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Regulation of groundwater arsenic concentrations in the Ravi, Beas, and Sutlej floodplains of Punjab, India

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Abstract

Recent testing has shown that shallow aquifers of the Ravi River floodplain are more frequently affected by groundwater arsenic (As) contamination than other floodplains of the upper Indus River basin. In this study, we explore the geochemical origin of this contrast by comparing groundwater and aquifer sand composition in the 10–30 m depth range in 11 villages along the Ravi and adjacent Beas and Sutlej rivers. The drilling was preceded by testing wells in the same villages with field kits not only for As but also for nitrate (NO_3^-), iron (Fe), and sulfate (SO_4^{2-}). Concentrations of NO_3^- were $\geq$ 20 mg/L in a third of the wells throughout the study area, although conditions were also sufficiently reducing to maintain > 1 mg/L dissolved Fe in half of all the wells. The grey to grey-brown color of sand cuttings quantified with reflectance measurements confirms extensive reduction of Fe oxides in aquifers of the affected villages. Remarkably high levels of leachable As in the sand cuttings determined with the field kit and As concentration up to 40 mg/kg measured by X-ray fluorescence correspond to depth intervals of high As in groundwater. Anion-exchange separation in the field and synchrotron-based X-ray spectroscopy of sand cuttings preserved in glycerol indicate speciation in both groundwater and aquifer sands that is dominated by As(V) in the most enriched depth intervals. These findings and SO_4^{2-} concentrations $\geq$ 20 mg/L in three-quarters of the sampled wells suggest that high levels of NO_3^-, presumably from extensive fertilizer application, may have triggered the release of As by oxidizing sulfide-bound As supplied by erosion of black shale and slate in the Himalayas. Radiocarbon dating of sub-surface clay cuttings indicates that multiple episodes of inferred As-sulfide input reached the Ravi floodplain over the past 30 kyr. Why the other river basins apparently did not receive similar inputs of As-sulfide remains unclear. High NO_3^- in groundwater may at the same time limit concentrations of As in groundwater to levels lower than they could have been by oxidizing both Fe(II) and As(III). In this particular setting, a kit can be used to analyze sand cuttings for As while drilling in order to target As-safe depths for installing domestic wells by avoiding intervals with high concentrations of As in aquifer sands with the well screen.

Keywords: Arsenic; Release mechanisms; Groundwater; Sediment; Indus Basin

1. INTRODUCTION

Exposure to arsenic (As) from drinking water that does not meet the World Health Organization guideline of 10 μg/L is a major public health threat causing spontaneous abortions, stillbirths and infant mortality, inhibited

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intellectual and motor functions in children, as well as adult mortality from cardio-vascular disease and cancers of the lung, liver, and bladder (Smith et al., 2000; Flanagan et al., 2012; Rahman et al., 2009; Quansah et al., 2015; Wasserman et al., 2016). Globally, over 100 million people in 70 countries are chronically exposed to high levels of As by drinking untreated well water (Ravenscroft et al., 2009; Sankar et al., 2014). The extent of As exposure is particularly widespread in rural South and South East Asia and has been referred to as the "world's biggest calamity" due to the combination of high rural population density and widespread reliance on groundwater for domestic consumption (Das et al., 1995).

Extensive studies have been conducted across the major floodplains of South and Southeast Asia, including the Bengal basin (BGS/DPHE, 2001; Dowling et al., 2002; Harvey et al., 2002; Ahmed et al., 2004; Ravenscroft et al., 2005; van Geen et al., 2003; Khan et al., 2016; Knappett et al., 2016), the Indo-Gangetic basin (Acharyya et al., 2000; Chakraborti et al., 2003; McArthur et al., 2018), the Mekong floodplain and delta (Kocar et al., 2008; Hoang et al., 2010; Wang et al., 2018), Hetao basin (Guo et al., 2008; 2011; Cao et al., 2018), Datong basin (Guo et al., 2003; Xie et al., 2015; Zhang et al., 2018) and the Red River basin (Berg et al., 2001; Postma et al; 2007; Winkel et al., 2011; van Geen et al., 2013; Postma et al., 2012; Postma et al., 2016a; Postma et al., 2016b; Postma et al., 2017) to understand how groundwater becomes elevated in As. There is a general agreement that microbially-mediated reductive dissolution of iron (Fe) oxides in anoxic aquifers driven by a reactive carbon source, sedimentary or advected, plays a key role in release of As to groundwater in these environments (Nickson et al., 1998; McArthur et al., 2001; Harvey et al., 2002; Postma et al., 2007; Fendorf et al., 2010; Mailloux et al., 2013; Whaley-Martin et al., 2017; Duan et al., 2019) even though oxidative dissolution has been proposed in other aquifers (Farooqi et al., 2007; Shakoor et al., 2018).

Less explored alternative pathways for the release of As to groundwater have been documented in other settings including the Punjab plains (Nickson et al., 2005; Farooqi et al., 2007). One of these is desorption of As in alkaline groundwater, possibly enhanced by evaporative concentration, which is believed to play an important role in some oxic aquifers (Welch et al., 2000; Nickson et al., 2005; Farooqi et al., 2007; Mushtaq et al., 2018; Shakoor et al., 2018). Another mechanism for As release to groundwater invoked in areas of high nitrate (NO_3^-) input from agricultural activities is the oxidation of As-containing pyrite (van Beek et al., 1988; Postma et al., 1991; Zhang et al., 2009; Jessen et al., 2017; Farooq et al., 2010). In this case, pyrite can act as the electron donor for reduction of O_2 and NO_3^- in aquifers resulting in a release of As, Fe^{2+} and SO_4^{2-} to groundwater. In contrast, NO_3^- input to reducing aquifers can also lead to the oxidation of Fe(II) and As (III) resulting in precipitation of Fe-oxides and removal of As from groundwater (Senn and Hemond, 2002; Smith et al., 2017; Naseem and McArthur, 2018). Another potential sink in high sulfate groundwater is the formation of As-sulfides by the reduction of sulfate in groundwater (Kirk et al., 2004; Islam et al., 2005; Lowers et al., 2007; Buschmann and Berg, 2009; Aziz et al., 2017; Naseem and McArthur, 2018).

All the mechanisms referred to above and others may play a role in the Punjab plains. A recent survey has shown that the proportion of wells contaminated with As (defined hereon as As wells with > 10 μg/L) in the Ravi floodplain is much higher than along other rivers of the region such as the Beas, Sutlej, Chenab, and Jhelum (van Geen et al., 2019). It is unclear why the Ravi floodplain stands out in this respect given the generally similar upstream geology of all these rivers originating from Himalayas. In the current study, we rely on drilling a subset of villages to examine more closely the mechanisms of As release in different floodplains of the Punjab plains of northern India. We targeted villages with contrasting groundwater As levels along with different local and watershed geologies. The study also sets the stage for future study of the potential impact of long-term groundwater pumping on aquifer As levels given that the hydrology of the Punjab plains has been perturbed for over a century. One reason for the perturbation is the supply of irrigation water by a large network of irrigation canals starting in the 19th century (Greenman et al., 1967). In more recent decades, the impact of canal irrigation has been supplanted by massive over-pumping of groundwater for irrigation throughout the region (Rodell et al., 2009; CGWB, 2013; McDonald et al., 2016; Lapworth et al., 2017).

2. MATERIAL AND METHODS

2.1. Study area

The Punjab basin is the alluvial floodplain of the major tributaries of the Indus River. From west to east in India, the Ravi, Beas, and Sutlej rivers divide the Punjab plains into three geographic regions called doabs formed of older alluvium: the Bari doab lying between the Beas and Ravi rivers, the Bist doab between the Beas and the Sutlej, and the South Sutlej doab lying south of the Sutlej river, also referred to as the Sirhind Tract (Fig. 1). The older alluvium includes sand to loam with calcareous concretions (Saini et al., 2016), sticky clay, and medium to coarse sand containing mica (Bonsor et al., 2017). There are also Late to Early Pleistocene sediments of the upper Siwalik group containing red clay and micaceous sand in the upper reaches of the three rivers (GSI, 2004). The newer alluvium along the active river channel is comprised of loose grey micaceous sand, grey to light blue micaceous sand, with some purple red clay (Bowen, 1985). The newer alluvium is less calcareous and further divided into recent floodplains, abandoned floodplains, and bar upland areas. There are also deposits of wind-blown sand in some portions of the study region (Fig. 1).

Land use in the area is dominated by agriculture, with rice grown during the wet summer alternating with wheat during the dry winter (Singh et al., 2009; Erenstein, 2010). Almost 75% of current irrigation in Punjab relies on groundwater pumped from an extensive aquifer up to 450 m thick with an average yield of 150 m^3/hr (Ambast

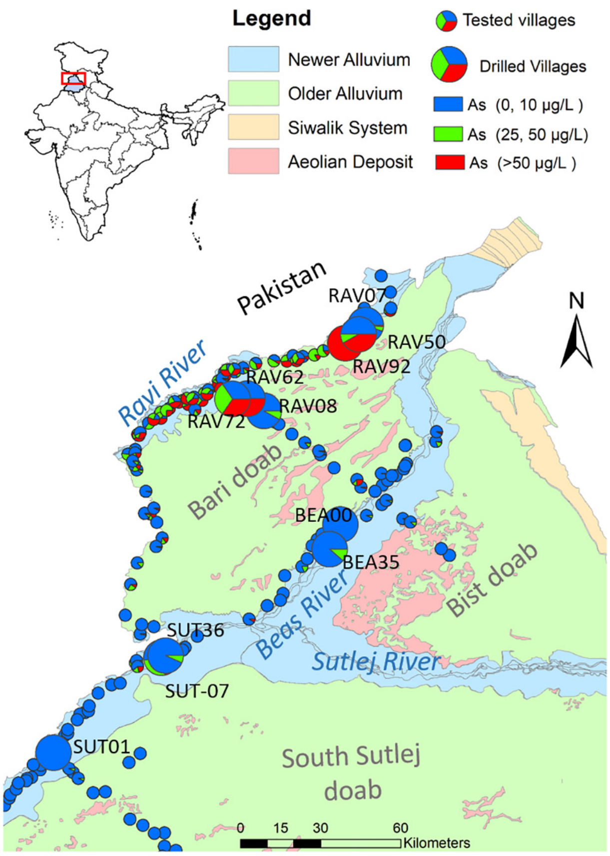

Fig. 1. Map of a portion of the state of Punjab, India, showing the location of the study villages in the context of the regional geology (GSI, 2018). Also shown as pie-diagrams are the proportions of tested wells in each village with ≤10 (blue), >10–50 (green), and >50 µg/L As (red). The small pie shows results of blanket survey in all villages and the larger pie represents results of subsequent testing in selected villages for drilling. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

et al., 2006). The Upper Bari doab canal supplying surface water from the north passes through the study region along with several sub-branches, but poor maintenance has led farmers throughout the region to shift to groundwater as their main source of irrigation and drinking water. As a result of over pumping, water levels have been dropping by up to 4 cm/yr in some parts of the Punjab plains (Tiwari et al., 2009; Rodell et al., 2009).

