Pre and Post-Monsoon Quality of Dissolved Organic Matter and Arsenic Mobilization Processes in Bengal Basin

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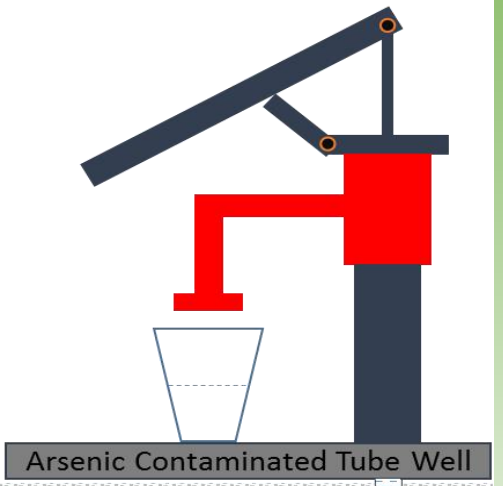
Outline

- Dissolved organic matter (DOM) and Arsenic Mobilization
- Design of study
- Results and Discussions
- Conclusions

Arsenic Mobilization



Soil Layer

FLOW

Organic Carbon

Bacteria

Inorganic Carbon

e^-

Oxidized Humics

Reduced Humics

e^-

e^-

Fe^{3+} Mineral

As

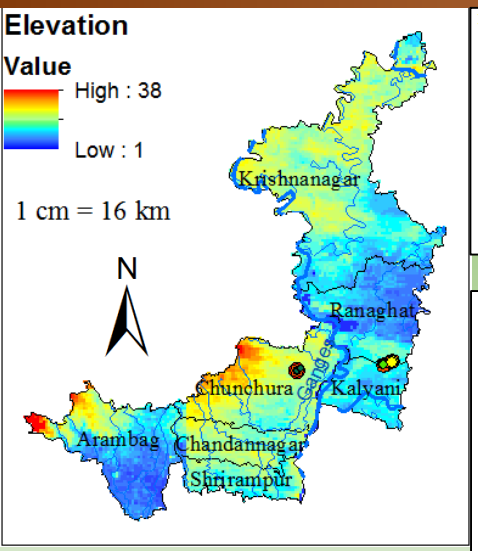
Fe^{2+}

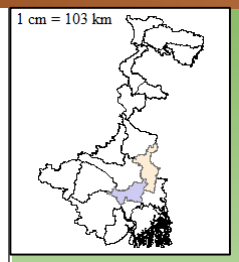
As – Humic Complex

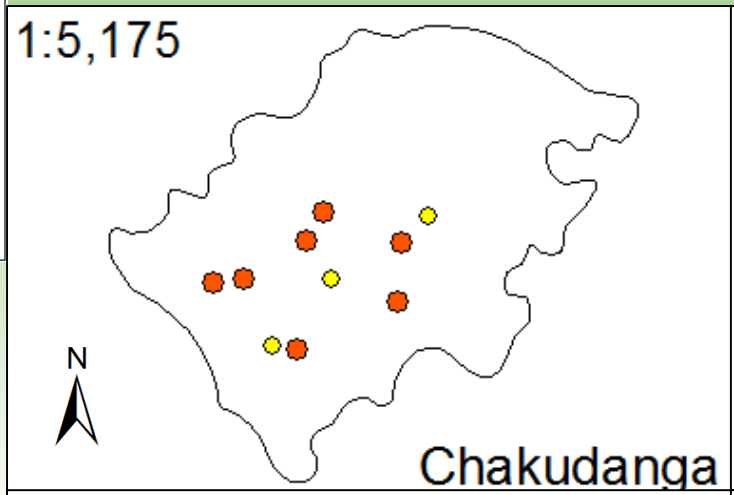
As – Fe -Humic Complex

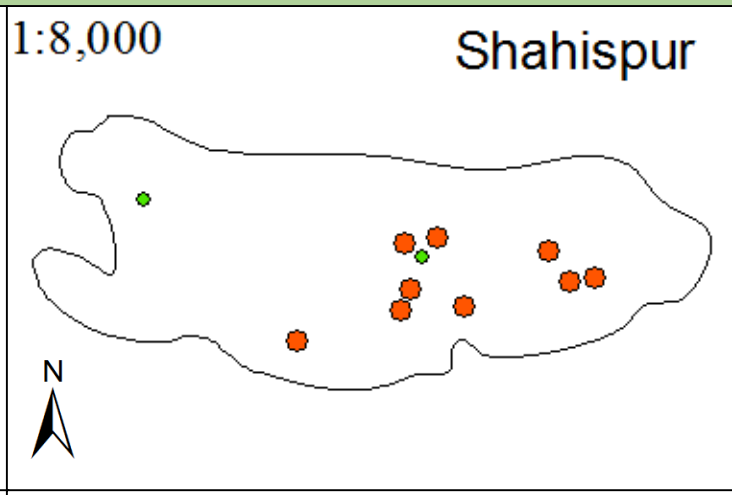
Reducing Aquifer (< 40m)

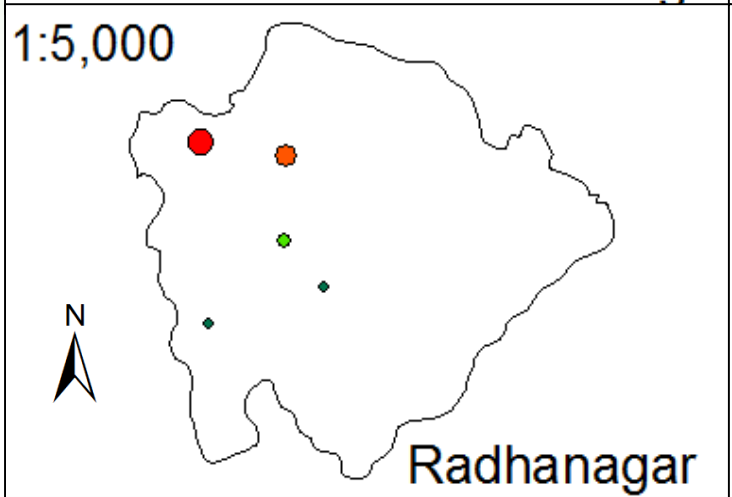
Study Site

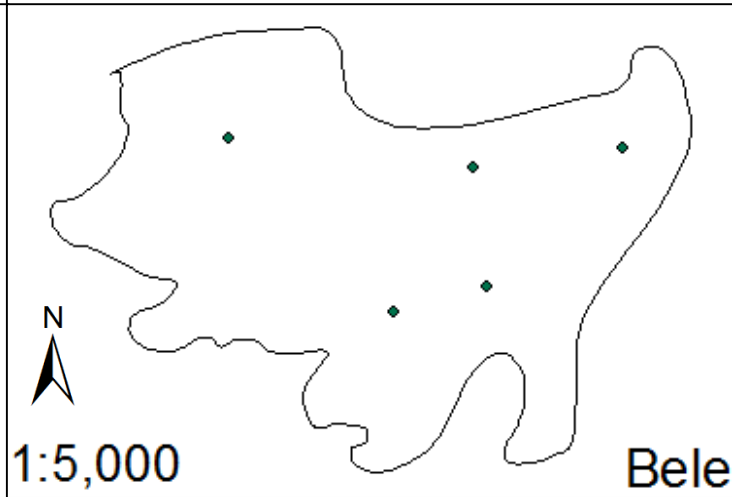












Arsenic (ppb)

Field4

- **0 - 10**
- **10 - 50**
- **50 - 100**
- **100 - 500**
- **> 500**

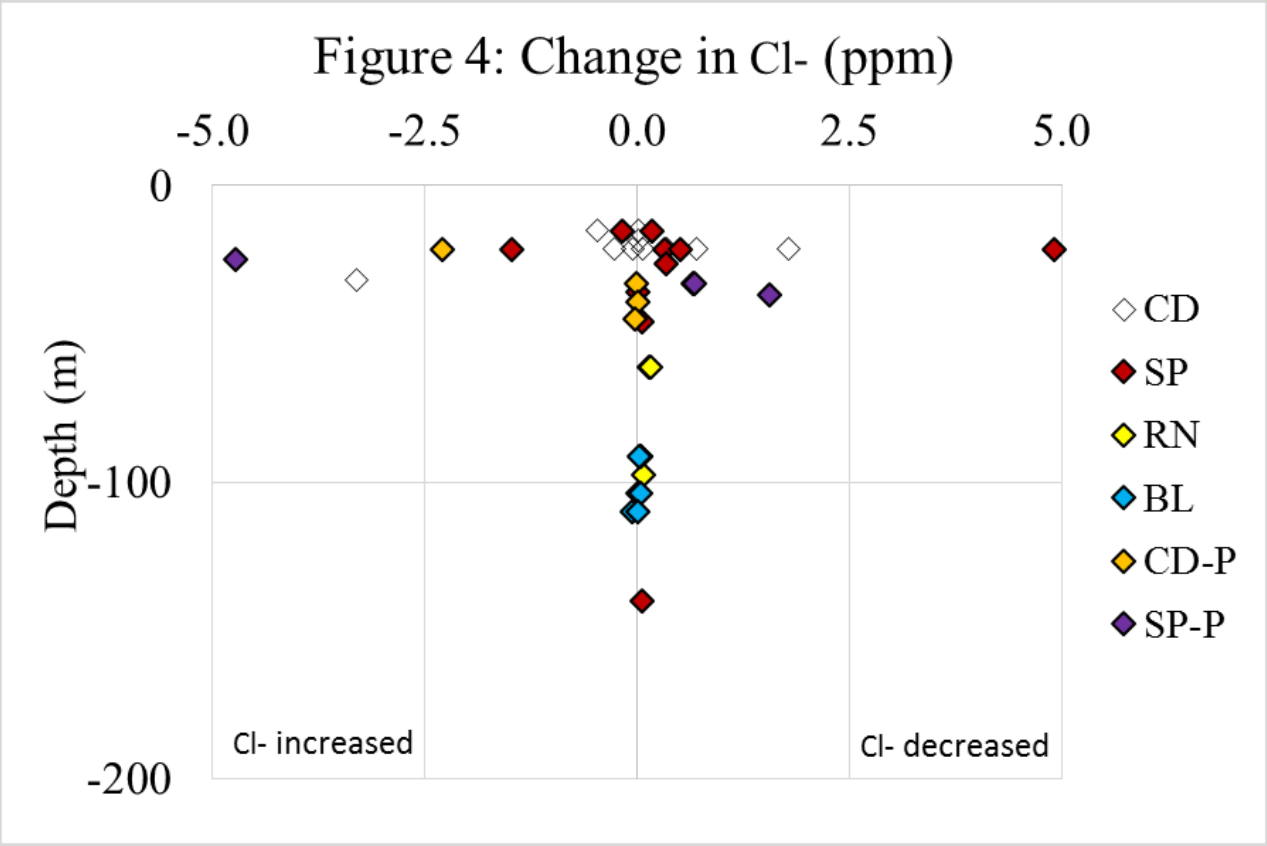
Sampling

Drinking Water
Tube Wells

Piezometers
(*Biwas et al., 2011*)

