

# Mineralogical hosts of reactive arsenic within reduced deltaic soils and sediments of Southeast Asia

Jason W. Stuckey<sup>1</sup> and Scott Fendorf<sup>1</sup>

<sup>1</sup>Department of Environmental Earth System Science, Stanford, CA 94305

## Introduction/Objectives

Millions of people in the deltaic regions of S/SE Asia regularly consume arsenic contaminated groundwater. Within the Mekong Delta of Cambodia, for example, arsenic persists within the groundwater despite being flushed by several pore volumes of recharge. The identity and reactivity of the minerals contributing to the persistence of arsenic in the deltaic aquifers remain elusive. Here we seek to define the molecular form of the arsenic and its host phases along two defined flow paths: i) in a seasonally saturated wetland (Seasonal Site) and ii) in a continuously saturated wetland (Flooded Site).

## Seasonal Site



## Flooded Site



## Methods

### Total and Reactive Arsenic

Sediment cores were retrieved from depths of 0.2 to 6 m at the Seasonal Site and from 0.2 to 4 m at the Flooded Site. Sediments were dried under 95%N<sub>2</sub>/5%H<sub>2</sub> atmosphere. A 1 M hydrochloric acid (HCl) extraction was performed on the bulk sediments to quantify the “reactive” As pool – from the dissolution of amorphous Fe/Mn oxides, acid volatile sulfides, and carbonates (Keon et al., 2001). Total arsenic concentrations were determined by X-ray fluorescence (XRF). The reactive and total arsenic concentrations are displayed as a function of depth for each site (Figure 1).

### X-ray Absorption Spectroscopy

Arsenic speciation was determined for the bulk sediments and clay size fraction (< 2 μm) by X-ray absorption near-edge structure (XANES) spectroscopy – the clay size fraction was isolated by sonication for 10 h followed by gravity separation in anoxic deionized water. Linear combination fitting of XANES fluorescence spectra was optimized over a range of 11850 to 11890 eV using normalized spectra of five standards representing the potential As species within the aquifers. The results of the linear combination fits are displayed as a function of depth for each site (Figures 1 and 2). Iron extended X-ray absorption fine structure (EXAFS) spectroscopy was used to determine the iron mineralogy of the bulk sediments. Energy scans for Fe EXAFS were collected from -230 to +900 eV about the Fe foil edge. A spline function was fit through the absorption envelope and subtracted from each spectrum. The resulting EXAFS function (chi) was transformed from eV to k-space (Å<sup>-1</sup>) and weighted by k<sup>3</sup>. Linear combination fitting of the Fe EXAFS chi function was performed over a k range of 3 to 12 Å<sup>-1</sup> using 30 different iron mineral standard spectra. The chi functions and linear combination fits are shown for four depths at each site (Figure 3). The fits were constrained by synchrotron X-ray diffraction.

## Results and Discussion

Arsenic (especially AsO<sub>3</sub><sup>3-</sup>) is often associated with iron oxides, which are concentrated in the fine grains of the sediment, and therefore we would expect to see a disproportionately high amount of As in the < 2 μm fraction and perhaps a difference in speciation. Nevertheless, in the Seasonal Site, the arsenic speciation is consistent between the bulk sediment and clay size fraction (Figure 1a & 1b). Arsenic exists as 100% As(V) from 0 to 4 m. Here the sediment profile drains in the dry season, allowing oxygen to penetrate. In addition, the top 4 m has hues of oxidized iron, and low organic content (0.3 – 0.5 % C). The sediment remains saturated year-around below 4 m, and as a result, we observe a relative decrease in AsO<sub>4</sub><sup>3-</sup> – the oxo As(V):As(III) ratio is approximately 1:1 at 5 m. Arsenic (III) predominates below 5 m as AsO<sub>3</sub><sup>3-</sup> and arsenic sulfides. Realgar (AsS) is present in both the bulk and clay fraction, and arsenopyrite (FeAsS) is found in the bulk sediment. The 5.5 m sample is from a greyish black, organic-rich (5.5 % C) layer, and the 6.10 m sample is black peat (21.5 % C). Under anaerobic conditions, sulfate and iron oxides will be reduced, forming iron sulfides to which arsenic can partition, explaining the 10 to 15-fold increase in total As concentration in the peat relative to the mineral-dominated sediment of the top 5 m (Figure 1c). However, only 2 % of the arsenic in the peat is reactive compared to the 11 – 25 % observed higher in the profile.