2.2. Field testing to select drill sites

2.2.1. Previous well testing

The present study was guided by the testing of groundwater for As with a field kit from 11,000 wells across 195 villages along portions of the floodplains of the Ravi, Beas and Sutlej rivers located within India (van Geen et al., 2019). The campaign was part of a broader study on both sides of the border with Pakistan that showed 54% of the 9,175 wells sampled in the floodplain of the Ravi River did not meet the WHO guideline for As, whereas this was the case for only 7% of 7,599 wells tested in floodplains of the other four rivers. Previous inter calibrations have shown that the ITS Econo-Quick kit (part no. 481298) effectively differentiates wells that meet the WHO guideline of 10 µg/L for As from those that do not, even if the kit overestimates As concentrations by about a factor of two at higher levels (George et al., 2012; van Geen et al., 2014, 2019).

The well testing was conducted in several phases. During the phase conducted between November 2013 to Oct 2014 and January 2015 to April 2015, not all wells in a village were necessarily tested (van Geen et al., 2019). In addition to testing for As with the field kit, most of these wells were also tested for NO_3^- using the CHEMet test kit (part no. K-6909D) based on the Cd-reduction method using evacuated glass ampoules. Most measurements were within the calibrated concentration range (0–132 mg/L NO_3^-) of the kit.

Before this well testing campaign, in July 2013, samples from 62 wells in another 7 villages of the region were collected in polyethylene scintillation vials and analyzed by ion chromatography to check the reliability of the NO_3^- kit. The samples were analyzed using a Dionex DX2000 ion chromatograph in gradient mode equipped with an AS-11HC column (Dionex, Sunnyvale, CA). The instrument was calibrated by inserting a combined reference standard spanning the relevant range of concentrations every 5 samples. Comparison between kit and laboratory results indicates that the CHEMet kit provides a reliable measure of the concentration of NO_3^- in well water (Fig. 2).

2.2.2. Retesting and selection of drill sites

In December 2016, all wells in all but one of the villages selected for drilling were re-tested using field kits for As, SO_4^{2-}, and dissolved Fe. We used the visual HANNA field kits based on the widely used phenanthroline method for Fe (no. HI3834) and the barium chloride turbidimetric method for sulfate (no. HI38000), respectively. In the case of SO_4^{2-},

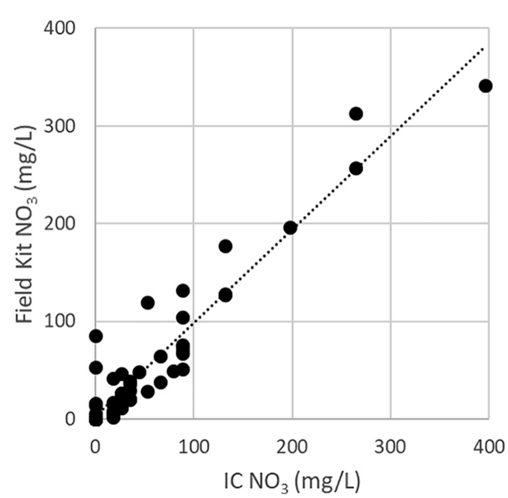

Fig. 2. Comparison of field-kit data and ion chromatography measurements of nitrate (shown as mg/L of NO_3^-) in well-water from a pilot study conducted in the northern Punjab in July 2013. The same Chemets K-6909D kit was subsequently used for testing wells for nitrate in the villages selected for drilling.

many wells exceeded the calibrated range of readings of 100 mg/L SO_4^{2-}.

Several villages were selected for well drilling and sediment collection based on prior well testing. These villages are identified hereon according to the name of the closest river and the proportion of wells with > 10 µg/L As, as determined by whichever of the two campaigns covered the largest number of wells in that village. In the northern portion of the Ravi floodplain, high-As village Adi was drilled at two different locations. In this village referred to as RAV92, 92% of 86 wells tested in the second survey contained > 10 µg/L As (Table 1). The low-As village Jainpur (RAV07; 7% of 72 wells > 10 µg/L As) located only 10 km to the northeast was drilled at one location. The mixed-As village Sanghor (RAV50; n = 119) located in between them was drilled at two locations (Fig. 1, Fig. 3a). Another group of 3 contrasting villages was selected further south along the Ravi River including high-As village Makowal (RAV78; n = 93), low-As village Khokhar (RAV08, n = 130), both of which were drilled once, and the considerably larger mixed-As village Samrai (RAV62, n = 154) which was drilled at two contrasting locations (Fig. 3b).

Along the Beas River, villages Desal (BEA35; n = 72), and Bhalojala (BEA00; n = 80) were selected for drilling once (Fig. 3c). Finally, along the Sutlej River, mixed-As village Alewala (SUT36; n = 45), and low-As villages Kamalwala (SUT07; n = 46), and Jhugge Chiliyan (SUT01; n = 69) were selected for drilling also once (Fig. 3d).

2.3. Well drilling

Groundwater aquifers were drilled at a total of 14 sites in 11 villages between March 15 and 27, 2017. The local manual drilling method relies on gradually advancing connected sections of 6″ (0.15 m) diameter metal casing by removing sand from within using a metal scooping device with a one-way flapper that is repeatedly dropped, raised, and emptied using a manual winch (Fig. S1). The drilling ended when thick clay was reached or at the maximum possible depth reachable using the flapper method within a single day. Maximum depths of 21 m were reached in the 3 northern villages in the Ravi floodplain (RAV07, RAV50, and RAV92), 36 m in the 3 southern villages of the same floodplain (RAV08, RAV62, and RAV78), and again 20 m in BEA00, BEA35, SUT01, SUT07, and SUT36.

2.4. Field-based sediment analysis

Drill cuttings were collected at 1.5 m intervals, washed with bottled water to remove clay from the recycled drilling water, pressed to reduce the moisture content, and packaged in cling wrap. The cling-wrapped pellets were analyzed in the field for bulk As and other elements using a portable InnovX Delta Premium X-Ray fluorescence analyzer mounted in a stand. The calibration of the instrument was checked against National Institute of Standards and Technology (NIST) reference material 2711 (contaminated Montana Soil) each day at the start and end of analysis of the sediments. The instrument was run in soil mode for

Table 1
Proportion of wells in each drilled village relative to various thresholds for parameters measured in the field.

Village Name (District)	Latitude	Longitude	Population (Census 2011)	Village Code	No. wells 1st survey	% wells > 10 µg/L As	% wells NO_3 ≥ 18 mg/L		No. wells 2nd survey	% wells > 10 mg/L As	% wells Fe ≥ 1 mg/L		% wells SO_4 ≥ 60 mg/L	
							Among wells ≤ 10 ug/L As	Among wells > 10 ug/L As			Among wells ≤ 10 ug/L As	Among wells > 10 ug/L As	Among wells ≤ 10 ug/L As	Among wells > 10 ug/L As
Jainpur (Gurdaspur)	32.153	75.340	526	RAV07	69	17	79	50	72	7	34	40	97	100
Khokhar (Gurdaspur)	31.865	74.998	1282	RAV08	74	1	21	0	130	8	42	64	68	73
Sanghor (Gurdaspur)	32.122	75.316	825	RAV50	51	57	23	28	119	50	51	40	53	25
Samrai (Gurdaspur)	31.906	74.942	1369	RAV62	100	70	37	4	154	62	19	46	90	82
Makowal (Amritsar)	31.905	74.892	1446	RAV78	93	78	10	0	51	76	50	58	75	59
Adi (Gurdaspur)	32.092	75.272	1470	RAV92	NA				86	92	43	96	29	89
Bhalojala (Taran Taran)	31.483	75.255	2610	BEA00	80	0	98		47	0	13		0	
Jhugge Chilliyan	30.715	74.290	NA	SUT01	69	1	100	100						
Kamalwala (Firozpur)	31.042	74.667	1007	SUT07	40	0	15		46	7	67	100	67	100
Desal (Kapurthala)	31.400	75.219	1433	BEA35	72	35	11	0	36	11	78	100	16	50
Alewala (Firozpur)	31.035	74.653	618	SUT36	45	36	10	13	23	48	63	67	88	100