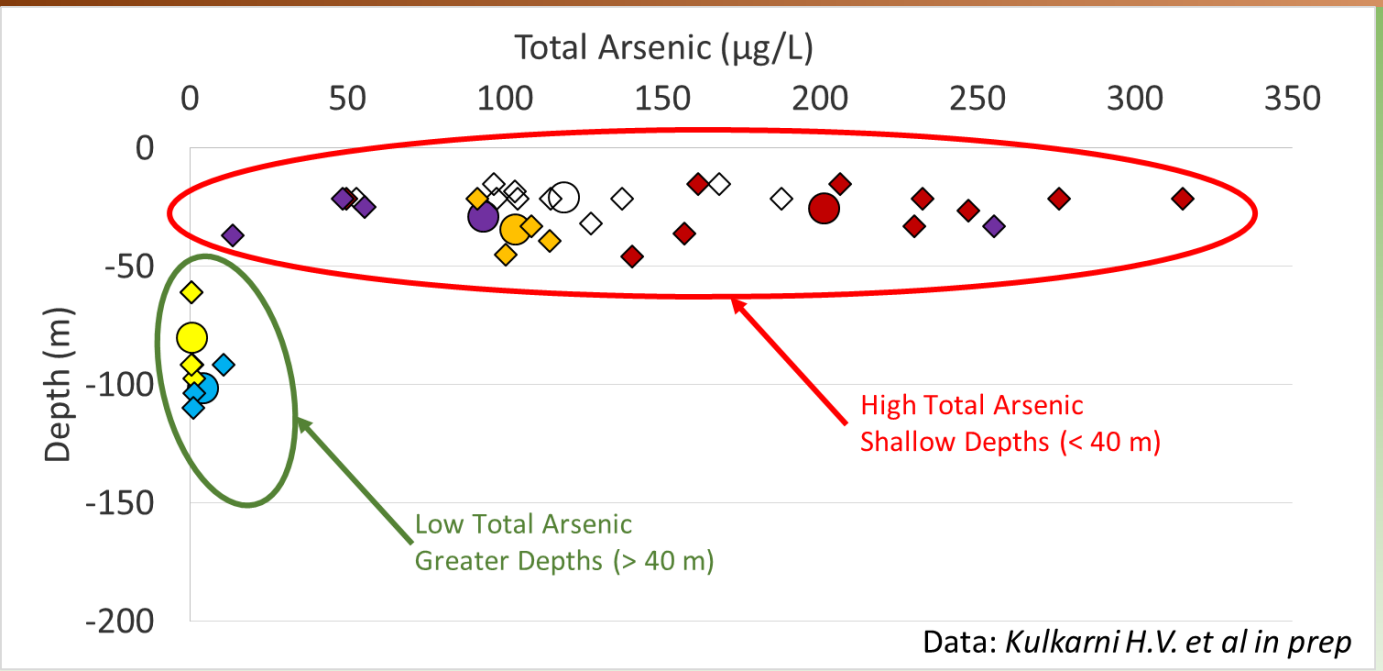
Pre-Monsoon (PRM) Sampling : 29th May – 8th June, 2015
Post-Monsoon (PSTM) Sampling: 20th July – 13th August, 2015

Results: Cl^-



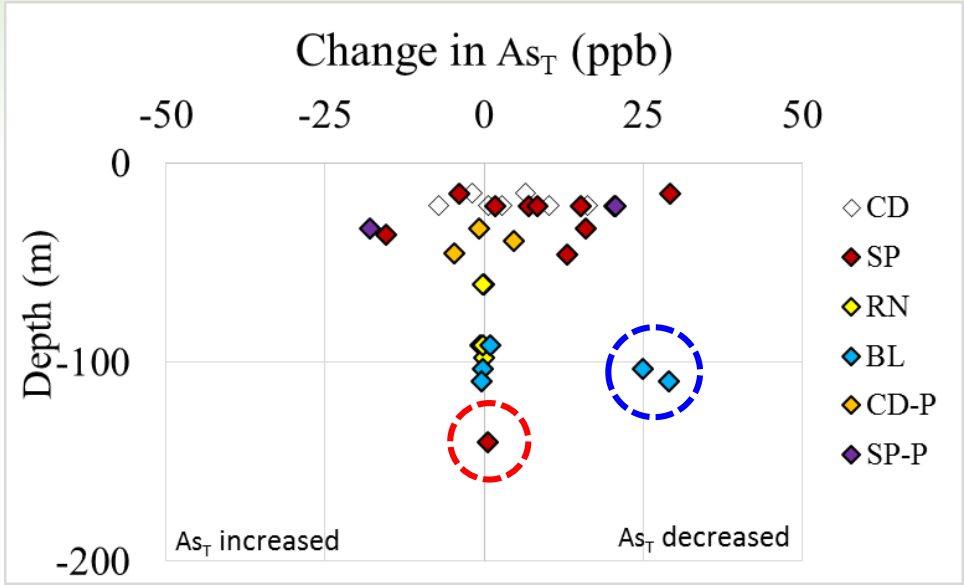
- A natural tracer (conservative anion)
- PRM – PSTM variations were observed only at shallow (< 40 m) depths.
- Suggests that variations in other parameters at greater depths may not be directly linked to the vertical mixing.

Results: Arsenic

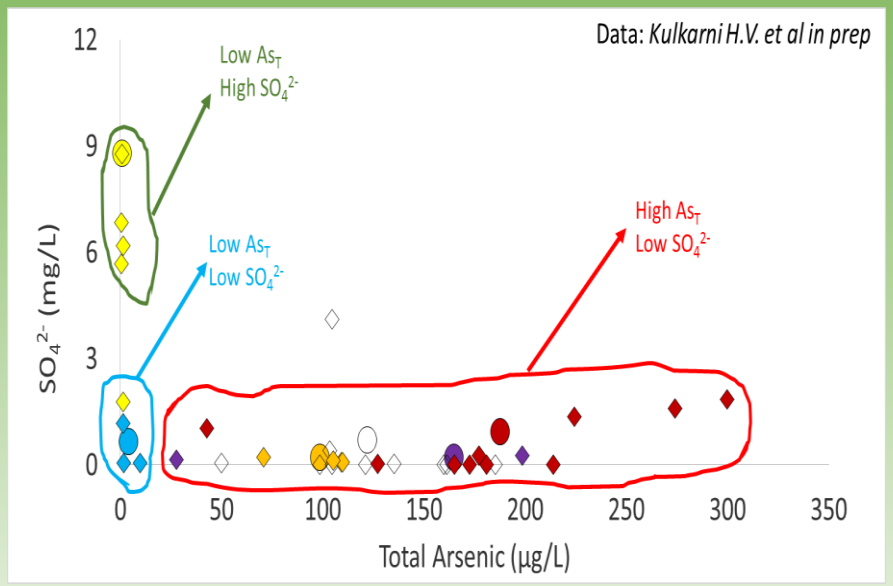


- ✓ Well # 28, 29 have exceptionally high As at BL site.
- ✓ Well # 22, has exceptionally low As at SP site.

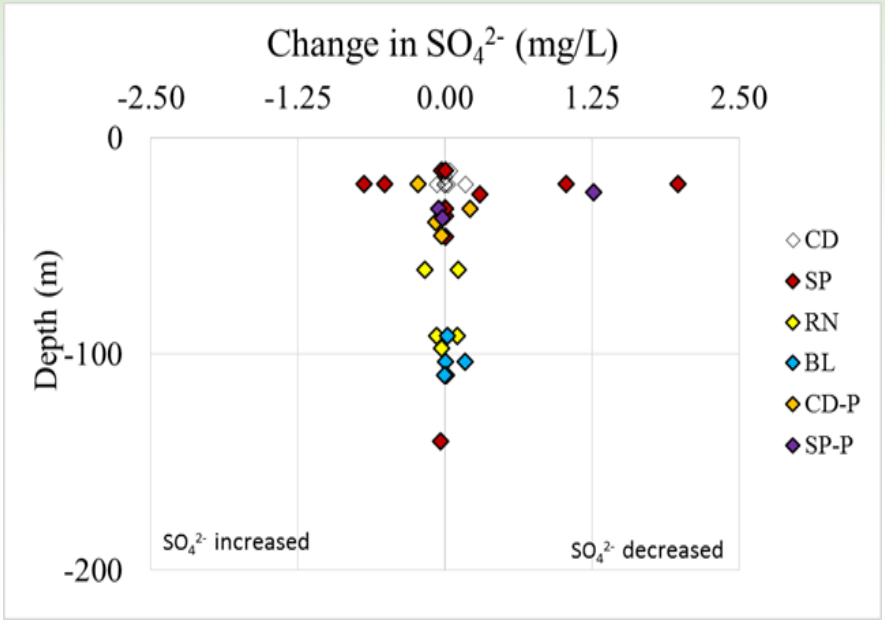
- ➢ Shallow depths ~ Holocene Gray Sediments ~ High As
- ➢ Greater depths ~ Pleistocene Orange Sediments ~ Low As

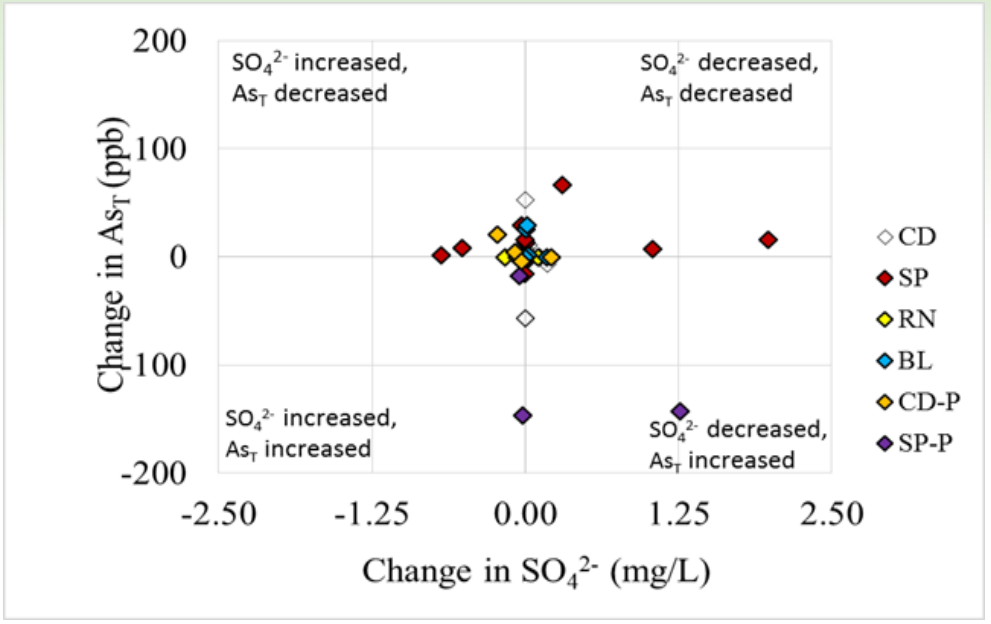


Results: SO_4^{2-}



- High As ~ Low SO_4^{2-} / Low As ~ High SO_4^{2-}
- CD & SP sites are High As – Low SO_4^{2-}, consistent with dominant microbial Fe (III) reduction and As release.
- RN site is Low As – High SO_4^{2-}, consistent with lack of microbial Fe (III) reduction. Comparatively less reducing conditions.
- BL site is Low As – Low SO_4^{2-}, interestingly, two wells (28,29) at this site had exceptionally high As. May explain overall low SO_4^{2-} concentrations.