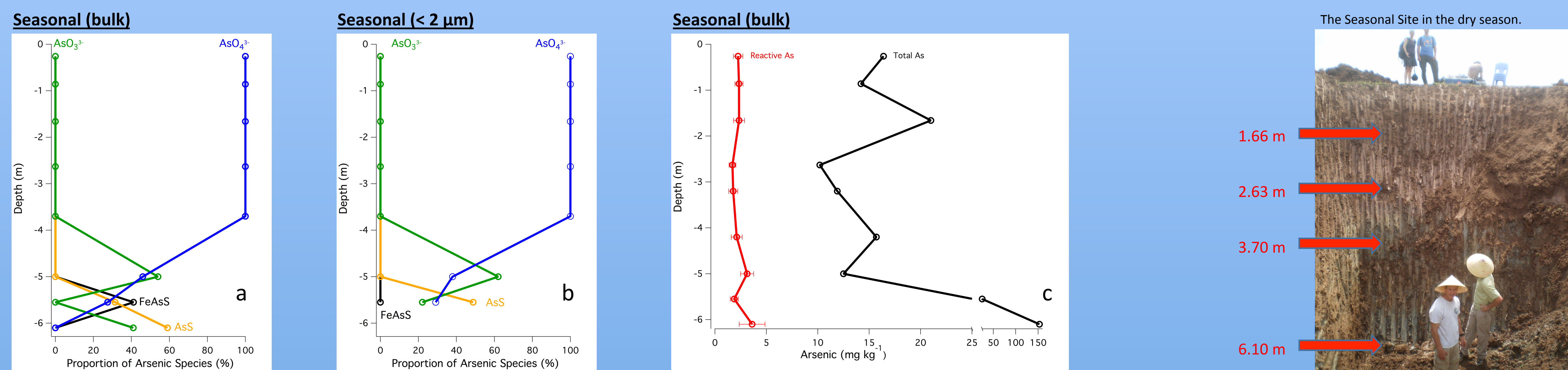


Figure 1. Arsenic speciation in the bulk (a) and < 2 μm sediment fraction (b), the “reactive” and total As (c), and sediment profile of the Seasonal Site.

In the Flooded Site the As(V):As(III) ratio decreases as a function of depth in both the bulk sediment and < 2 μm fraction, indicating arsenic reduction is occurring over time. Here As(V) disappears in the clay size fraction below 2.5 m and in the bulk sediment at 4 m, indicating reducing conditions occur closer to the land surface than in the Seasonal Site. Arsenic sulfide (realgar) was detected at 3 m. The generally higher proportion of As(V) in the bulk relative to the clay size fraction (especially at 0.26 m) may be attributed to the greater array of mineral surfaces (e.g., silicates) to which As(V) can sorb. Arsenic reactivity is greatest at the surface, indicating active arsenic reduction is most likely to occur here.