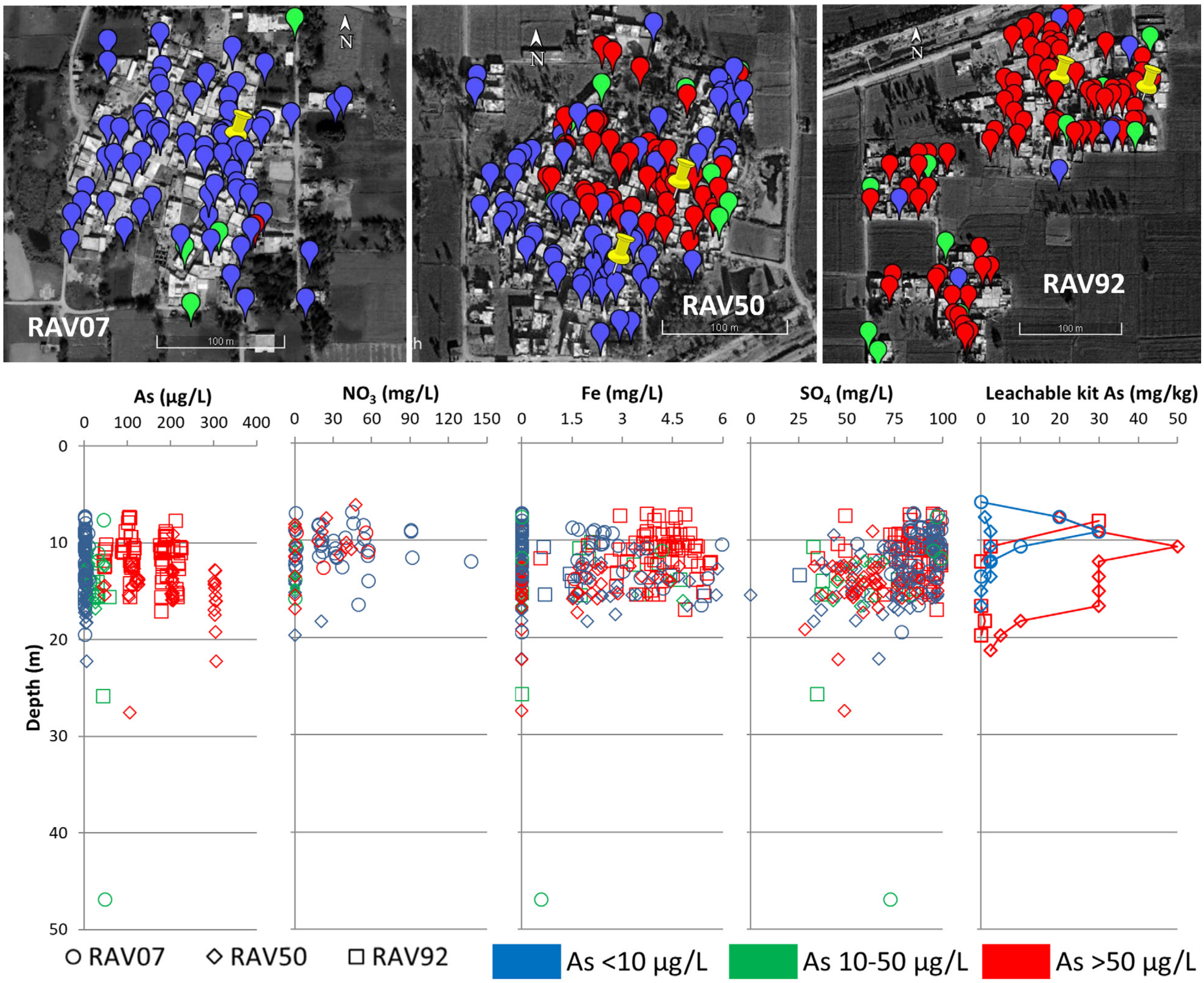

Fig. 3a. Satellite images of drilled village and profiles of groundwater As, NO_3^-, Fe, and SO_4^{2-} and leachable As in aquifer sands based on field tests conducted in the 3 northern study villages along Ravi River. Field testing for As and NO_3^- (neither available for RAV92) was conducted in between 2013 to 2015, before another round of testing for As (including for a first time in RAV92), Fe, and SO_4^{2-} in December 2016. Wells numbers and depths therefore don't necessarily correspond across measurements. The yellow pin indicates the drilling locations.

a total duration of 3 min at three incident X-ray energies. The average As concentration of 104 ± 3 (n = 16) measured in the NIST soil was consistent with the certified value of 105 ± 8 mg/kg. The detection limit calculated by the manufacturer's software under these conditions was 0.8 mg/kg As.

Sand cuttings were also analyzed using the field kit to estimate the easily exchanged As fraction (Choudhury et al., 2018). About 0.5 g of washed sand cuttings was added to the kit's reaction bottle along with 50 mL of bottled low-As water. The slurry was shaken for 1 min, after which the usual reagents were added and the procedure for testing water was followed. The color of the test strip was visually matched to a reference chart provided with the kit after a reaction time of 10 minutes.

As a more quantitative proxy for the sediment iron oxidation state than the color of sand perceived visually, the diffuse spectral reflectance spectrum of the sand cuttings was recorded through a single layer of cling wrap using a handheld CM700d (Minolta Crop., USA) instrument. The spectrometer was calibrated every day before analysis using a white barium sulfate reference plate. Each sample was analyzed three times and the difference in reflectance at 530 nm and 520 nm was calculated as a proxy for the Fe(II)/Fe ratio in the acid-leachable fraction in the sand cuttings (Horneman et al., 2004).

2.5. Household well installation

After noting that elevated levels of As in sand cuttings and well-water As coincided across several villages of the Ravi floodplain, an exploratory drinking-water well was installed in RAV78 by targeting a relatively shallow interval with a low-As concentration of sand cuttings analyzed with

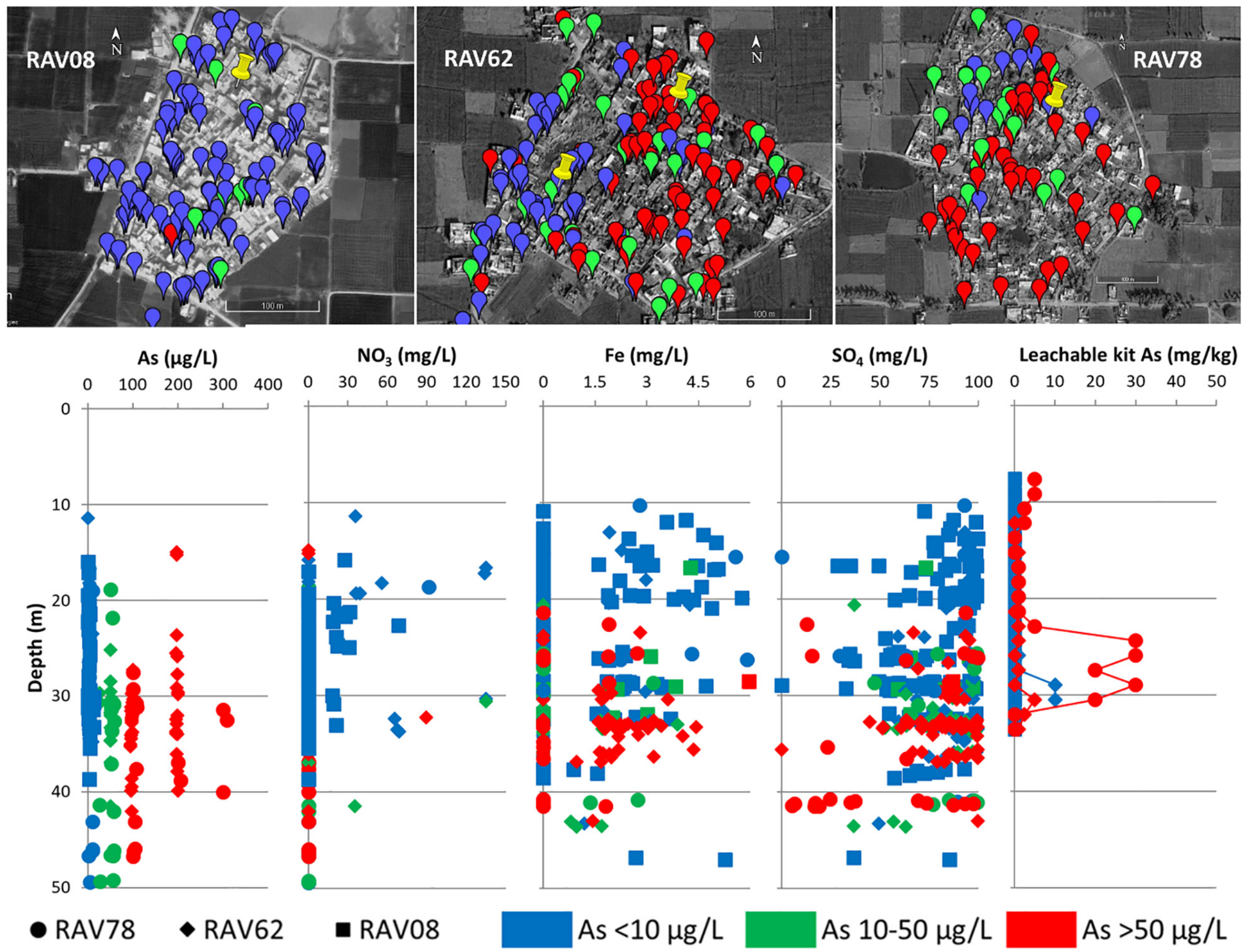

Fig. 3b. Satellite images of drilled village and profiles of groundwater and aquifer sand properties in the 3 southern study villages along Ravi River. Field testing for As and NO_3^- was conducted in between 2013 to 2015 before another round of testing for As, Fe, and SO_4^{2-} in December 2016 except RAV78 which was tested in March 2017. Wells therefore don't correspond across measurements. The yellow pin indicates the drilling locations.

the kit and by XRF. The driller used sections of 6-inch (0.15 m) diameter PVC pipe including a slotted screen extending from 17 to 19 m depth on March 27, 2017. The household owning the land transferred its submersible pump from its deeper high-As well to this new well and has been testing it under routine use with the kit.

2.6. Arsenic speciation in groundwater

In a subset of 4 villages in the Ravi floodplain, wells with > 100 μg/L As were sampled again in February 2018 to determine the speciation of As in groundwater. A 50 mL syringe was purged twice to eliminate air bubbles, after which an aliquot of groundwater was gently forced through an anion-exchange column that retains As(V) and not As(III) (http://metalsoftcenter.com/new-products/arsenic-speciation-cartridge). After passing through the column, the sample was analyzed with the ITS kit along with a sample of groundwater taken directly from the well.

2.7. Radiocarbon dating of clay

Five samples of clay cuttings free of sand or gravel from the 15–26 m depth range in 5 different villages were sent to the National Oceanic Science Accelerator Mass Spectrometry Facility in Woods Hole, Massachusetts, USA, for radiocarbon analysis of their organic carbon content.

2.8. X-ray absorption near edge structure (XANES) analysis

A total of 8 sand cuttings from RAV78 (15.2 m, 18.2 m, 27.4 m), RAV50 (9.1 m, 12.1 m, 15.2 m) at the drill site in the high As portion of the village, RAV62 (30.4 m) at the drill site in the low As section of the village, and SUT01 (18.2 m) were selected on the basis of their elevated As concentration measured by XRF of 17–24 mg/kg for As speciation analysis by X-ray absorption near edge structure (XANES) at the Stanford Synchrotron Radiation Laboratory. These sand cuttings were immersed in glycerol soon after collection and stored in 20 mL scintillation vials to