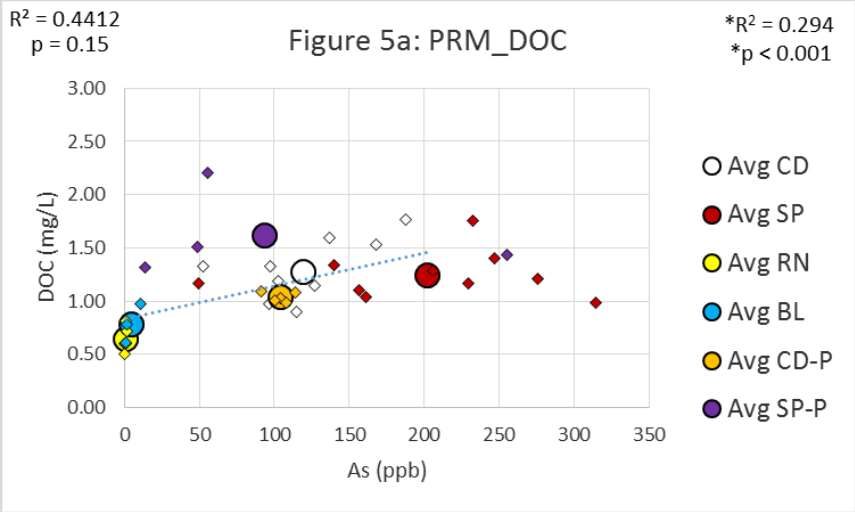


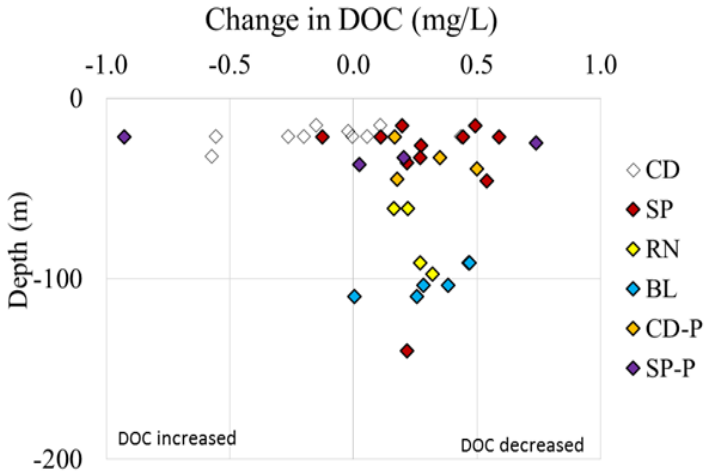


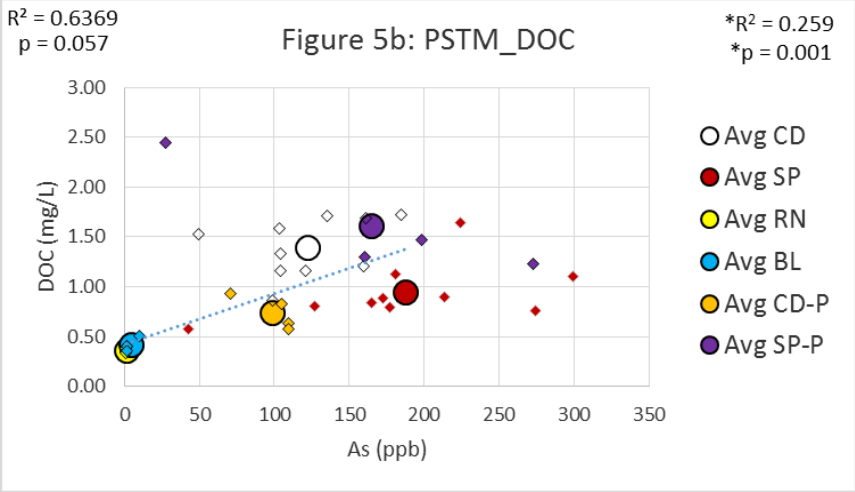
Results: DOC

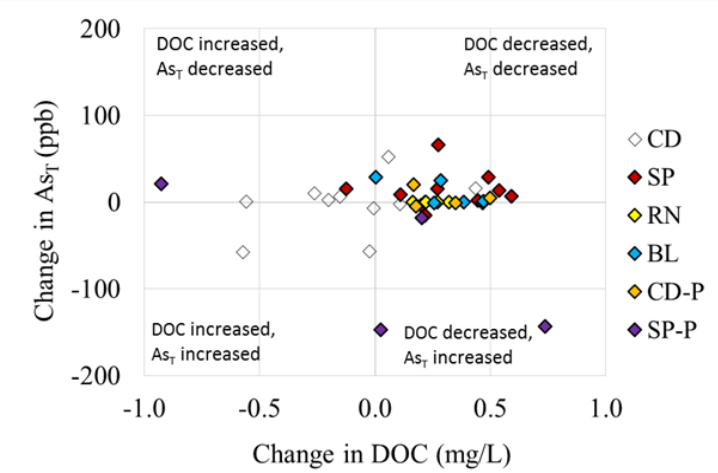
R^2 and p values from linear regression of average values, n = 6.

*R2 and *p values from linear regression of all samples, n = 39







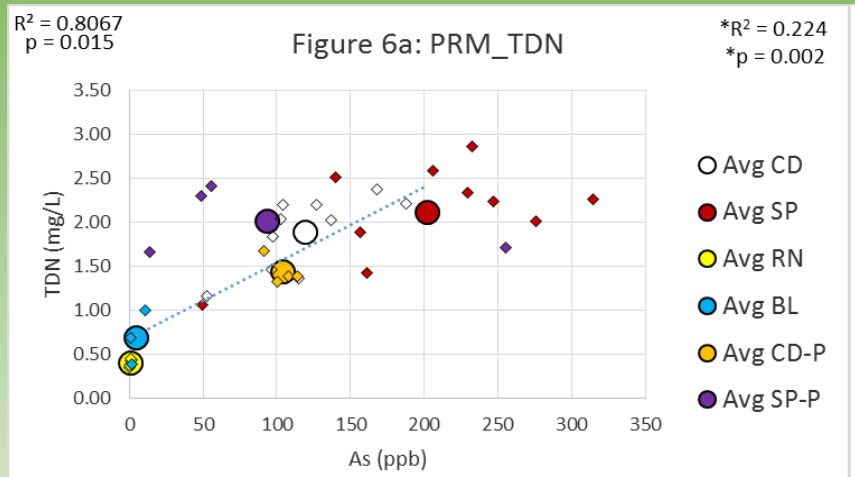


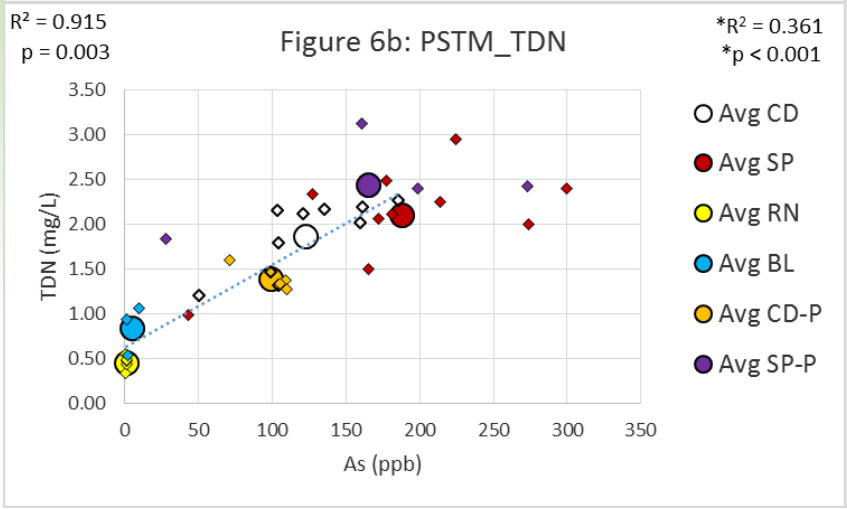
- Wells at CD & SP sites have 1 ppm > DOC < 2.5 ppm, consistent with high As, low SO_4^{2-}
- Wells at RN & BL sites have DOC < 1 ppm, consistent with low As, high SO_4^{2-}
- PRM-PSTM DOC varied (mostly decreased) in both shallow and deep samples.

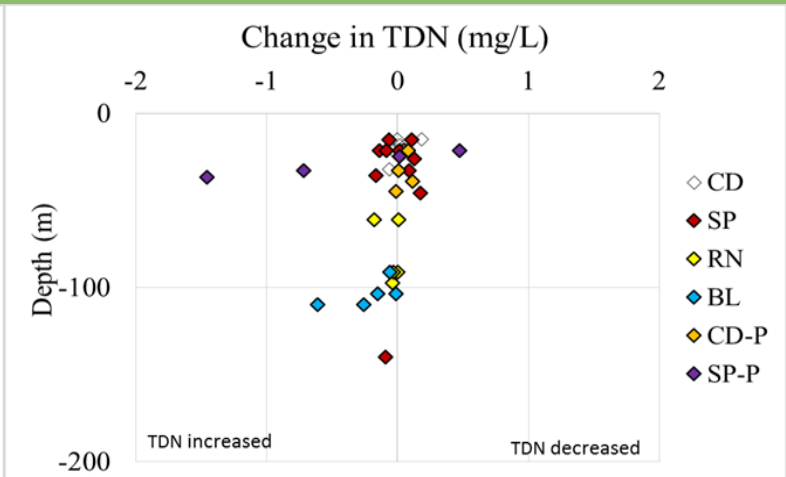
Results: TDN

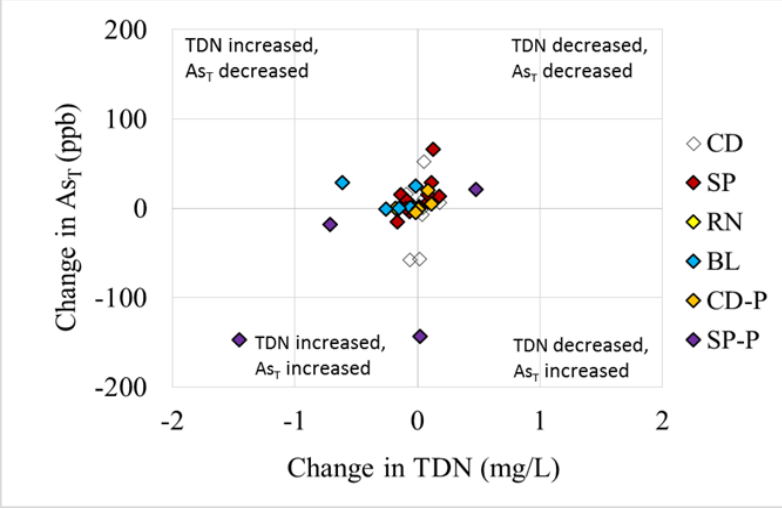
R^2 and p values from linear regression of average values, n = 6.

*R2 and *p values from linear regression of all samples, n = 39



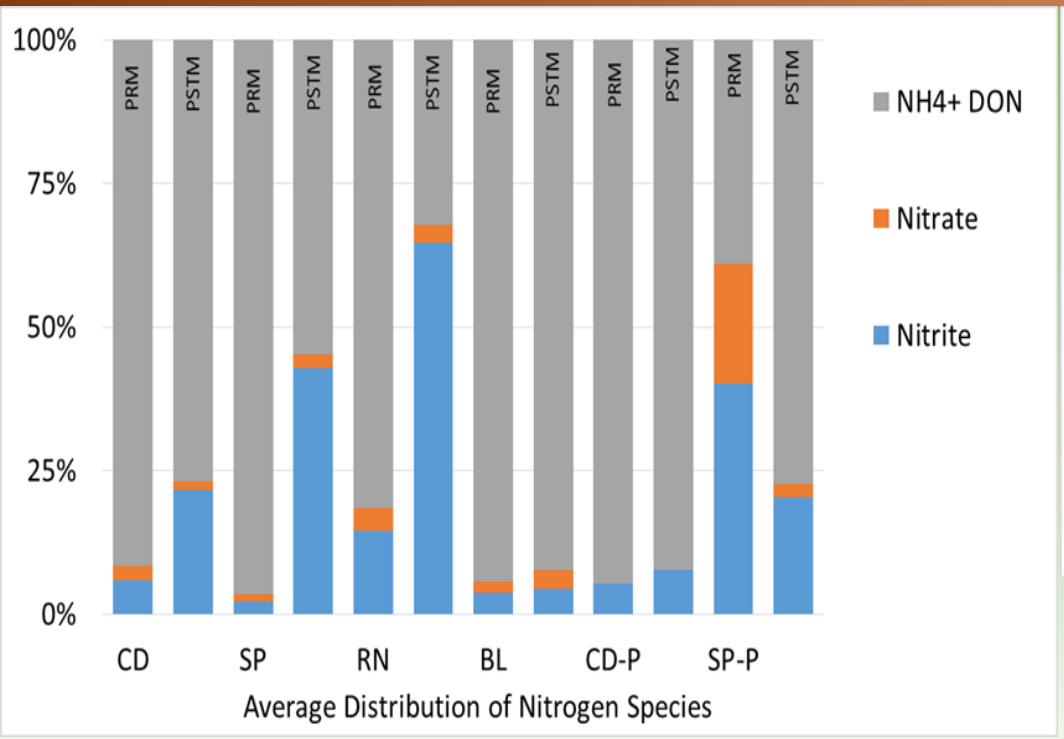


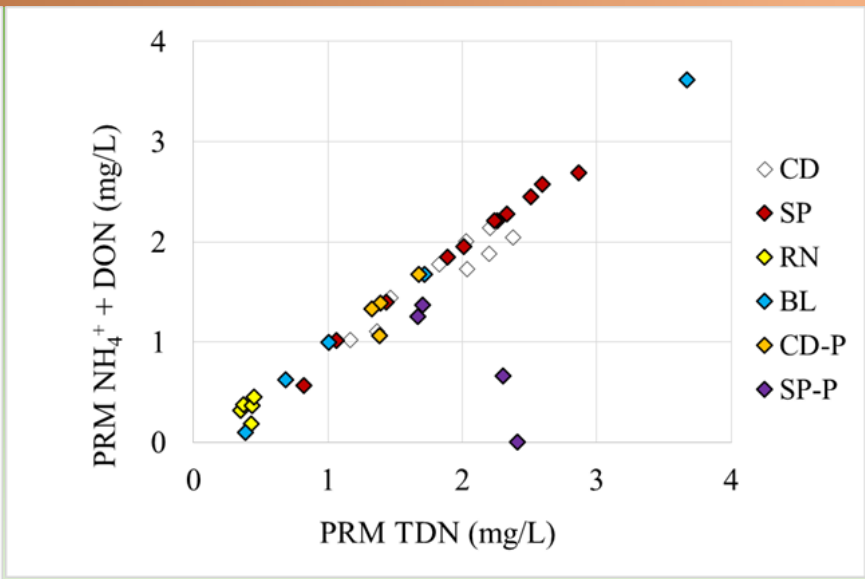




- Wells at CD & SP sites have 1 ppm > TDN < 3 ppm, consistent with high As, high H:P, high DOC and low SO_4^{2-}.
- Wells at RN and BL sites have TDN < 1 ppm, consistent with low As, low H:P, low DOC and high SO_4^{2-}.