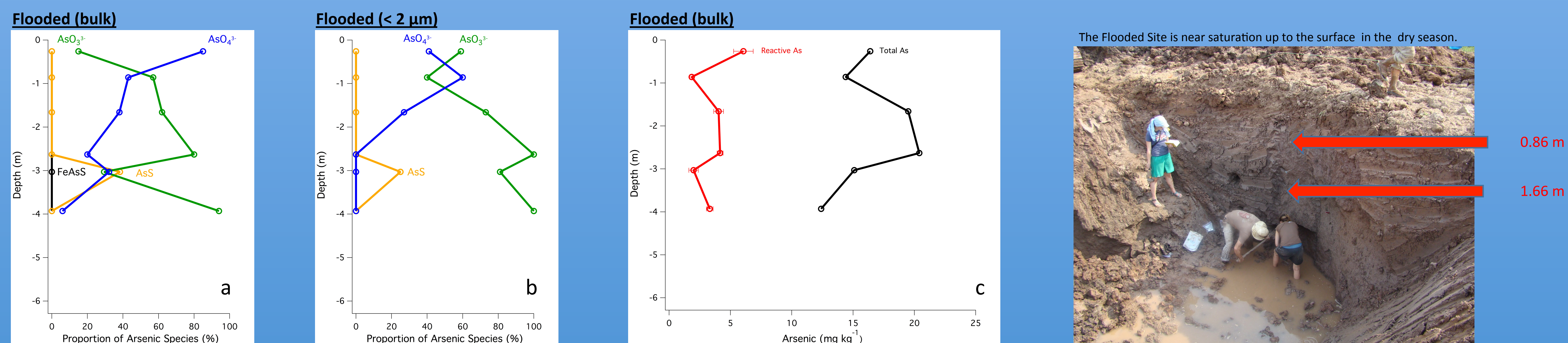


Figure 2. Arsenic speciation in the bulk (a) and < 2 μm sediment fraction (b), the “reactive” and total As (c), and sediment profile of the Flooded Site (d).

### Seasonal Site – Iron Mineralogy

Depth (m)	Component (%)							
	Ferrihydrite	Goethite	Hematite	Fe-Smectite	Hornblende	Augite	Pyrite	Siderite
-1.66	35	14	18	11	22			
-2.63	32	16	16	15	21			
-3.70	34	23		25	18			
-6.10		20			28	28	24	

### Flooded Site – Iron Mineralogy

Depth (m)	Component (%)							
	Ferrihydrite	Goethite	Hematite	Fe-Smectite	Hornblende	Augite	Pyrite	Siderite
-0.86	31	11	15	18	25			
-1.66		10	22	30	38			
-2.63		16	14		13	39		18
-3.93	31		14	12	43			