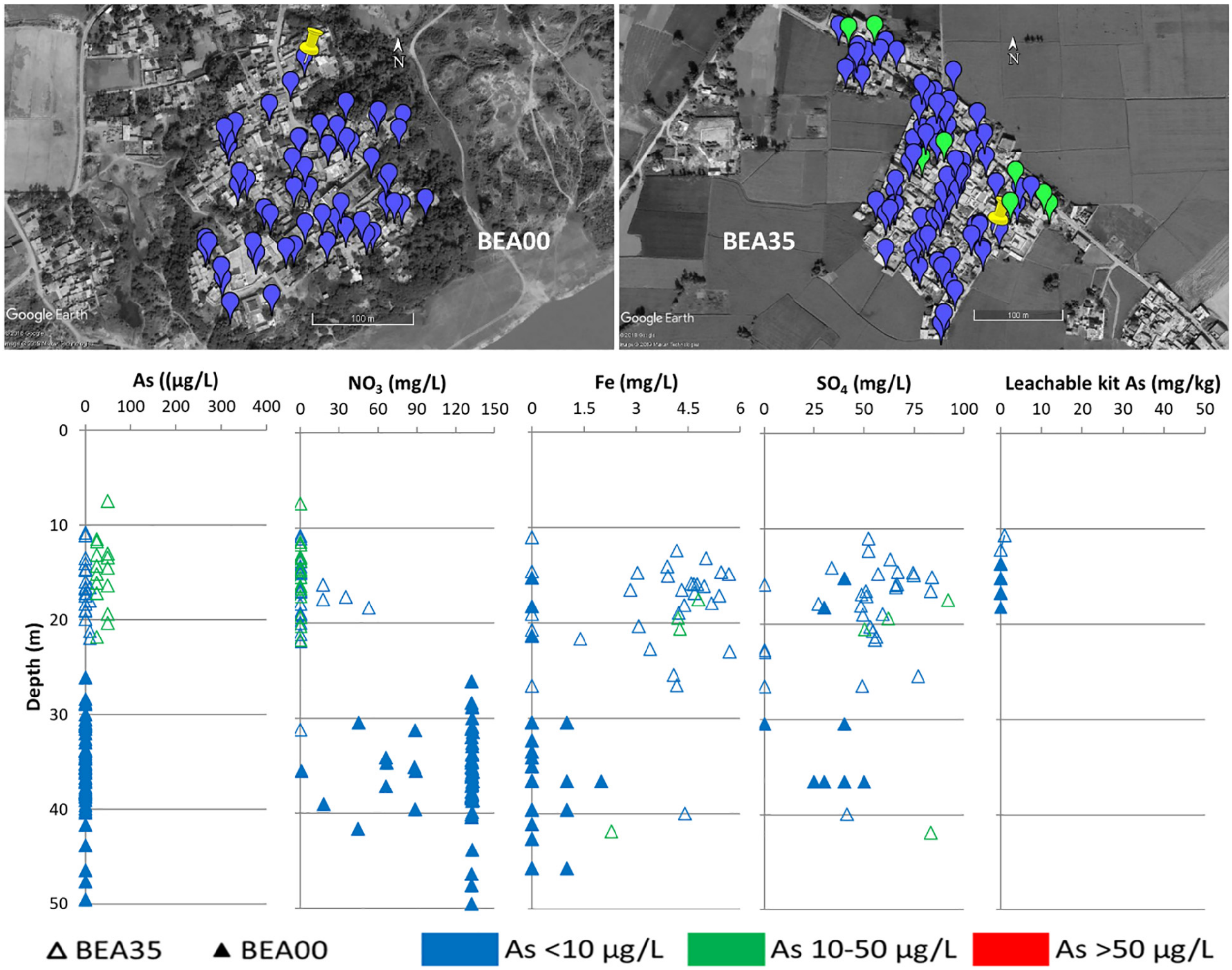

Fig. 3c. Satellite images of drilled village and profiles of groundwater and aquifer sand properties in the 2 study villages along Beas River. Field testing for As and NO_3^- was conducted in between 2013 to 2015 before another round of testing for As, Fe, and SO_4^{2-} in March 2017. Wells therefore don't necessarily correspond across measurements. The yellow pin indicates the drilling locations.

avoid contact with atmospheric oxygen. The samples were brought to the lab in a cooler and stored at −20 °C prior to analysis, except while in transit from India to the US.

The sand cuttings were analyzed within 5 weeks of collection by XANES on beamline 4–1 following methods described in Aziz et al. (2017). Briefly, As XANES spectra were collected from −235 to 425 eV around the As K edge. Scans were calibrated by setting sodium arsenate edge inflection to 11,874.0 eV. All data averaging, normalization, and linear combination fitting was done with SIXPack software (Webb, 2005). As XANES fits were performed on normalized spectra using an energy range of 11,865–11,890 eV. Arsenate and arsenite adsorbed on ferrihydrite (100 g As/kg ferrihydrite, pH 7) were used to represent adsorbed As(V) and As(III), and orpiment (As_2S_3) was used to model arsenic sulfides. Orpiment and realgar (AsS) have similar XANES spectra and are thus not easily differentiated using XANES. Arsenopyrite (FeAsS), which contains As(-I), was also used in fitting but was not required to fit any spectra. The estimated errors reported by SIXPack are determined from sensitivity analysis and are sensitive to fit quality, spectrum noise levels, and reference spectrum characteristics (e.g., noise, similarity to other reference materials), and are commonly a few percent or better for As XANES fits.

3. RESULTS

3.1. Groundwater properties measured in the field

Within the 3 northern Ravi floodplain villages where wells span the 8–20 m depth range, levels of As > 10 µg/L are concentrated in the northern half of RAV50 and distributed throughout RAV92 (Fig. 3a). In the 3 southern Ravi floodplain villages, high- and low-As wells are more interspersed geographically. In RAV62 and RAV78, respectively, 90 out of 96 and all 39 high-As wells are > 25 m deep (Fig. 3b). The depth range of low As wells in RAV07 and RAV08 overlaps with that of the fewer high As wells in these two villages.

Wells target primarily the 10–30 and 25–50 m depth ranges in BEA35 and BEA00, respectively (Fig. 3c). Even in BEA35, the As concentration of none of the wells exceeds 50 μg/L. Further downstream in the Sutlej floodplain, wells with >50 μg/L are limited to the 10–30 m depth range in SUT36. The vast majority of wells contain no more than 10 μg/L across the 10–50 m depth range in both SUT01 and SUT07. Groundwater As does not show any systematic relation with Fe (ranging from 1–5 mg/L), however, most of the high As groundwater in the northern Ravi floodplain is elevated (>30 mg/L) in SO_4^{2-} (Fig. 4).

Remarkably, a considerable proportion of the As in groundwater of the region is oxidized. For the 40 samples analyzed in the field with the anion exchange column, 25 and 60% of the As from RAV92 and RAV50, respectively, was on average in the form As(V). The proportion of As(V) in well water ranged more widely in RAV82 and RAV63 but averaged about half (Figs. 5a–5d).

There are no systematic patterns in the depth distributions of NO_3^-, Fe, and SO_4^{2-} in well water from the 11 drilled villages (Figs. 3a–3d). Overall, however, 51% of 466 wells with ≤ 10 μg/L As contain detectable (≥20 mg/L) levels of NO_3^-, whereas this is the case for only 9% of 227 wells with > 10 μg/L As. The contrast is less pronounced for Fe, with 41% of 456 wells with ≤ 10 μg/L As containing detectable (≥1 mg/L) levels of Fe based on the kit while this is case for 63% of 307 wells with > 10 μg/L As. The proportion of wells with detectable (≥20 mg/L) concentrations of SO_4^{2-} is identical at 70% for 417 wells with ≤ 10 μg/L As and 308 wells with > 10 μg/L As (Fig. 4).

3.2. Concentrations of As in sand cuttings measured in the field

The shallow sandy aquifer was capped by a clay and/or silt layer extending to 5–14 m depth at all sites. Measurements are reported only for sandy intervals below the water table encountered at the time of drilling because domestic wells are not installed at shallower depths. Concentrations of As in these sand cuttings measured by XRF ranged from ≤ 0.8 mg/kg to 40 mg/kg (Figs. 5a–5d). The slurries of sand cuttings produced kit readings spanning the 0 to

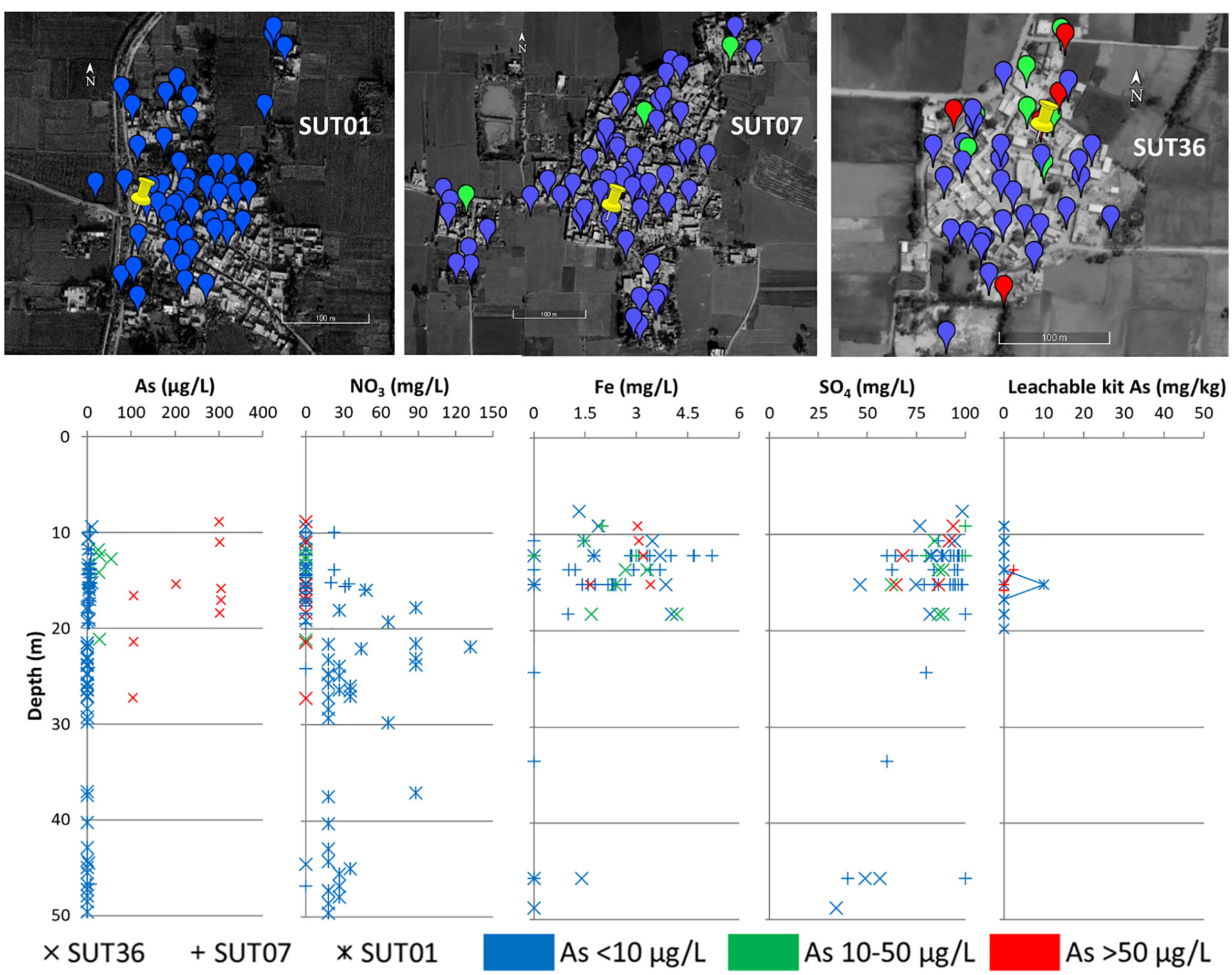

Fig. 3d. Satellite images of drilled village and profiles of groundwater and aquifer sand properties in the 3 study villages along the Sutlej River. Field testing for As and NO_3^- was conducted in between 2013 to 2015 before another round of testing for As, Fe, and SO_4^{2-} in March 2017. Wells therefore don't necessarily correspond across measurements. The yellow pin indicates the drilling locations.