Results: TDN



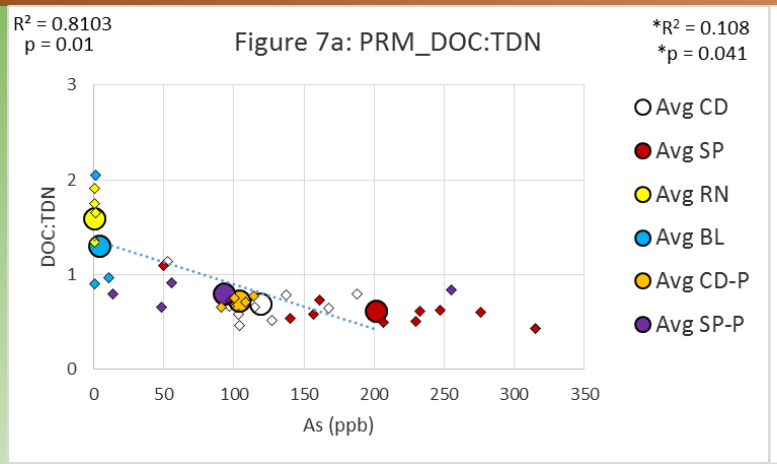


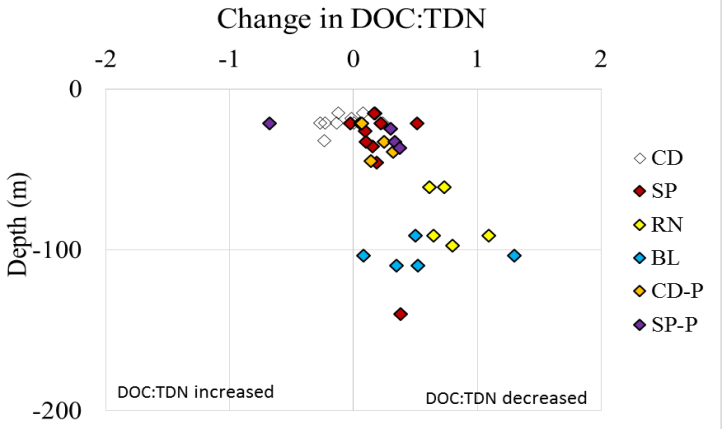
- TDN = NO_3^- + NO_2^- + NH_4^+ + DON
- Considerable NO_2^- increased at CD and SP sites in PSTM samples, may indicate some nitrate/nitrite using bacteria activity due to mixing of oxygenated rainwater at shallow depths (?).
- Considerable increase in NO_2^- at RN (deep wells) site also occurred. RN and BL sites are comparatively less reducing than CD & SP sites. But this increase in PSTM NO_2^- at RN alone, may not be associated with mixing of oxygenated rainwater at such greater depths.
- (NH_4^+ + DON) is strongly correlated with TDN, and hence also with As_T

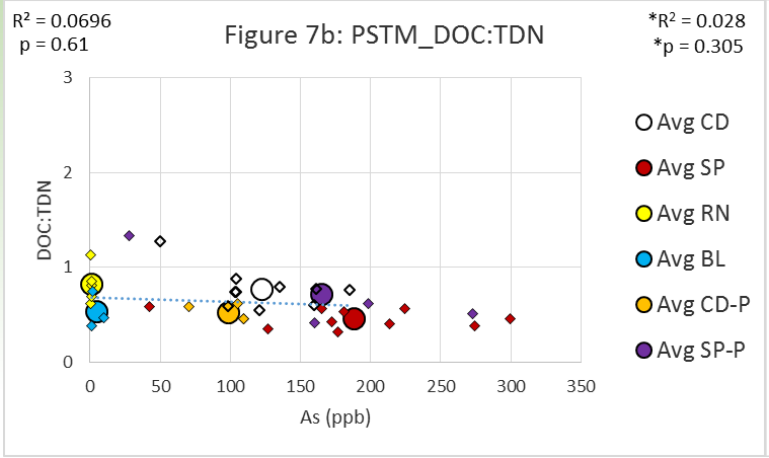
Results: (DOC:TDN)

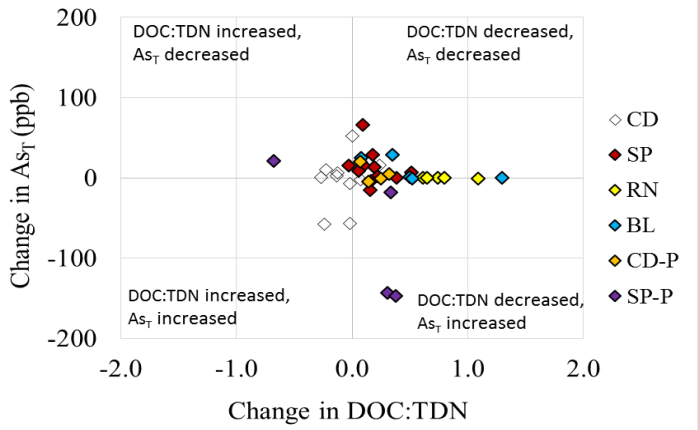
R^2 and p values from linear regression of average values, n = 6.

*R2 and *p values from linear regression of all samples, n = 39

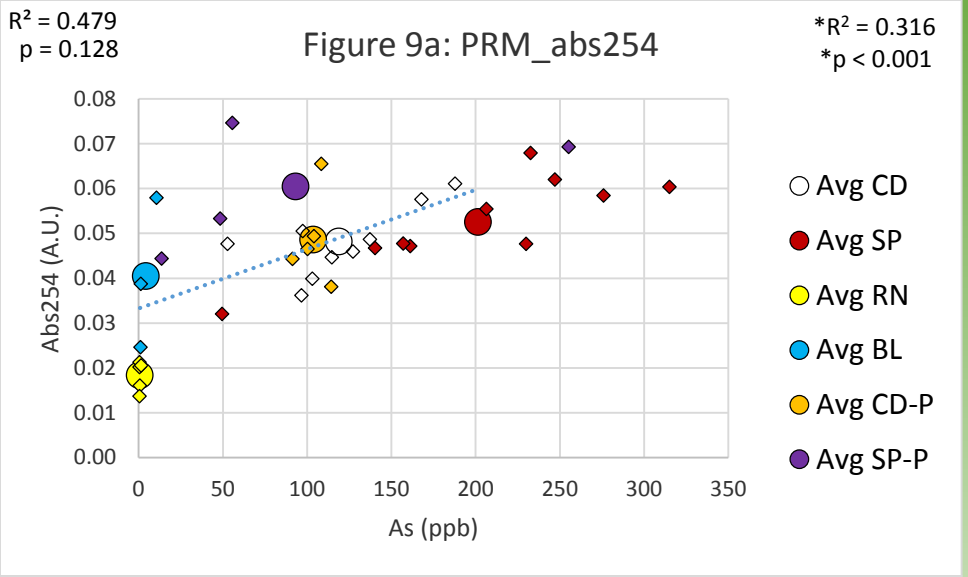


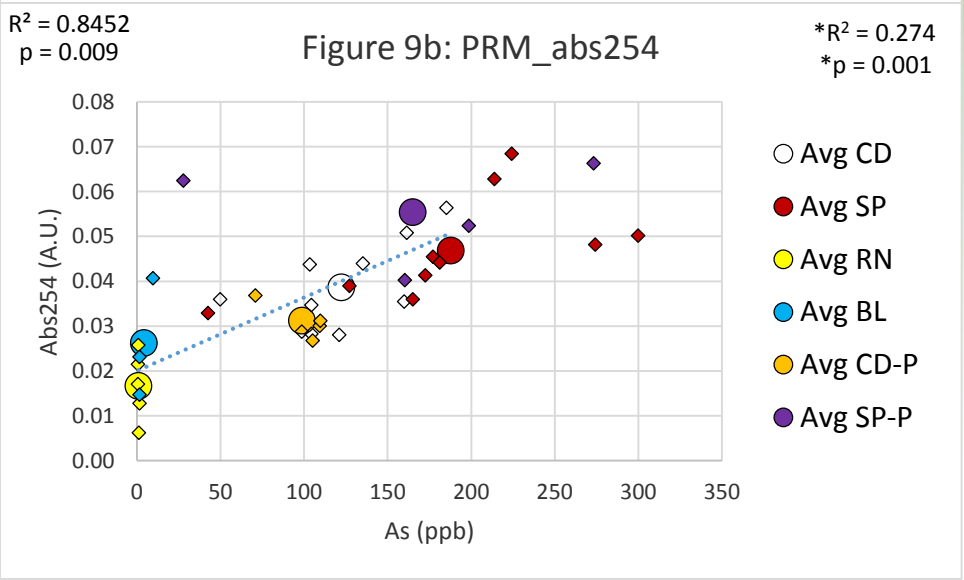




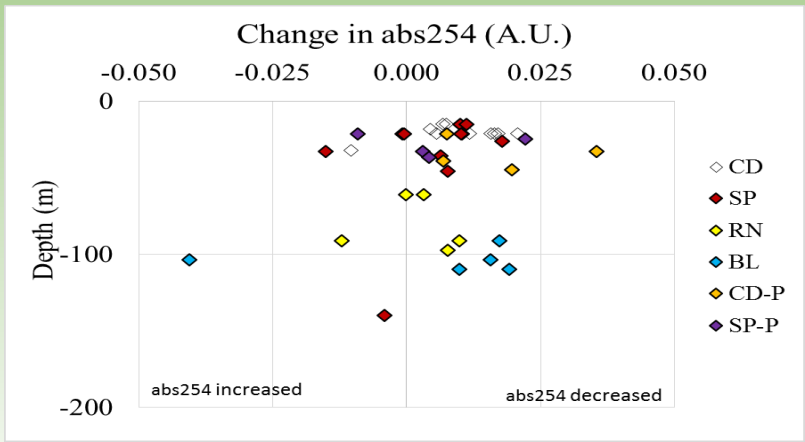


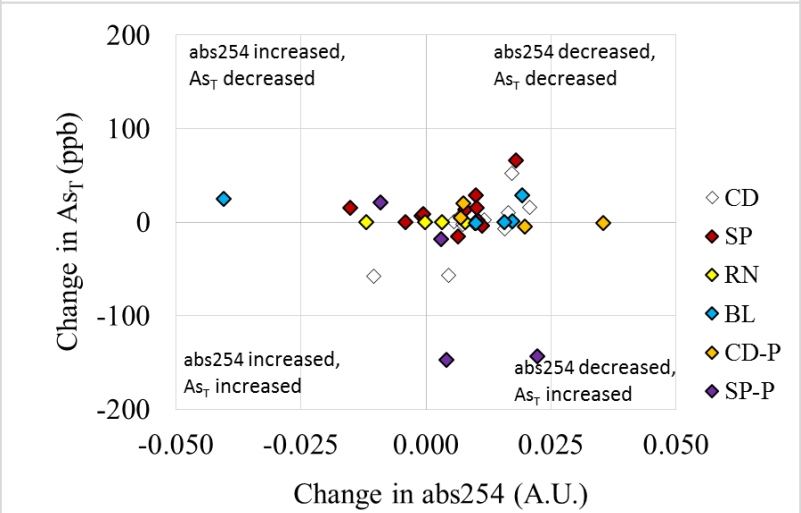
- High As ~ Low DOC:TDN during PRM. No correlation during PSTM.
- Wells at CD & SP sites have DOC:TDN < 1 (i.e. DOC < TDN) during both PRM and PSTM.
- Wells at RN & BL sites have DOC:TDN >1 (i.e. DOC > TDN) during PRM and DOC:TDN < 1 (i.e. DOC < TDN) during PSTM.





