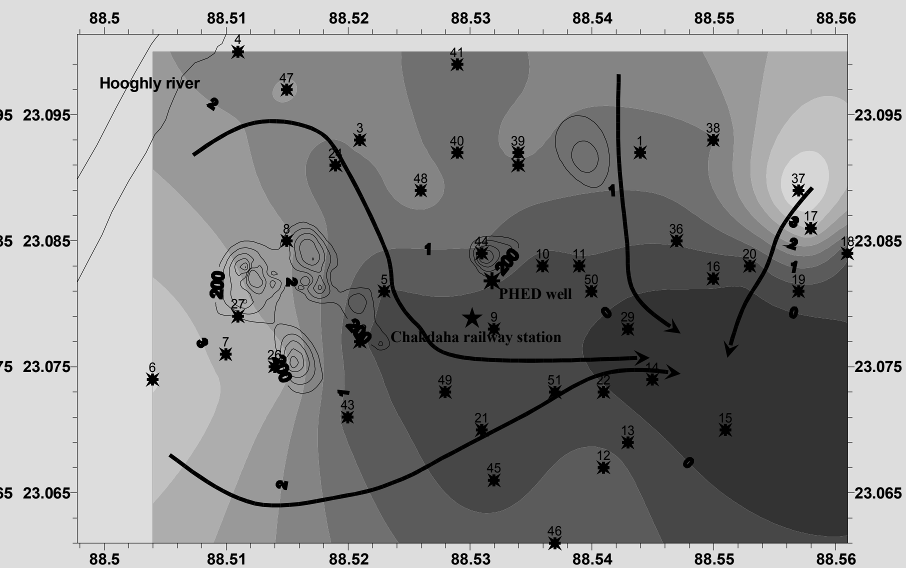
Surface resistivity contour [low resistivity values (whitish colour) indicates fine-grained surface layer]; a) plotted against geomorphological signature, and b) plotted against arsenic distribution

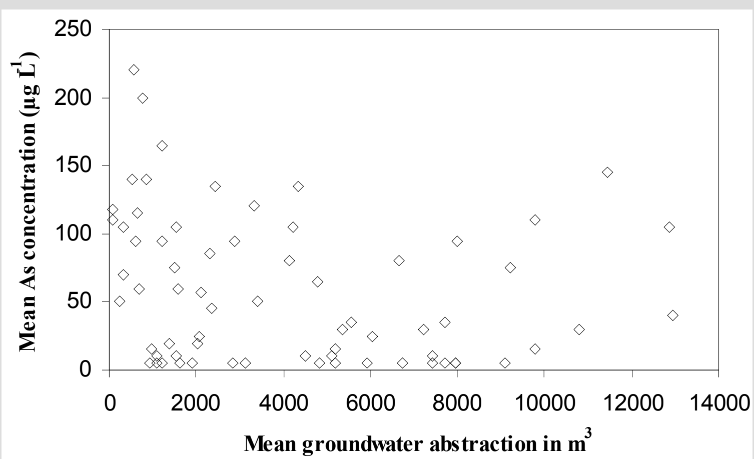


Resistivity profile (marked with red line above) at high arsenic sites demonstrate the dominance of fine-grained material at top of the aquifer. This possibly help in maintaining redox status (reduced) of the aquifer

Hydrogeology and As contamination





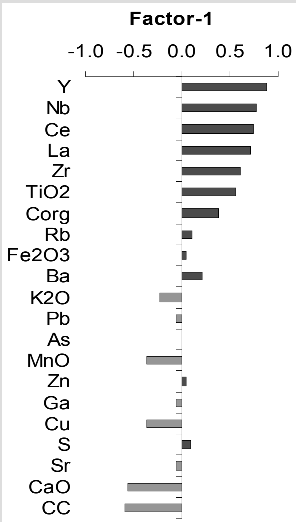


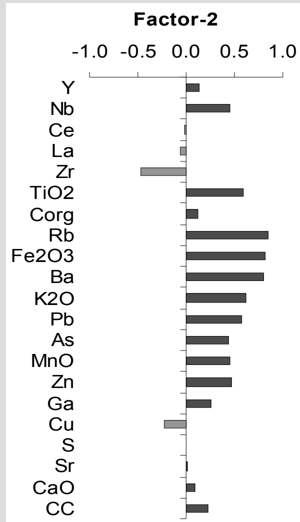
Pre-monsoon (2000 and 2002) water level contour shows cone of depression at the central and southeastern part of the study area (Hooghly acting as effluent river)

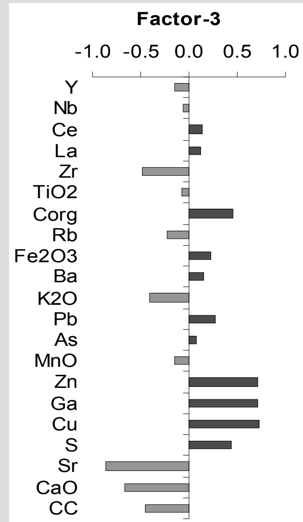
Groundwater flow lines are deviating away from the high As aquifer and making high As areas as dead zone for groundwater movement. This makes the aquifer having low permeability, longer sediment-water interaction and possibly helps in arsenic mobilization. The observation is also corresponds with close association of high As aquifer with geomorphological features.