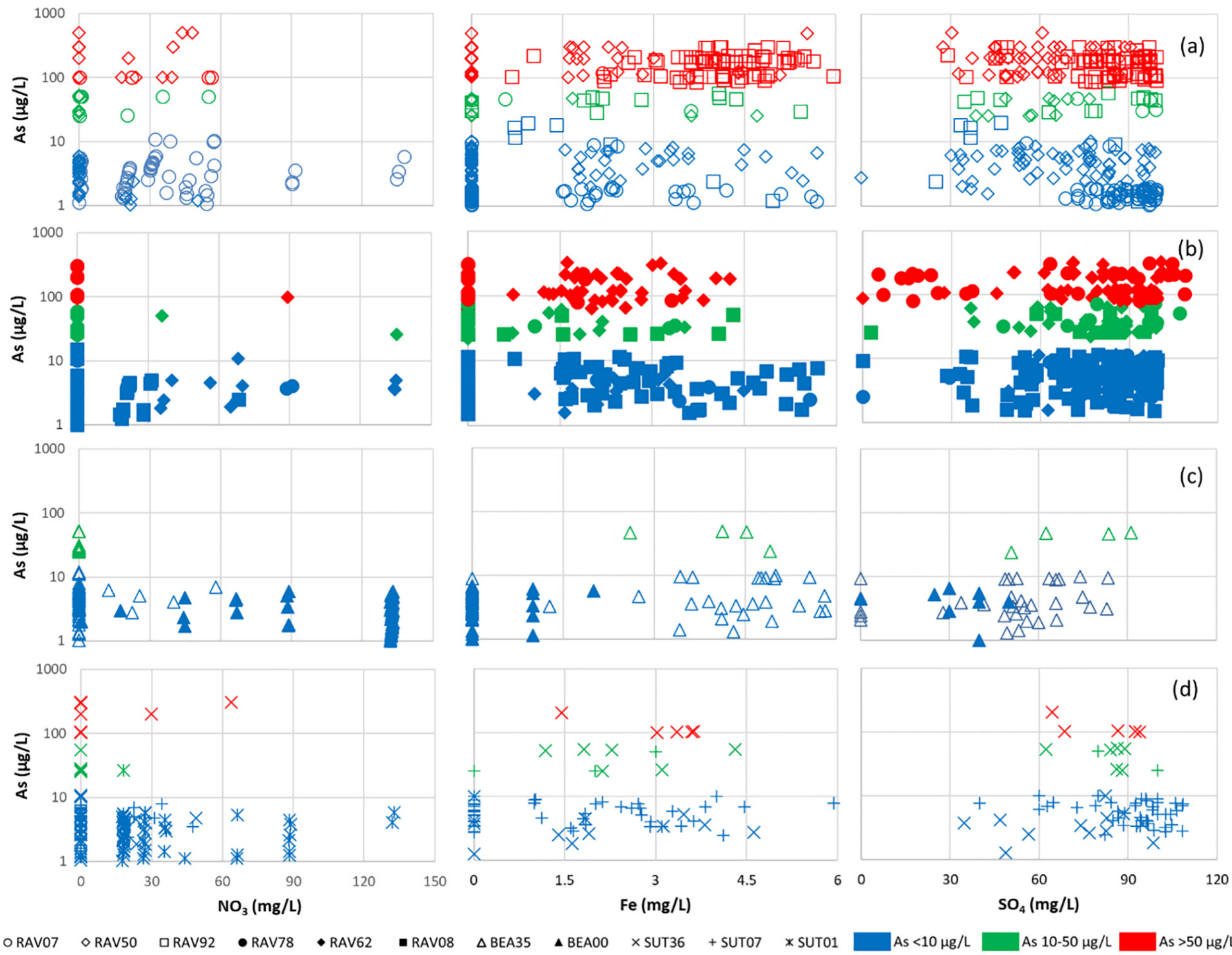

Fig. 4. Relation of As with other field parameters in Indus basin, Punjab, India. Villages are in the same order and use the same symbols and color code as in Figs. 3a–3d: (a) RAV06, RAV50, RAV92 in northern Ravi; (b) RAV82, RAV63, RAV09in southern Ravi, (c) BEA06, BEA00 in Beas; (d) SUT05, SUT28, SUT01 in Sutlej. The samples up to 50 m depth are only shown.

500 µg/L range, which correspond to concentrations of 0–50 mg/kg As in the solid phase after correcting for dilution (Figs. 3a–3d).

The correlation between the two sets of field measurements of As in cuttings is striking (Fig. 6). However, comparing individual samples shows that the kit overestimates As concentrations by at least 40% compared to XRF because leachable As concentrations can in reality not exceed total As concentrations, which are well quantified by XRF. Assuming that the 2-fold over-estimate of As concentrations in groundwater with the kit applies to slurries of cuttings (George et al., 2012), this suggest that nearly all the As present in the cuttings is released within the 10 min reaction time in the mildly acidic slurry used in the kit.

The two drill sites with the largest number of cuttings with leachable As $\geq$ 5 mg/kg are in the high-As portion of RAV50, with 9 such intervals in the 8–21 m depth range, and in RAV78 with 9 such intervals between 8 and 30 m depth (Figs. 3a and 3b). Additional intervals with cuttings containing $>$ 5 mg/kg As in the Ravi floodplain were encountered in RAV07 (3 intervals at 6–11 m), RAV92 (2 at 9–11 m), and both drill sites in RAV62 (1 at 30 m in the high-As portion, 2 at 29–30 m in the low-As portion). Outside the Ravi floodplain, leachable As $\geq$ 5 mg/kg was measured only in cuttings from a single interval at 16 m in SUT01.

3.3. Diffuse reflectance of cuttings measured in the field

Sandy intervals encountered while drilling before the water table was reached were often brown in color, indicating Fe oxides dominated by Fe(III). Reflectance data are presented here only for sand cuttings collected below the level of the water table at the time of drilling because shallower intervals are not targeted by household wells. These cuttings span a more limited range from grey to grey-brown in color (Figs. 5a–5d). Out of the 13 available reflectance profiles, 9 show advanced reduction of Fe oxides within the upper 5 m of the aquifer corresponding to 0.1–0.2% in the difference in reflectance between 530 and 520 nm (Horneman et al., 2004).

Broadly speaking, reflectance profiles from the Ravi floodplain fall into two groups. Profiles with the most reduced sand cuttings average 0.1% or less in reflectance

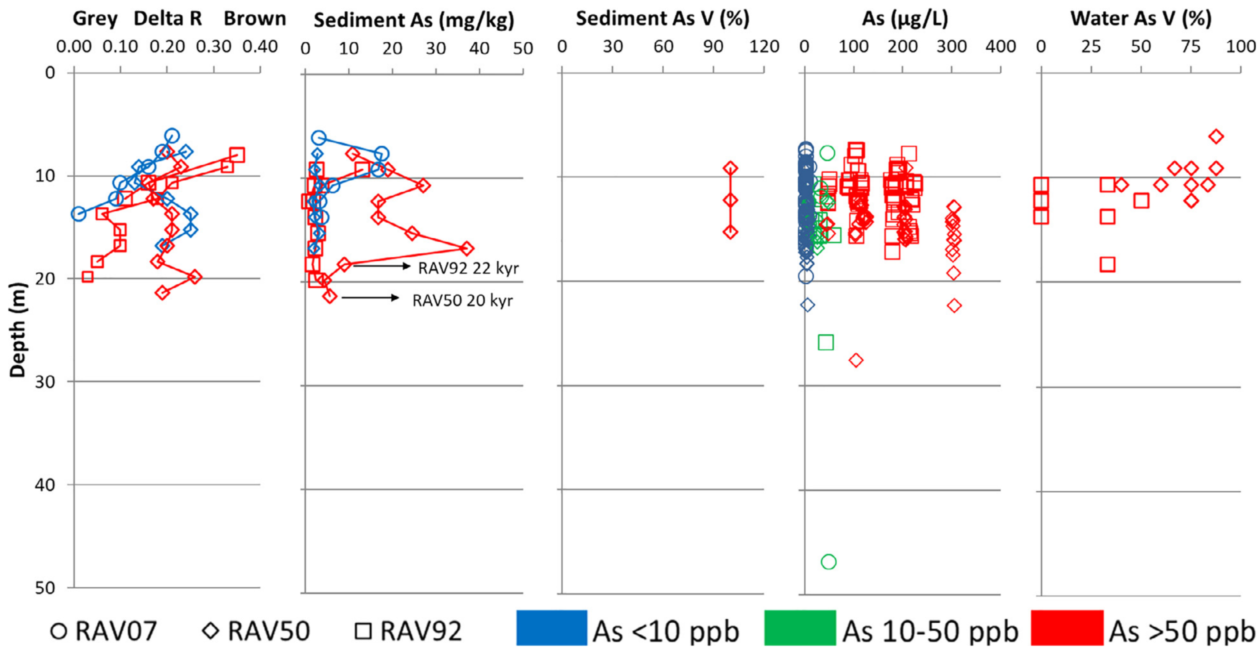

Fig. 5a. Depth profiles of sediment and groundwater properties in 3 northern Ravi villages RAV92, RAV50, RAV07. Delta R refers to the difference in diffuse spectral reflectance (%) of fresh cuttings between 530 and 520 nm (Horneman et al., 2004). The arrow in panel 2 shows the depth and radiocarbon age of the clay.