- High AS ~ High abs254
- CD & SP sites had higher abs254 than RN & BL sites, consistent with higher H:P ratio, higher DOC and higher dissolved iron (?) at CD & SP.
- Post-Monsoon changes: Significant, p = 0.002, t-test, n = 39. At all sites, PSTM abs254 intensity decreased. This decrease was correlated with decrease in arsenic in majority of samples.

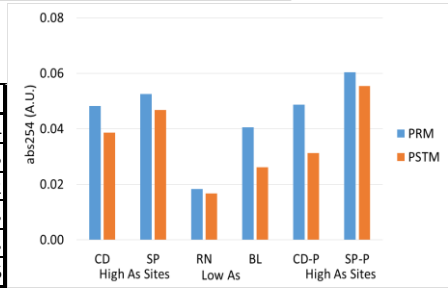


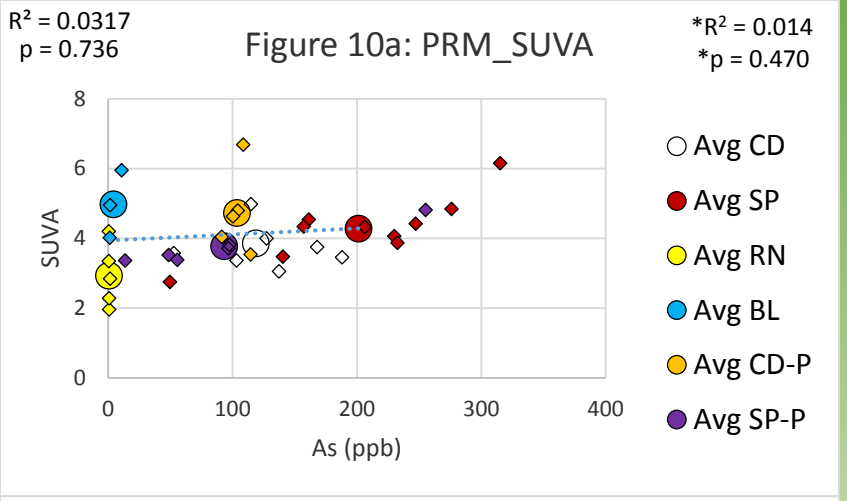


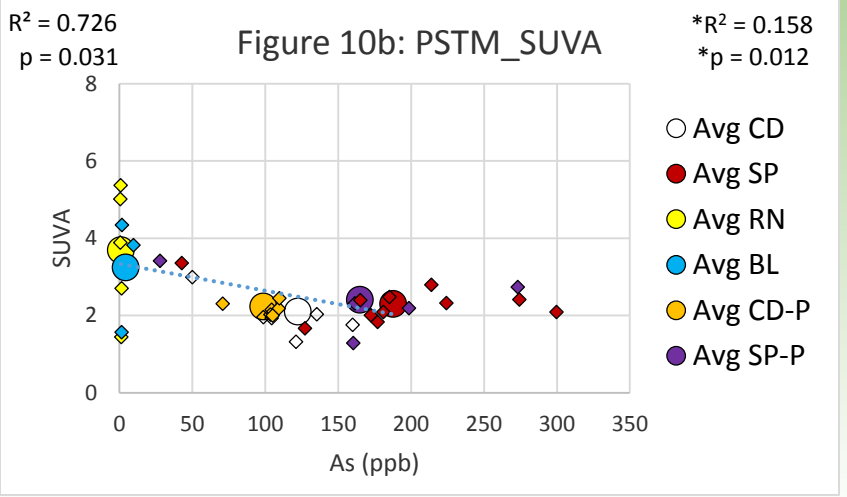
- R^2 and p values from linear regression of average values, n = 6. Trend line shows average trend.
- *R2 and *p values from linear regression of all samples, n = 39

Avg. abs254 (A.U.)

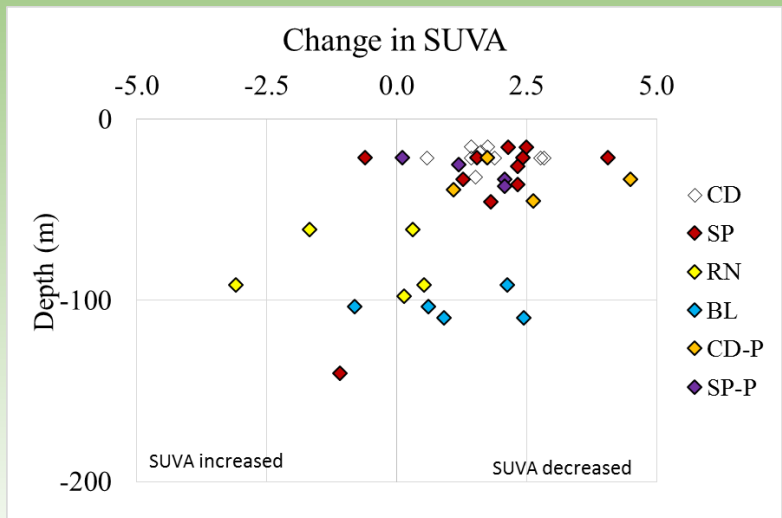
SITE	PRM	PSTM
CD	0.05	0.04
SP	0.05	0.05
RN	0.02	0.02
BL	0.04	0.03
CD-P	0.05	0.03
SP-P	0.06	0.06

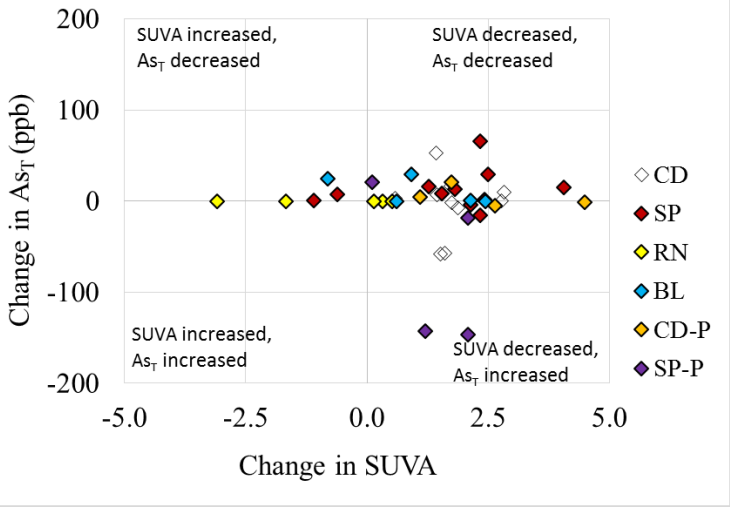






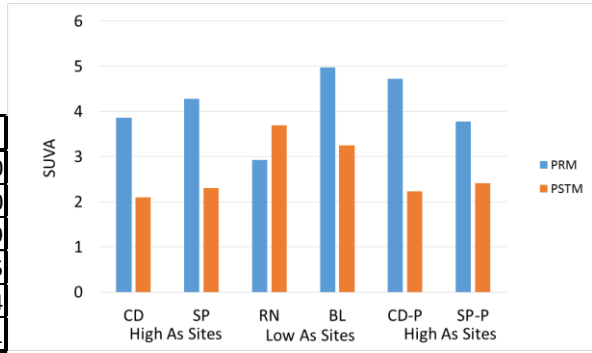
- No correlation with As during PRM.
- Post-Monsoon changes: Significant, $p < 0.001$, t-test, $n = 39$.
- During PRM, all sites have SUVA in the similar range. PSTM SUVA of shallower samples seems to decrease significantly than that of deeper samples. Dilution at shallower depths.
- Decrease in SUVA consistent with decrease in DOC and abs254, but contrasting with seemingly increase in H:P ratio.

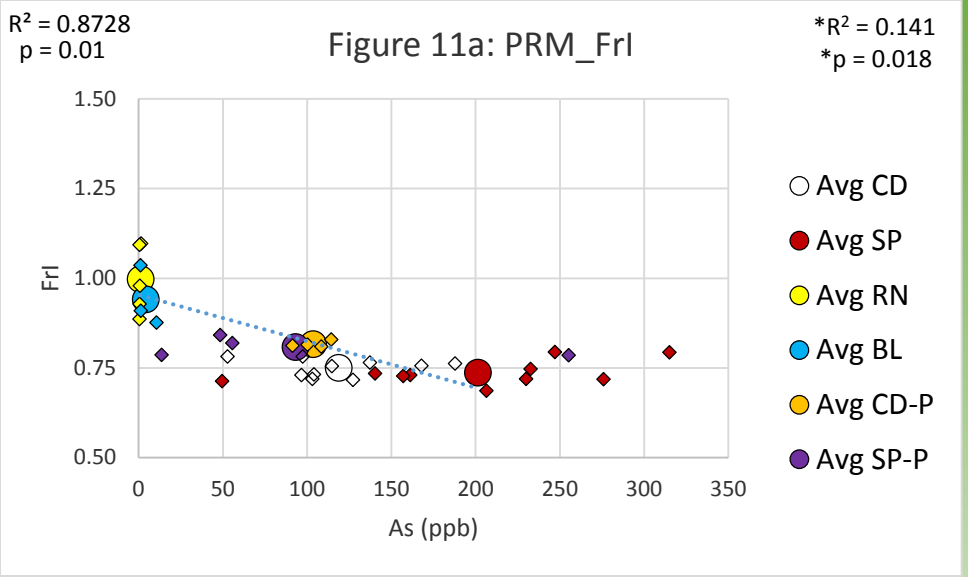


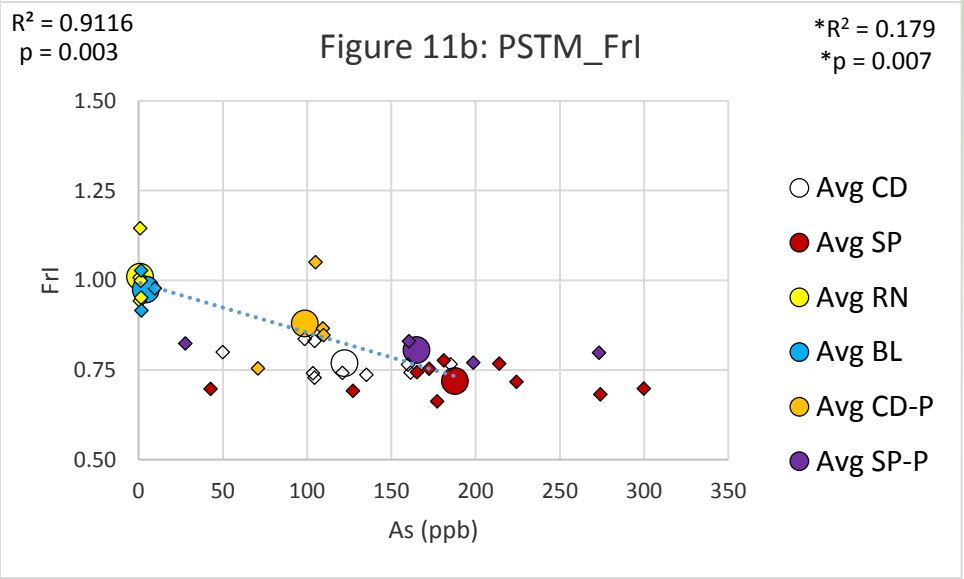


- R^2 and p values from linear regression of average values, n = 6. Trend line shows average trend.
- *R2 and *p values from linear regression of all samples, n = 39