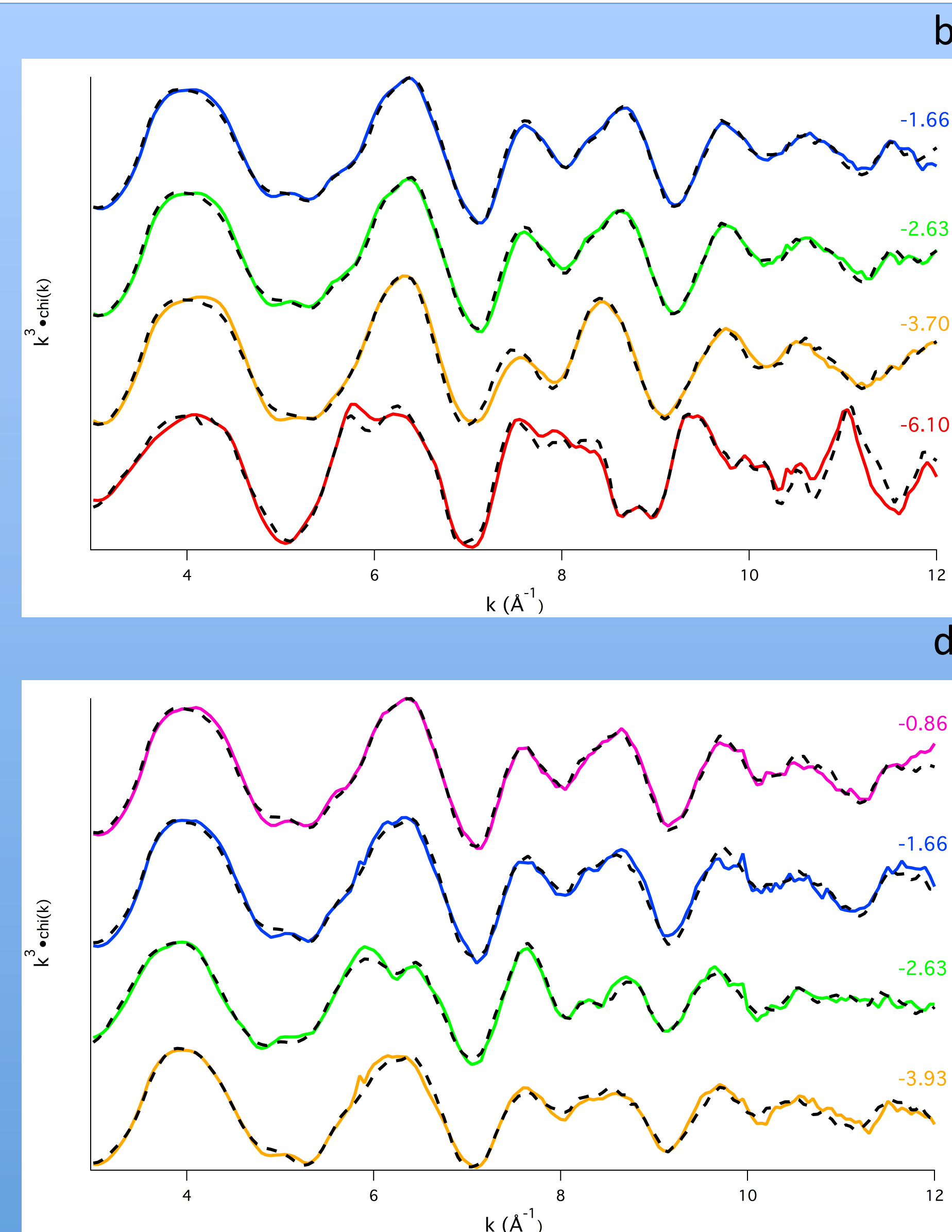


Figure 3. Results of the linear combination fitting of the k<sup>3</sup> – weighted chi function of Fe EXAFS spectra for four sediment samples from each site (a, c). The numbers provided are the % contribution of each mineral to the total Fe concentration. The k<sup>3</sup> – weighted chi functions are displayed as solid colored lines, and the black dashed lines are the fits (b, d). The colors in the tables correspond to the colors in the graphs. The sampling depths are given.

The iron mineralogy is consistent for both sediment profiles, and is predominantly comprised of iron oxides (ferrihydrite, goethite & hematite) and silicates (smectite, hornblende & augite). The two exceptions are the pyrite found in the peat layer (6.10 m) in the Seasonal Site, and the siderite found in the Flooded Site at a depth of 2.63 m. The co-associate of arsenic with iron and sulfur in the peat layer is shown in the pink region of Figure 4.