There is no correlation between mean groundwater abstraction and mean As concentration in the study area

Sediment geochemistry and As associated phases





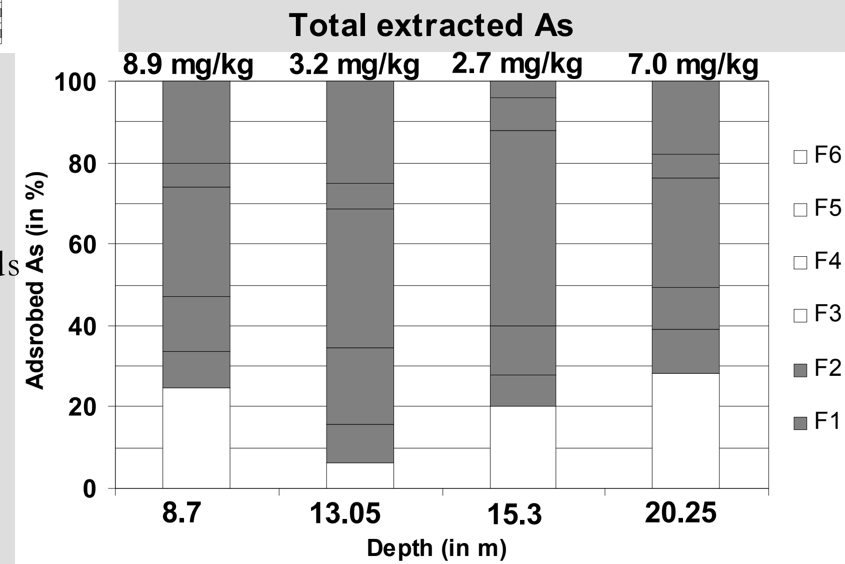


F1: Heavy-mineral factor [e.g., rutile (Ti), zircon (Zr, La, Ce, Y and Nb)]

F2: Phylosilicates and/or biotite

F3: Sulphidic mineral factor [e.g., chalcocite (Cu, S), galenite (Pb), sphlarite (Zn, S)]

F1: Ionically bound As
F2: As strongly adsorbed on Fe-oxyhydroxides and humic acids
F3: As coprecipitated with AVS, carbonates, Mn-oxides and very amorphous Fe-oxyhydroxides
F4: As coprecipitated with amorphous Fe oxyhydroxides
F5: As coprecipitated with crystalline Fe oxyhydroxides
F6: Orpiment and remaining recalcitrant As minerals