SITE	PRM	PSTM
CD	3.86	2.10
SP	4.28	2.30
RN	2.93	3.69
BL	4.98	3.25
CD-P	4.73	2.24
SP-P	3.78	2.41

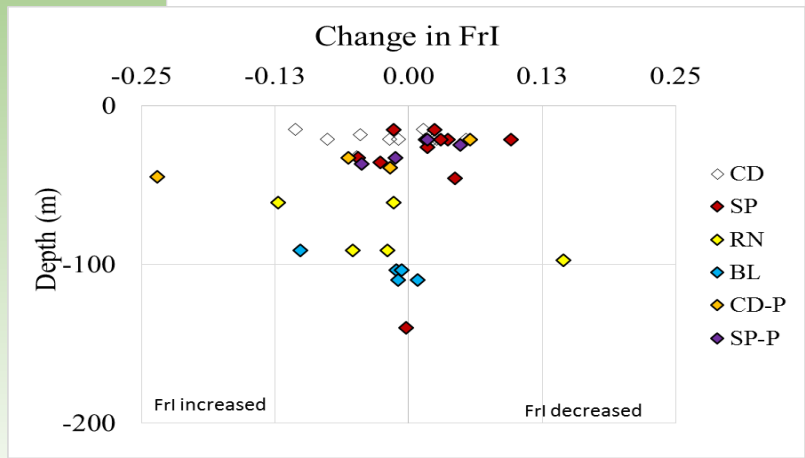


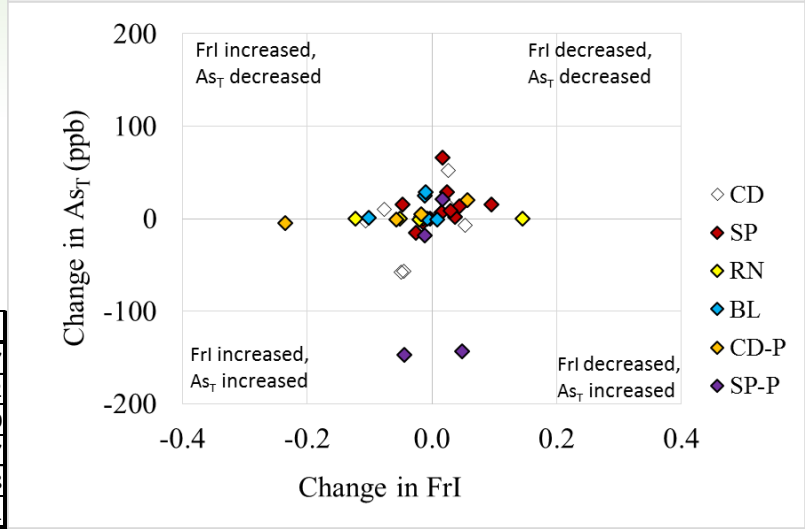




- R^2 and p values from linear regression of average values, n = 6. Trend line shows average trend.
- *R2 and *p values from linear regression of all samples, n = 39

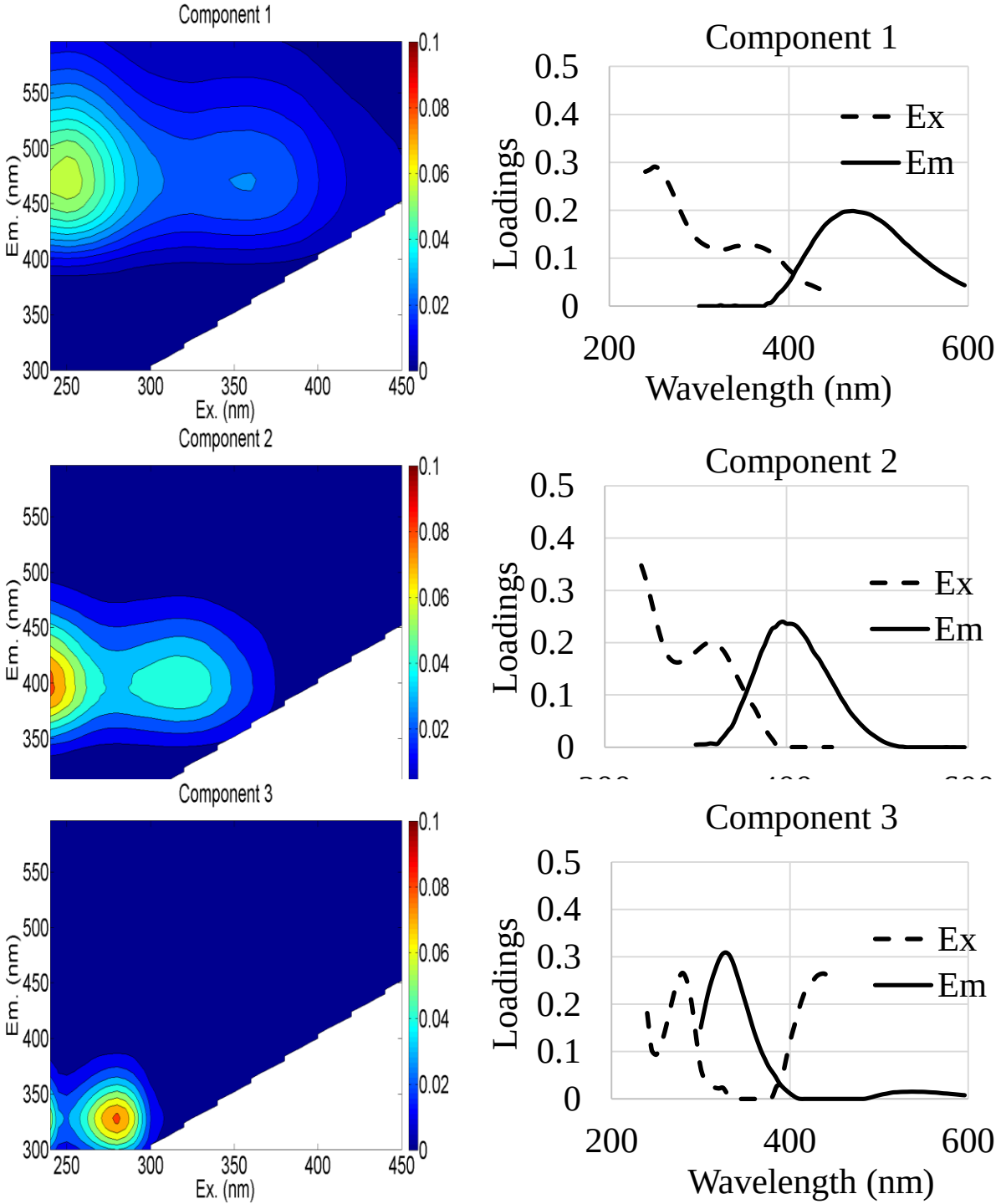
- High As ~ Low FrI / Low As ~ High FrI
- CD & SP sites have lower FrI than RN & BL sites, consistent with Murshidabad study.
- Post-Monsoon changes: <u>Not Significant, p = 0.279, t-test, n = 39</u>





Avg. FrI

SITE	PRM	PSTM
CD	0.75	0.77
SP	0.74	0.72
RN	1.00	1.00
BL	0.94	0.97
CD-P	0.82	0.88
SP-P	0.81	0.81

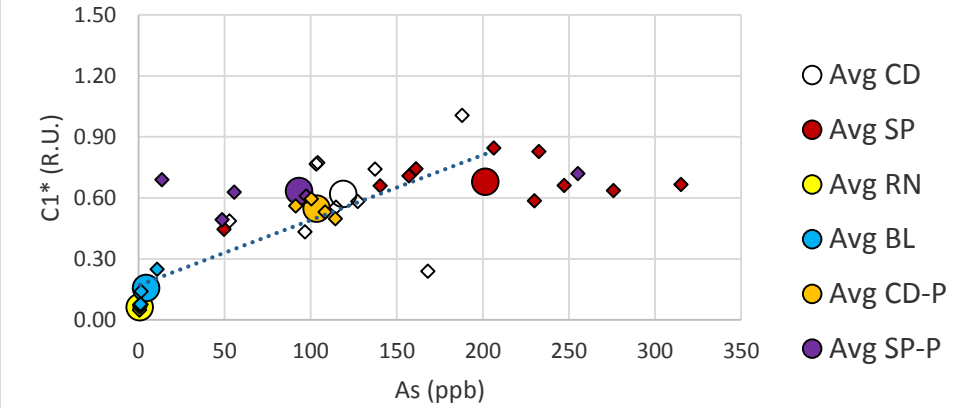


EEM spectra (left) and emission-excitation curve (right) showing loadings of three PARAFAC components identified in the model

R^2 = 0.8183
p = 0.013

Figure 13a: PRM_C1*

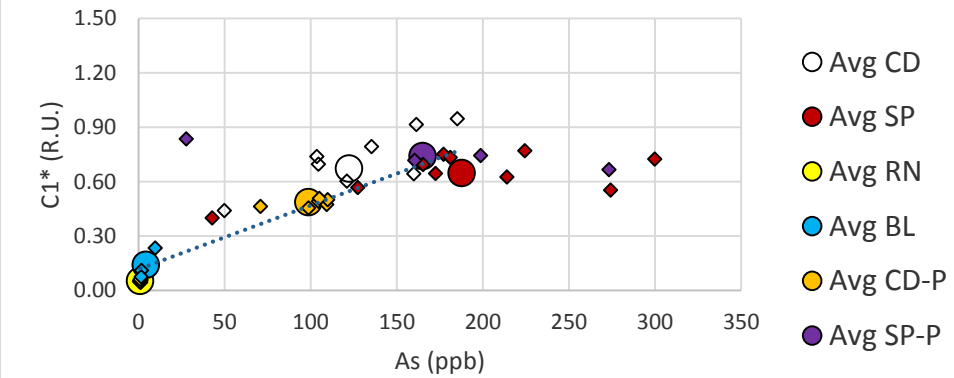
*R^2 = 0.121
*p = 0.03



R^2 = 0.9069
p = 0.003

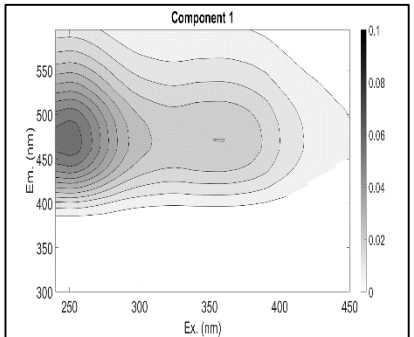
Figure 13b: PSTM_C1*

*R^2 = 0.341
*p < 0.001



- R^2 and p values from linear regression of average values, n = 6. Trend line shows average trend.
- *R2 and *p values from linear regression of all samples, n = 39

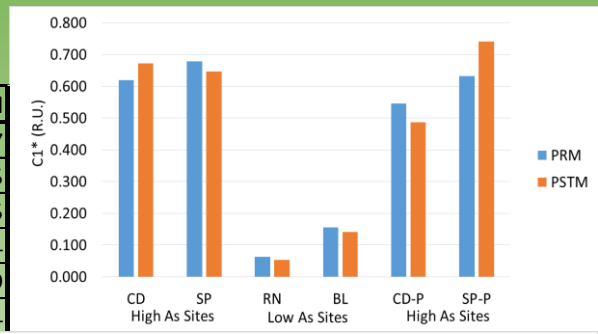
C1*: Terrestrial Humic-like
240 (360) / 460