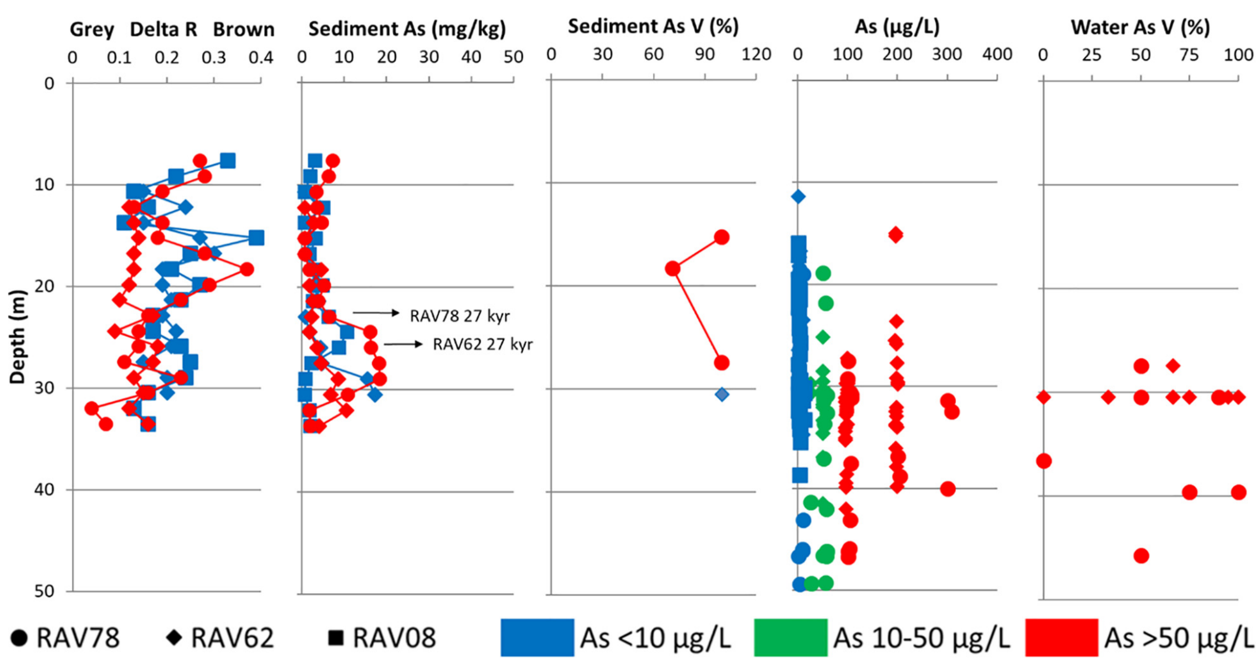

Fig. 5b. Depth profiles of sediment and groundwater properties in 3 southern Ravi villages RAV78, RAV08, and RAV62). The arrow in panel 2 shows the depth and radiocarbon age of the clay.

difference between 530 and 520 nm at RAV07, the high-As drill site in RAV62, and RAV92. Villages with less reduced sand cuttings and an average difference in reflectance closer to 0.2% are RAV08, both drill sites at RAV50, the low-As drill site in RAV62, and RAV78. Profiles of sand cuttings from villages outside the Ravi floodplain are less reduced, with reflectance differences averaging about 0.2% at SUT01, SUT07, BEA35, and SUT36.

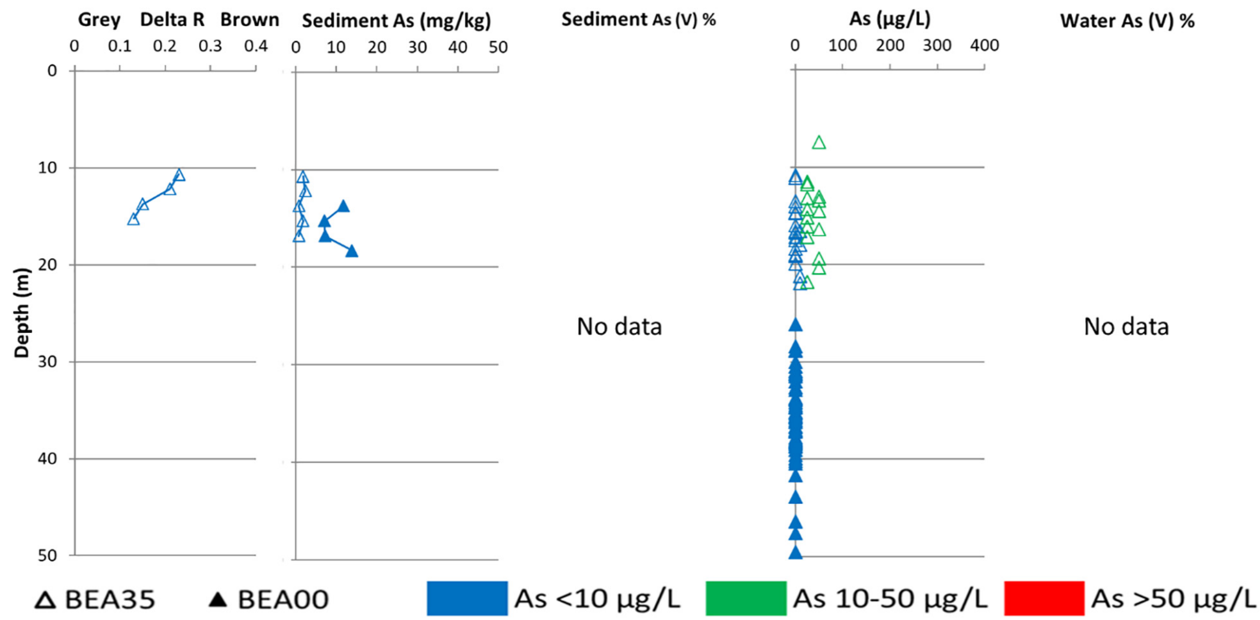

Fig. 5c. Depth profiles of sediment and groundwater properties in 2 Beas villages BEA00 and BEA35.

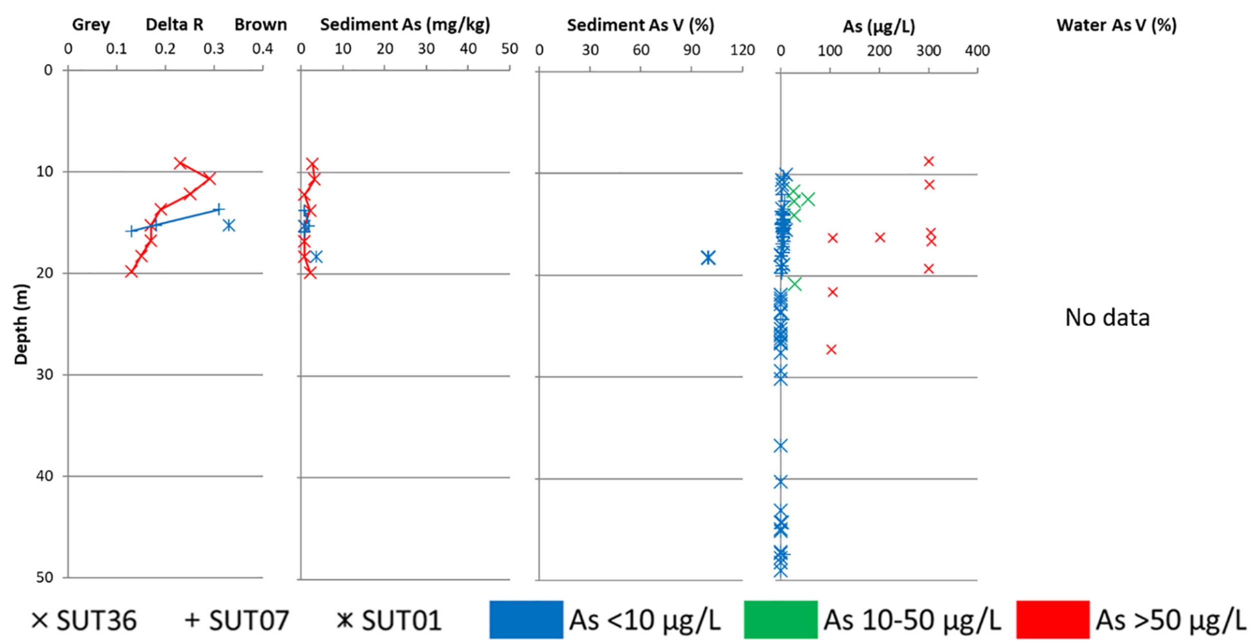

Fig. 5d. Depth profiles of sediment and groundwater properties in 3 Sutlej villages SUT36, SUT07, and SUT01. Reflectance in SUT01 is >0.4 at 15.2 and 18.2 m (1.53 and 0.43 respectively) so not visible.

3.4. Properties of cuttings measured in the laboratory

Uncorrected radiocarbon ages of organic matter in clay recovered from the bottom of the shallow aquifer of RAV07, RAV50, and RAV92 at depths of 15–26 m range from to 20.5 to 27.2 kyr (Table 2). The Pleistocene age of these clays does not rule out deposition of the overlying aquifer during the Holocene, although the villages are located in the area marked as older alluvium in the Geological Survey of India map (Fig. 1). The dating indicates that the intervals with high leachable As in the clay cuttings were deposited less than 20 kyr ago at RAV50 and less than 22 kyr ago RAV92 (Figs. 5a–5d). Further south in RAV 62 and RAV78, radiocarbon dates indicate that the high-As sand intervals were deposited more than 27 kyr ago, and therefore well before the deposition of high-As sands at RAV50 and RAV92.

The XANES spectra of preserved sand cuttings clearly show that the solid phase speciation is dominated by As (V) in 7 out of 8 sand cuttings collected in the 9–30 m depth

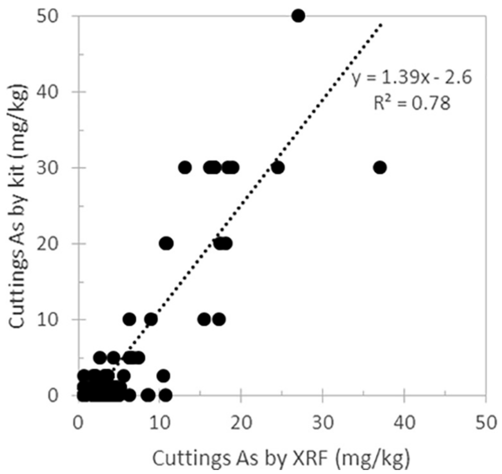

Fig. 6. Correlation among the As concentration in sediment using XRF and Leachable As from the sediment in water collected during the drilling of boreholes.

range from RAV50, RAV78, and SUT01 (Table 3). Only one sample from 18 m depth at RAV78 contained detectable levels of As(III) and As sulfides of 20 and 9%, respectively (Fig. 7).

3.5. Targeted installation of a household well

The original household well of the owner of the land in RAV78 where we drilled was 45 m deep and contained 200 μg/L As according to the kit. A comparison of the As concentration of the sand cuttings at this site with the distribution of As with depth throughout the village suggested a shallower well installed in the 15–20 m depth range had a good chance of being low in As (Fig. 8). This was the basis for installing a new well for the landowner who then shifted his submersible pump to it and started using it for his domestic supply. The new well was tested by the household for As using the kit every week for the first 6 months after installation in March 2017 and twice a month after that. As of May 2019, all the kit readings had remained below 10 μg/L As.