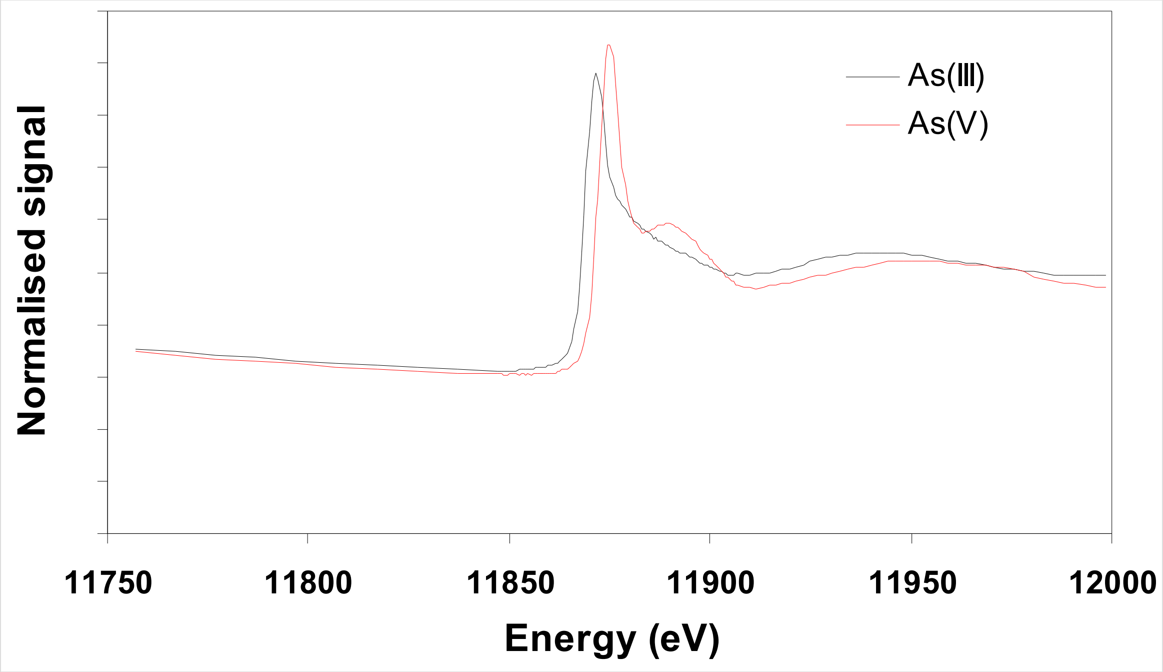
Saturation indices

	Low As well					Med As well				High As well		
	WB-03	WB-04	WB-05	WB-08	WB-13	WB-06	WB-07	WB-01	WB-02	WB-09	WB-10	WB-11
Anhydrite	-0.41	-0.45	-0.03	-1.36	-1.37	-1.3	-1.2	-1.33	-1.45	-1.43	-1.3	-1.45
Aragonite	2.13	2.1	2.23	2.08	2.63	2.16	2.03	2.03	2.05	2.24	2.22	2.49
Arsenolite	-8.07	-8.56	-8.27	-10.98	-8.35	-6.89	-6.79	-6.51	-5.45	-5.96	-5.81	-5.75
As_native	-10.3	-9.45	-10.85	-16.37	-12.58	-8.58	-9.1	-9.57	-6.85	-9.15	-9.37	-11.09
Calcite	2.28	2.25	2.37	2.22	2.77	2.3	2.17	2.18	2.2	2.38	2.37	2.63
Claudetite	-8.11	-8.6	-8.31	-11.01	-8.38	-6.93	-6.83	-6.55	-5.49	-6	-5.85	-5.79
Dolomite	3.74	3.87	3.98	3.84	5.1	3.95	3.67	3.42	3.5	4.16	4.12	4.72
Goethite	4.05	3.82	4.54	5.12	5.26	4.23	4.17	3.67	3.69	4.7	4.73	5.61
Halite	-4.89	-4.7	-4.38	-5.79	-5.83	-5.91	-5.46	-5.93	-5.22	-6.24	-6.22	-5.3
Hematite	10.11	9.65	11.09	12.26	12.53	10.48	10.35	9.35	9.4	11.42	11.48	13.23
Maghemite	-0.35	-0.83	0.63	1.7	2.02	0.01	-0.11	-1.06	-1.04	0.88	0.96	2.78
Magnesite	0.88	1.04	1.02	1.03	1.74	1.07	0.91	0.66	0.72	1.2	1.17	1.51
Magnetite	12.4	12.08	13.73	14.11	15.33	13.33	12.96	11.24	12.05	14.41	14.4	16.44
Manganite	-10.2	-10.65	-9.73	-8.75	-9.42	-10.39	-10.64	-11.15	-11.21	-9.98	-10.07	-8.73
Pyrolusite	-20.08	-20.86	-19.45	-16.9	-18.48	-20.63	-20.7	-21.11	-21.84	-19.74	-19.77	-17.97
Rhodochrosite	2.06	1.9	2.09	1.93	1.54	2.02	1.71	0.96	1.66	2.14	1.96	2.54
Scorodite	-9.81	-11.01	-9.11	-7.09	-7.29	-9.79	-9.42	-9.38	-10.29	-8.14	-7.85	-5.79
Siderite	2.7	2.75	2.75	2.11	2.56	3.03	2.91	2.21	2.96	3.15	3.1	3.28

- Saturation indices computed using PHREEQC for groundwater from West Bengal, India

- Positive values denotes precipitation, and negative values denotes dissolution of the special mineral

EXAFS and XANES studies



- Standard curve showing the As(III) and As(V) species in liquid (50 mgL^{-1}, respectively).

- The Taiwan Synchrotron radiation facilities (1.5 GeV) failed to detect arsenic species in both groundwater and sediments samples. However, we used HPLC-ICPMS technique to detect arsenic species in groundwater (results tabulated in slide 7).

Conclusions

- Arsenic distribution is patchy with the dominance of As(III) species.

- Surface geophysical studies indicate the dominance of fine-grained sediment at the high As sites, including the close association of geomorphological features. This possibly helps in maintaining low redox status of the aquifer.

- The hydrogeological study indicates that the high groundwater As aquifer is linked with lower permeability zone and is also associated with dead zone for groundwater movement, facilitating longer sediment-water interaction.

- The clay and silt sized fraction of the sediments is playing an important part in controlling the distribution of solid phase As.

- Multivariate statistical analysis showed the presence of three different mineral phases in sediments (e.g., heavy mineral fraction, phylosilicates/biotite/Fe-oxyhydroxides, and sulphides) and is validated through selective extraction studies, revealing that the amorphous Fe- oxyhydroxide acting as potential sink for As.

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Thank you for your attention!!