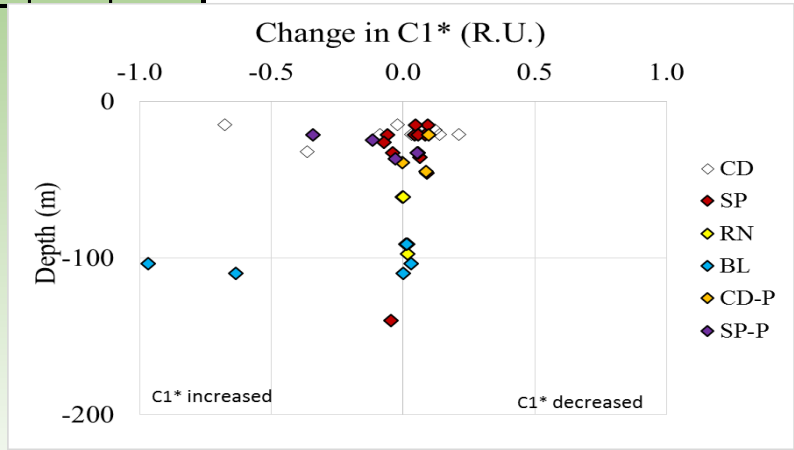


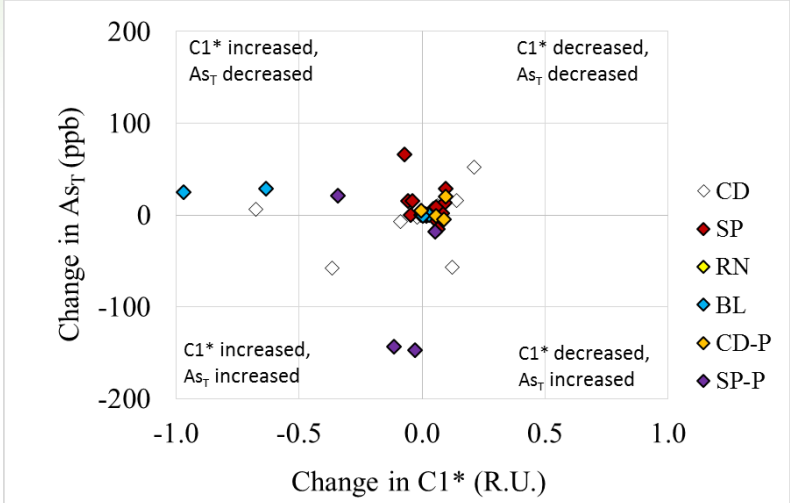
- Arsenic increases with increase in C1*
- Post-Monsoon changes: <u>Not Significant, p = 0.19, t-test, n = 39</u>

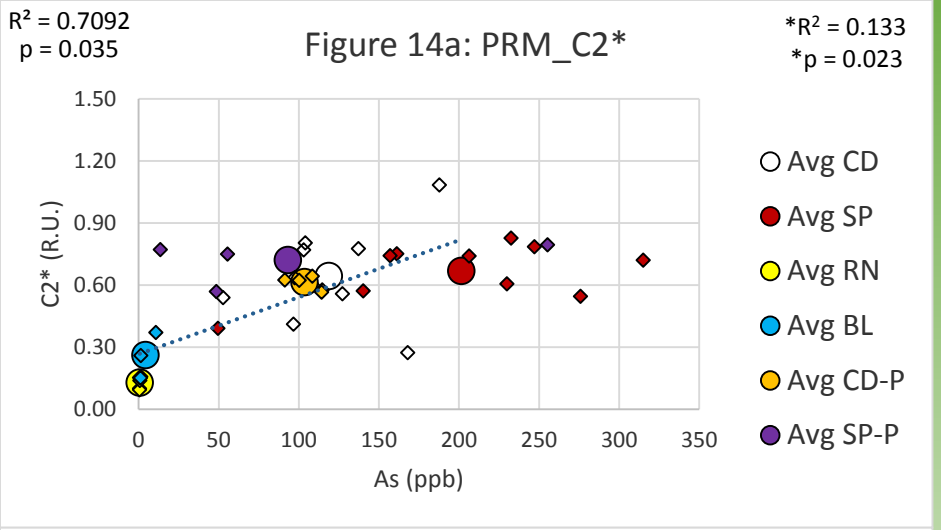
Avg. C1* (R.U.)

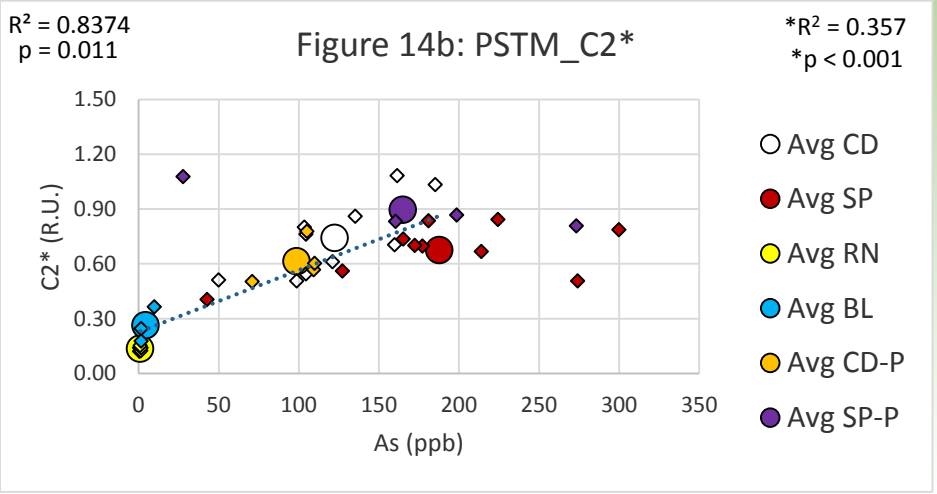
SITE	PRM	PSTM
CD	0.62	0.67
SP	0.68	0.65
RN	0.06	0.05
BL	0.16	0.14
CD-P	0.55	0.49
SP-P	0.63	0.74





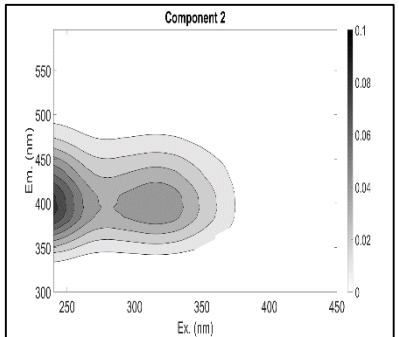






- R^2 and p values from linear regression of average values, n = 6. Trend line shows average trend.
- *R2 and *p values from linear regression of all samples, n = 39

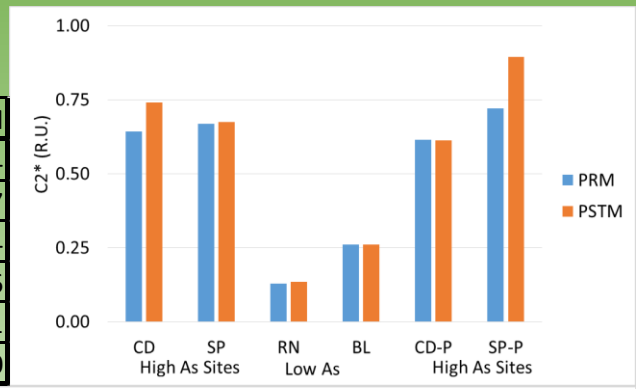
C2*: Humic-like, impacted by agriculture, wastewater activity
240 (320) / 400

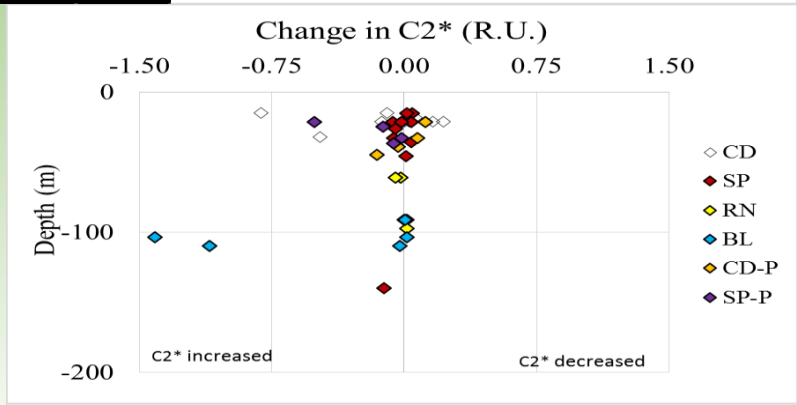


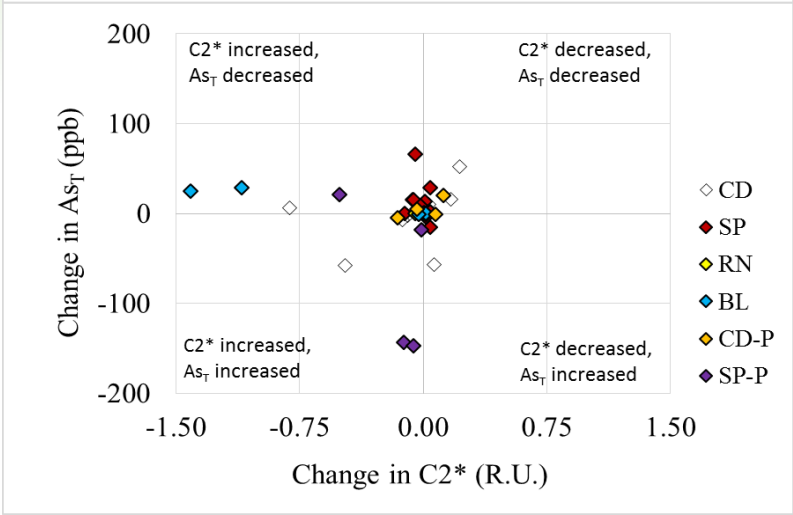
- Arsenic increases with increase in C2*
- Post-Monsoon changes: Significant, p = 0.037, t-test, n = 39

Avg. C2* (R.U.)