4. DISCUSSION

The data collected for this study present a challenge for identifying the mechanisms regulating As concentrations in groundwater of the Punjab plains. Groundwater quality parameters tested in the field do not show any clear association from which to infer a dominant mechanism, whether considered individually (Figs. 5a–5d) or with box-plots (Fig. 9). On one hand, the reflectance of aquifers sands and detectable dissolved Fe in many samples both indicate reductive dissolution of Fe oxides of the kind associated with the release of As to groundwater in the Bengal basin and other anoxic aquifers. With the exception of two intervals at SUT01, none of the sand cuttings were as orange and oxidized as Pleistocene sands associated with low-As groundwater in the Bengal basin (Horneman et al., 2004). On the other hand, the predominance of As(V) over As(III) in both aquifer sands and groundwater within the most affected depth intervals, combined with widespread occurrence of high levels of NO_3^- in groundwater, suggest oxidative As release could also have a significant role. The following discussion attempts to integrate the available evidence, while heeding the point made by Naseem and MacArthur (2018) that multiple mechanisms of release and removal may be at play in a complex system such as the Punjab.

4.1. Associations between sediment and well-water As

Although leachable As concentrations are well correlated with total sediment As (Fig. 6), comparing

Table 2
Radiocarbon dating of the clay samples collected during drilling of boreholes.

Drilling site	Depth (m)	Age (yr)	Age Err (yr)	$\delta^{13}C$(‰)	$\Delta^{14}C$(‰)
RAV07	15.2	23,600	220	−18.76	−947.43
RAV50-H	22.8	20,500	140	−21.62	−922.32
RAV92	18.8	22,000	180	−23.32	−935.92
RAV62-L	25.9	27,200	330	−26.12	−966.36
RAV78	22.0	27,000	320	−24.11	−965.57

Table 3
Sediment As species (%) in the selected samples.

Sample	Depth (m)	XRF As (mg/kg)	As_2S_3	As(V)	As(III)	As_2S_3 error	As(V) error	As(III) error
RAV78	15.2	0.8	0	100	0	2	1	2
RAV78	18.2	1.8	9	71	20	3	1	3
RAV78	27.4	18.4	0	100	0	1	1	1
RAV50-H	9.1	19.0	0	100	0	1	1	1
RAV50-H	12.1	16.8	0	100	0	1	1	1
RAV50-H	15.2	24.5	0	100	0	1	1	2
SUT01	18.2	3.6	0	100	0	1	1	1
RAV62-L	30.4	17.3	0	100	0	1	1	1

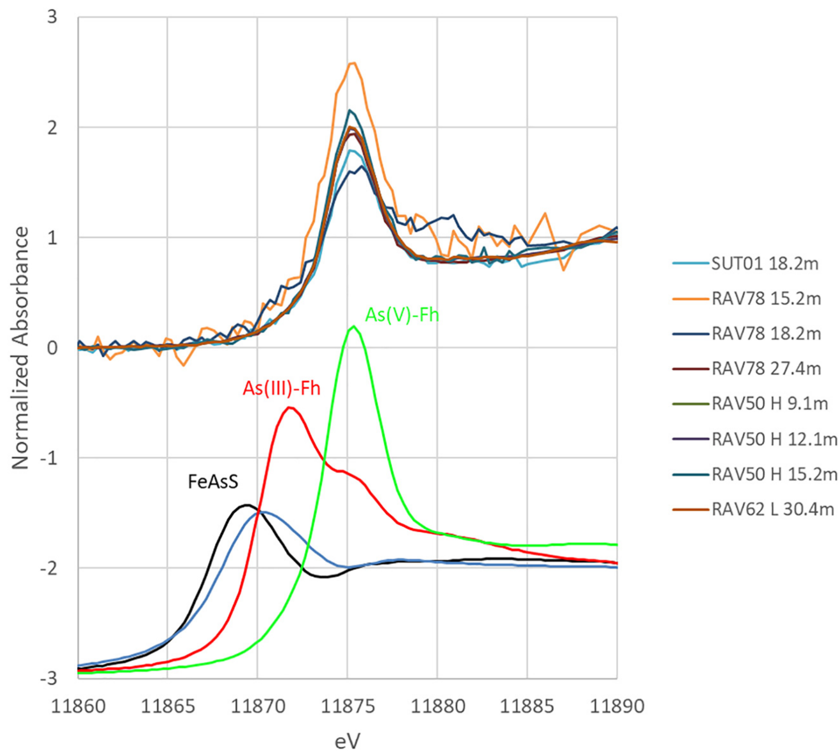

Fig. 7. Normalized XANES spectra of selected aquifer sands. All measured samples had As XANES spectra dominated by a single edge feature with a white line position of 11875.4 eV, coincident with arsenate, As(V). For comparison, As(III) has a white line feature at about 11873 eV, while arsenic sulfides have white lines features at <11871 eV.

groundwater As concentration with either extractable or total sediment As is more difficult because of the combination of spatial variability (vertically and laterally) and mismatched depths. Only in the case of the original and the re-installed household well in RAV78 can groundwater and sediment As concentration be compared directly (Fig. 8). To overcome this limitation, both leachable and total As concentrations were first averaged in 6-m (i.e. 4 sample) intervals. This averaging preserves the linear relation between the two properties for individual samples (Fig. 6), with a slope suggesting an over-estimate of leachable As concentrations relative to total As concentrations of at least 50% (Fig. 10a).

The main outliers from this relationship are three shallow 6 m intervals of aquifer sands containing 10–15 mg/kg total As concentrations at BEA00 that are not associated with any detectable levels of leachable As (Fig. 10a). Often out of range levels of NO_3^- and less frequently detected dissolved Fe at BEA00 compared to BEA06 within the same floodplain suggest perhaps less reducing conditions (Fig. 2c). The reflectance of BEA00 sediment was not measured but was visually closer to brown than to grey and therefore consistent with less reduction. With the exception of this site, the relationship between leachable and total As concentrations is remarkably consistent and, to our knowledge, has not been reported previously for South Asian sedimentary aquifers.

The relationship between groundwater As averaged over the same depth intervals as a function of average total As measured by XRF in the sediment is more scattered but remains striking (Fig. 10b). The higher end of the range of As concentrations in both groundwater and aquifer sands is populated by a dozen averaged intervals from RAV50, RAV63, and RAV82, all in the Ravi floodplain. Concentrations of 20 mg/kg total As are exceptionally high, especially when considering that fine-grained sediments were washed out of the sand cuttings, and an order to magnitude higher than typical As concentrations in the continental crust (BGS/DPHE, 2001). Concentrations of As in aquifer sands from other As-affected region in South and Southeast Asia are much closer to crustal values in the Bengal basin (1–3 mg/kg range; Harvey et al., 2002; Zheng et al., 2005; Choudhury et al., 2018), Hetao basin (7 ± 2 mg/kg; Wang et al., 2019), and the Mekong delta (up to 2 mg/kg; Kocar et al., 2008; Hoang et al., 2010; Sø et al., 2018).

Given the preferential partitioning of As into the solid phase (Fendorf et al., 2010; Sø et al., 2018), it is unlikely that the very high levels of As in aquifer sands could have accumulated by advection from elsewhere. At least 1000 pore volumes of 200 μg/L As groundwater would be necessary to retain 20 mg/kg As in sediments assuming complete adsorption and typical porosities. It is also telling that As concentration in the 10–20 m depth range are consistently low in the southern 3 villages in the Ravi floodplain in spite of conditions that are just as reducing based on reflectance and dissolved Fe as the deeper high As interval at 20–40 m depth (Fig. 4). The implication is that the As concentration of aquifer sands plays a significant role in regulating

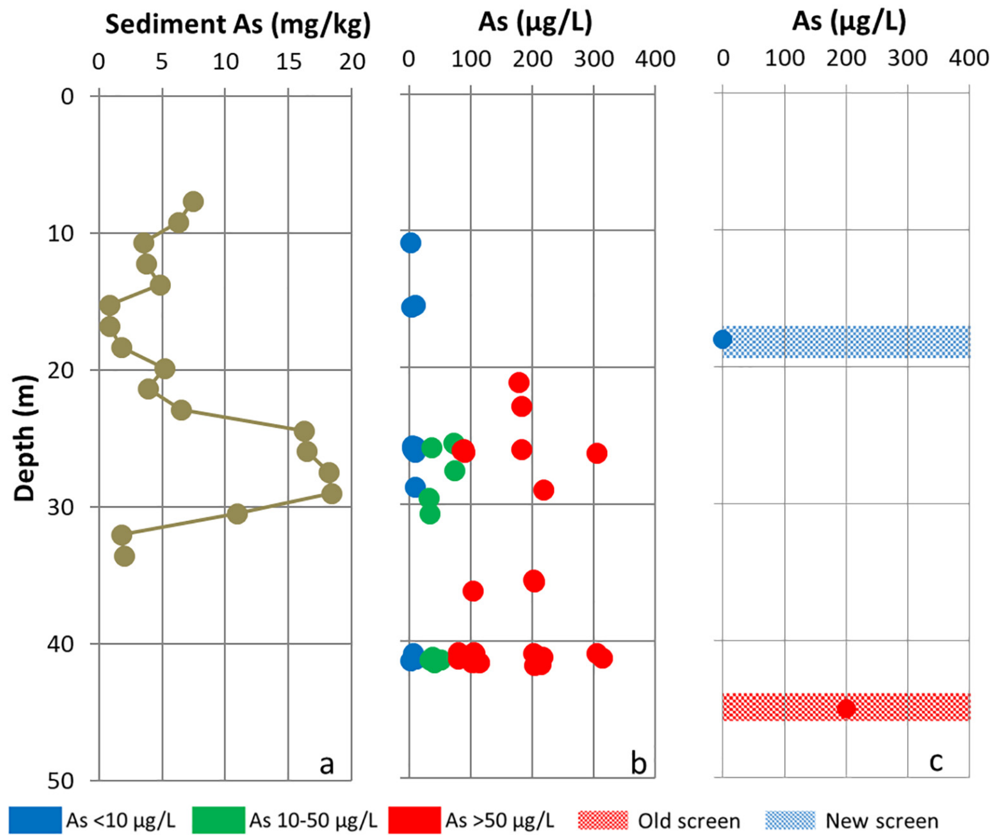

Fig. 8. (a) Depth profile of sediment As measured by XRF in study village RAV78. (b) Depth profiles of groundwater As measured with the kit in the same village. (c) Screened interval of a household well installed to target the lowest As levels in both sediment and groundwater. Field testing of this well after two years of household use using a submersible pump continues to show As < 10 μg/L.

groundwater As concentrations in the Ravi floodplain (Figs. 3a and 3b).

It is important not to overstate the role of the solid phase as the sole controlling factor, however. There are deviations from this relationship in RAV50, RAV63, and RAV82, i.e. even within the other Ravi floodplain villages. The most prominent outlier is RAV92 where high As concentrations in well water are associated with only modest levels of As in aquifer sands (Fig. 10b). Another is RAV07 where, instead, intermediate As levels in aquifer sands might have suggested higher As concentrations in groundwater based on the other villages in the Ravi floodplain.