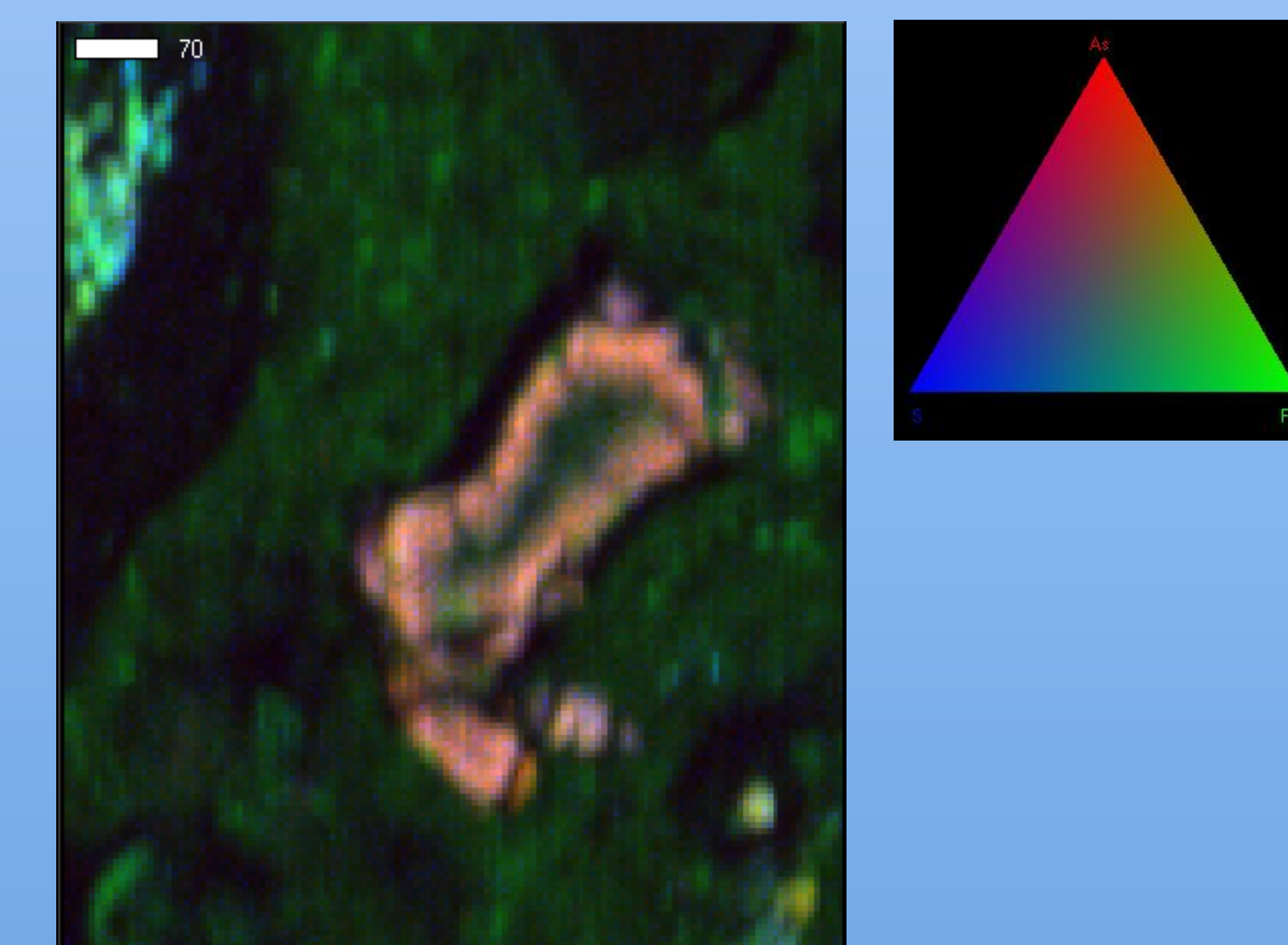


Figure 4. μX-ray fluorescence relative distribution of As, Fe, and S in the peat layer mapped at 11881 eV. The scale bar is in μm.

## Conclusion

Arsenic becomes more reduced as depth increases in both the Seasonal and Flooded Sites, with AsO<sub>3</sub><sup>3-</sup> predominating closer to the land surface at the Flooded Site. The reactive arsenic is within 11 – 27 % of the total As for all sediments with two important exceptions. First, arsenic reactivity is greatest (37 % of total) at the surface of the site where fresh iron oxides are codeposited with organic matter under continuously flooded conditions leading to active dissimilatory As/Fe reduction. Second, arsenic reactivity is lowest (2% of total) in the peat, which contains 10 – 15-fold more total As than any other sediment layer. The source of reactive arsenic in these sediments is most likely the (1 M HCl dissolvable) iron oxides. On the other hand, peat layers appear to be a sink for arsenic.

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