SITE	PRM	PSTM
CD	0.64	0.74
SP	0.67	0.67
RN	0.13	0.14
BL	0.26	0.26
CD-P	0.61	0.61
SP-P	0.72	0.90



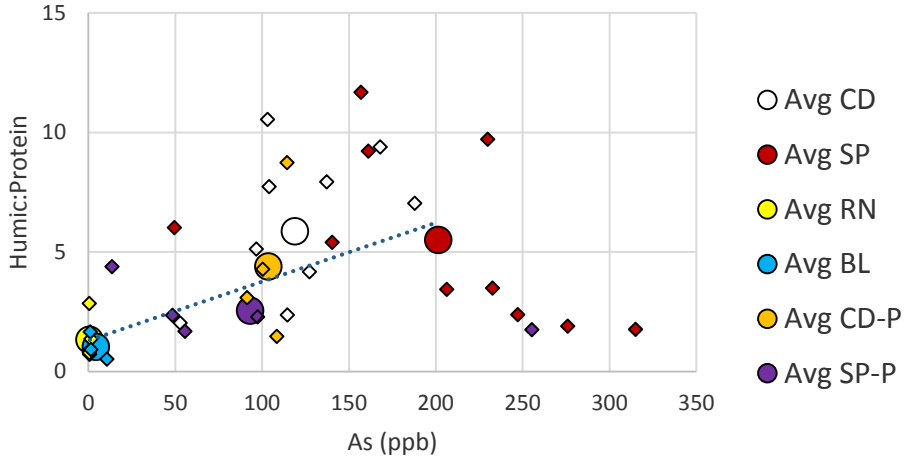




R^2 = 0.7835
p = 0.019

Figure 15a: PRM_Humic:Protein

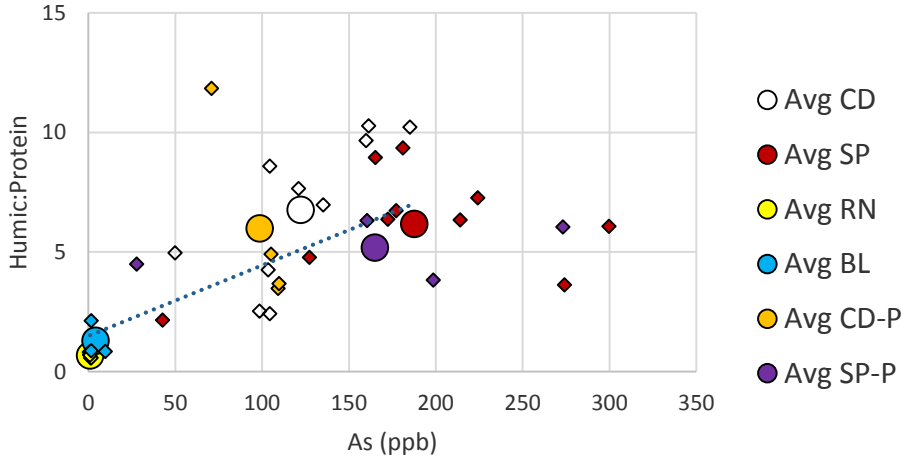
*R^2 = 0.159
*p = 0.012



R^2 = 0.7676
p = 0.022

Figure 15b: PSTM_Humic:Protein

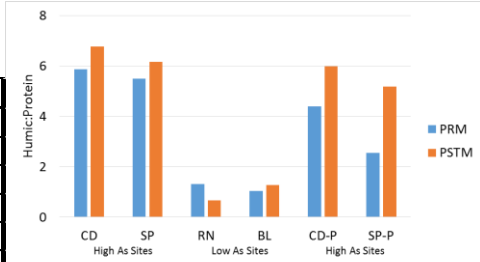
*R^2 = 0.35
*p < 0.001



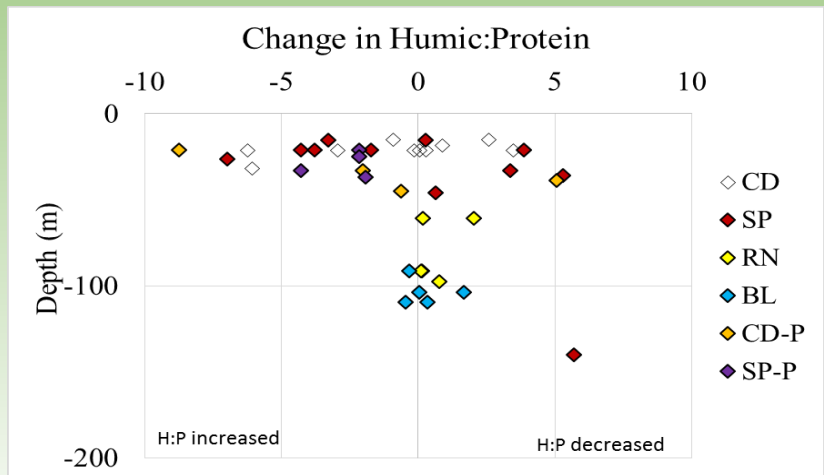
- R^2 and p values from linear regression of average values, n = 6. Trend line shows average trend.
- *R2 and *p values from linear regression of all samples, n = 39

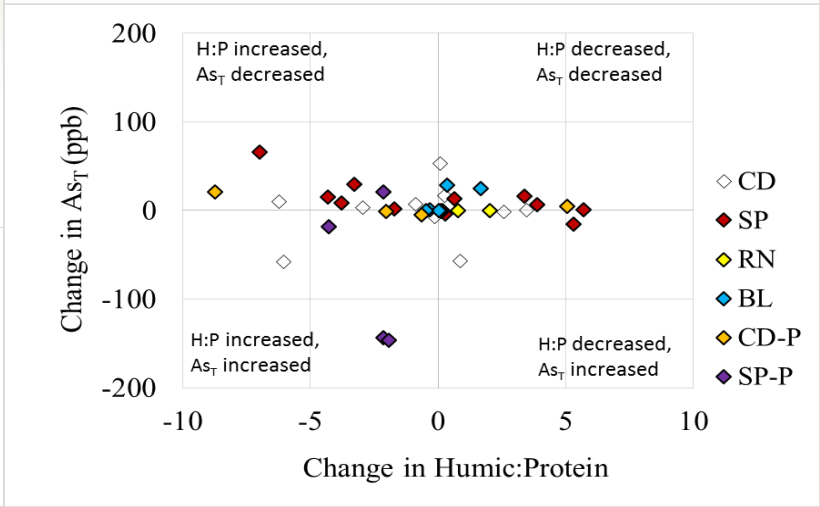
Avg. Humic:Protein

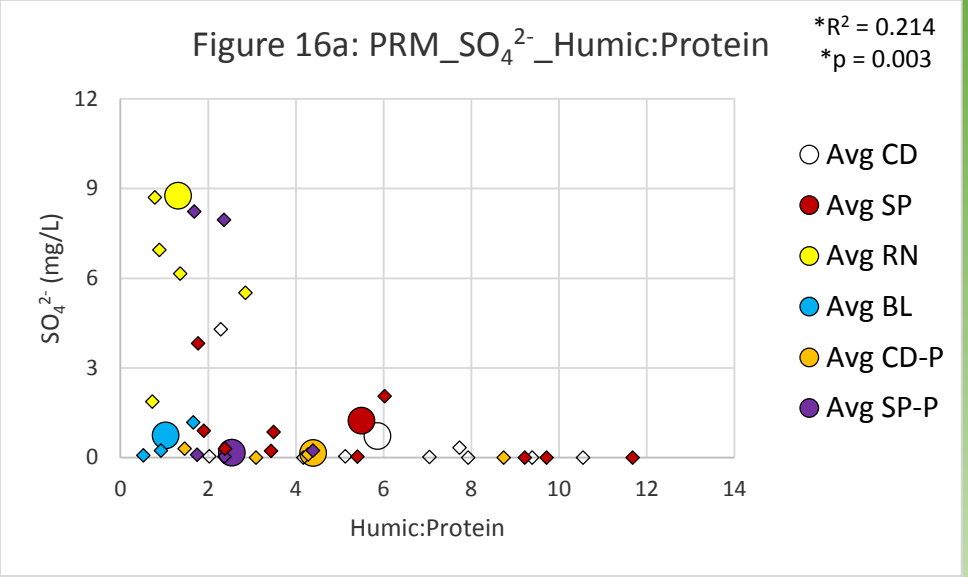
SITE	PRM	PSTM
CD	5.86	6.76
SP	5.50	6.16
RN	1.32	0.67
BL	1.03	1.28
CD-P	4.39	5.98
SP-P	2.55	5.17

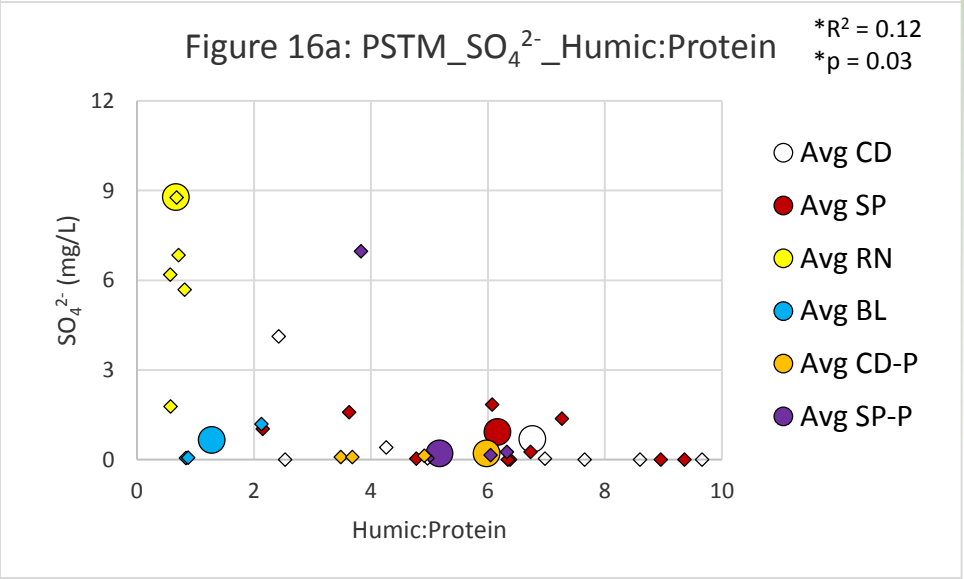


- High As ~ High Humic:Protein
- CD & SP sites have higher H:P than RN & BL sites, consistent with Murshidabad study. So, High As – High H:P – Low SO_4^{2-}
- PSTM changes: Not Significant, p = 0.292, t-test, n = 39. Increased in many shallow samples. The only deep well # 22 (140 m, SP site, exceptional low As) showed decrease in H:P ratio. All other deep wells at RN and BL sites, did not show such decrease in H:P.

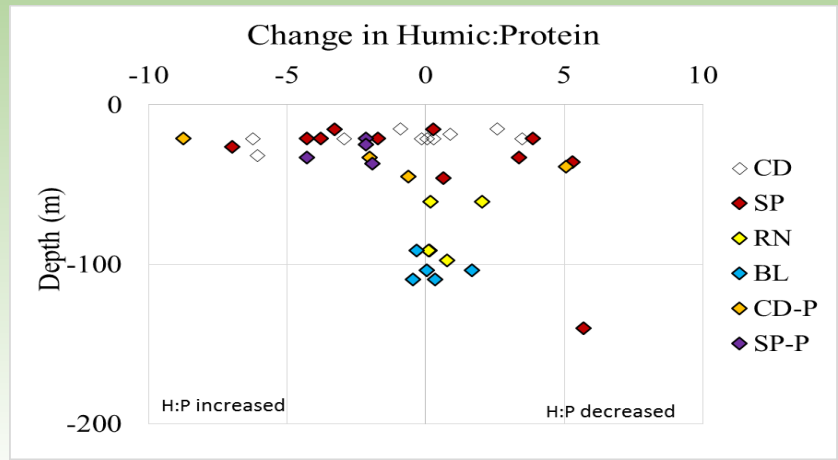


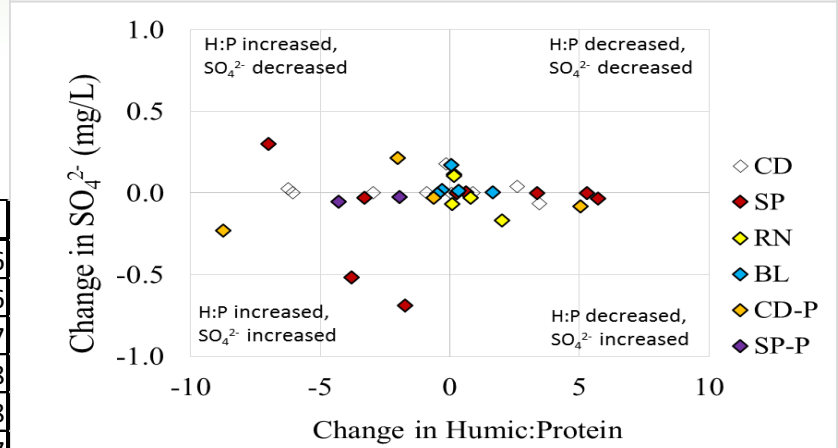






- High Humic:Protein ~ Low SO_4^{2-} / Low Humic:Protein ~ High SO_4^{2-}
- CD & SP sites are high Humic:Protein – low SO_4^{2-}, support humic-mediated microbial Fe (III) reduction and As release.
- Wells at RN site have high SO_4^{2-} and low Humic:Protein, supporting presence of less humified DOM associated with lower microbial reductive dissolution and less As release.
- Wells at BL have low SO_4^{2-} and Humic:Protein, consistent with As- SO_4^{2-}.
- PRM-PSTM Humic:Protein varied (mostly increased) at shallow depth, overall statistically not significant (p = 0.292, t-test, n = 39).





Avg. SO_4^{2-} (mg/L)

SITE	PRM	PSTM
CD	0.72	0.69
SP	1.23	0.92
RN	8.76	8.77
BL	0.74	0.65
CD-P	0.15	0.20
SP-P	0.16	0.20

Avg. Humic:Protein

SITE	PRM	PSTM
CD	5.86	6.76
SP	5.50	6.16
RN	1.32	0.67
BL	1.03	1.28
CD-P	4.39	5.98
SP-P	2.55	5.17

Summary

- Vertical mixing due to monsoonal recharge was limited to shallow depths (< 40m).
- Redox sensitive processes and DOM quality was affected even at greater depths.
- Shallow depths ~ High As ~ Low SO_4^{2-} ~ High DOC ~ High TDN ~ High abs254 ~ Low β: α ~ High Humic: Protein.
- At shallow depths, mixing effect, vertical movement exceeds lateral movement, less sedimentary DOC transported laterally.
- At greater depths, no mixing effect, irrigation pumping is stopped which slows down the lateral movement, less sedimentary DOC transported laterally.

Thank You

For Any Questions, Please Contact
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