4.2. An oxidative mechanism of As release to groundwater

Several features of the data point to a mechanism of As release to groundwater in the Punjab plains that differs from the reductive-dissolution of Fe oxides extensively documented in the Bengal basin. First, the As concentration in the sands is high and often correlated with groundwater As levels. Second, a large proportion of As(V) exists in both the solid and solution phase. The presence of oxidized As(V) is particularly striking given the clearly anaerobic conditions indicated by detectable levels of Fe in groundwater (Fig. 4). In the Bengal basin, As(III) typically dominates in both reduced aquifer sands and anoxic groundwater (Polizzotto et al., 2005; Lowers et al., 2007; Polizzotto et al., 2008; Gnanaprakasam et al., 2017). Another key differentiating feature is that the concentrations of NO_3^- and SO_4^{2-} in groundwater of the Punjab plains are much higher than in the Bengal basin (BGS/DPHE, 2001).

Our observations from the Ravi floodplain suggest that arsenic concentrations are not regulated solely by reductive dissolution of Fe oxides. Although reduction of secondary Fe phases occurs based on dissolved Fe levels, As release in groundwater appears to be predicated on or exacerbated by the dissolution of primary minerals. We conjecture that particularly high levels of As in groundwater of the Ravi floodplain could be due to the oxidation of As-bearing pyrite derived from slate and black shale upstream in the Greater Himalaya (Ganai and Rashid, 2015; Alizai et al., 2011). This oxidation could both release As(V) directly into groundwater, and form high levels of As-bearing Fe oxides within sediments downstream that are susceptible to reduction. One study of stream sediment composition in the floodplain of the Pin River, a tributary of the Spiti River, reports 47 out of 444 samples with As concentrations in the 15–100 mg/kg range from the watershed of the Sutlej (Kanwar and Ahluwalia, 1983).

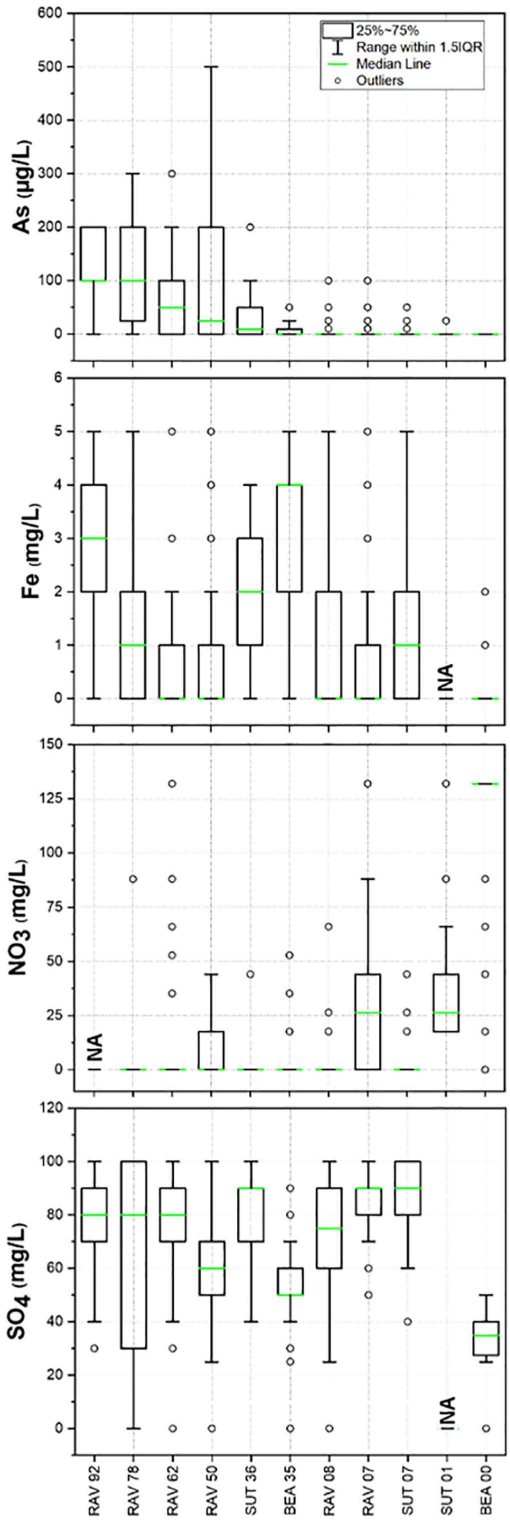

Fig. 9. Box Plot of groundwater field parameters across the study area (data not recorded = NA).

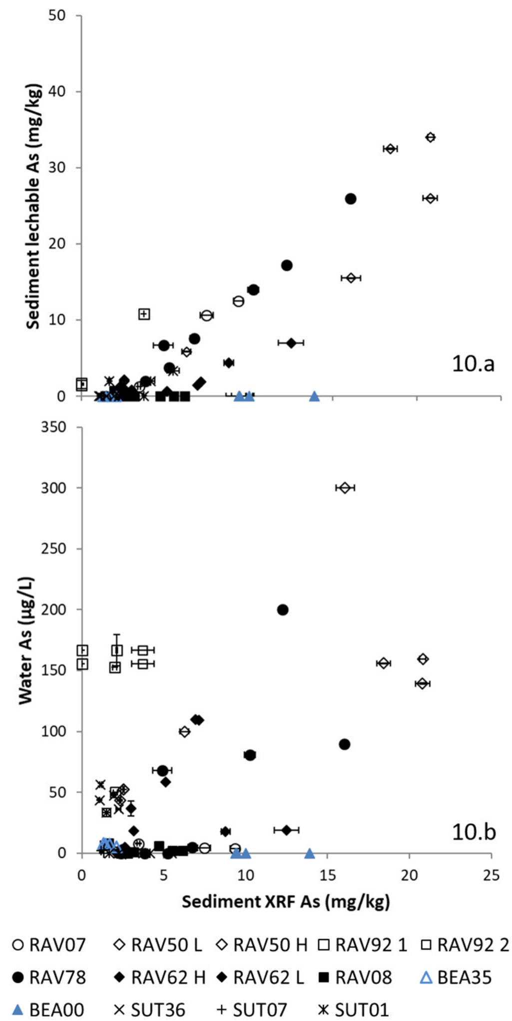

Fig. 10. (a) Sediment leachable As measured with the kit and (b) groundwater As measured with the kit averaged in 20-ft depth intervals as a function of sediment total As measured by XRF for the 11 study villages. Standard deviations are shown in both dimensions but are not necessarily visible. Symbol are the same as in Figs. 3a–3d, with the two villages with the lowest As concentrations in groundwater shown blue.

Under the proposed scenario, the oxidation of arsenic-pyrite could have been promoted by high levels of NO_3^- and resulted in high levels of SO_4^{2-}. The supply of nitrate may be anthropogenic given extensive use of fertilizer in the region (Rao et al., 2017). Oxidation of pyrite by NO_3^- is effective in oxidizing As and Fe, and has been invoked to explain elevated levels of As in groundwater in several aquifers (van Beek et al., 1988; Postma et al., 1991; Stollenwerk et al., 2007; Zhang et al., 2009; Jessen et al., 2017). Sulfide oxidation would produce sulfate in solution whereas the persistence of As in solution would depend on the persistence of Fe(II) in groundwater. The difference in age of aquifers sands containing As-enriched minerals in the northern and southern Ravi villages indicated by radiocarbon dating also suggests that the supply of As-enriched minerals from the Himalayas may have occurred over multiple periods of enhanced slate and shale erosion instead of a single catastrophic event.

The available data also point to some inconsistencies with this explanation, however. The upstream watersheds of the Ravi, Beas, and Sutlej rivers all contain slate and shale, including black shale (Ganai and Rashid, 2015; Misra and Tewari, 1988; Mushtaq et al., 2018; GSI, 2004). Nearly 59% of the 5,000 km^2 upstream watershed of the Ravi River is composed of slate and shale. This is about twice as much as in the upstream watershed of the Beas (29% of 15,000 km^2), but comparable to the proportion of slate and shale in the upstream watershed of the Sutlej River (55% of 27,000 km^2) (GHP, 2013; Rana et al., 2014). It therefore remains unclear based on watershed geology upstream why the Beas and Sutlej floodplains show a much lower proportion of wells with high levels of As compared to the Ravi (Fig. 1).

4.3. Oxidative As removal from groundwater

Whereas NO_3^- in groundwater could have oxidized primary sulfide minerals and caused an increase in groundwater As concentrations, the effect may have may have partially been countered by a different process. This is the re-oxidation of Fe(II) and even As(III) coupled to denitrification resulting from high levels of NO_3^- (Senn and Hemond, 2002; Smith et al., 2017). We do not have matched groundwater data for Fe and NO_3^- data from the same wells in the drilled villages because NO_3^- was measured with a kit on a first subset of samples and Fe was measured on a subsequent survey. We can therefore not verify that these two groundwater constituents are mutually exclusive, although it seems likely based on thermodynamics and kinetics, as well as observations elsewhere including Sindh province of Pakistan Naseem and MacArthur (2018). The available kit data do indicate that the proportion of wells elevated in NO_3^- is considerably higher for low-As wells compared to high-As wells.

4.4. Implications for reducing exposure

Blanket testing of the villages selected for drilling has confirmed that high spatial variability of As in groundwater is not limited to the Bengal basin (BGS/DPHE, 2001; van Geen et al., 2003; MacArthur et al., 2004) and extends to the Indus floodplain. The spatial variability of groundwater As in the Punjab appears to be controlled geochemically in two more ways besides the reductive dissolution of Fe oxides: (1) the total As concentration of aquifer sands which may have released from sulfides by NO_3^- in the past, (2) the current supply of NO_3^- which precipitates Fe(II) out of groundwater along with some As(V).

Excessive use of groundwater in the Punjab has altered the groundwater flow regime in the region (Wada et al., 2010) and may have transported contaminants from shallow aquifer to greater depth (Lapworth et al., 2017). Under the first additional mechanism listed above which implies a highly localized control determined by geology, perturbation of groundwater flow by irrigation pumping (Lapworth et al. 2017) is not very likely to lead to much spreading of elevated As in groundwater. Elevated levels of NO_3^- combined with elevated levels of Fe in adjacent (presumably not the same) wells also suggests little mixing between geochemically distinct shallow aquifers (Fig. 9). Under the second additional mechanism listed above, irrigation pumping combined with fertilizer application may actually have reduced groundwater As concentrations, as previously proposed by Naseem and MacArthur (2018).

The practical implication of these findings is that wells that are currently low in As are unlikely to become contaminated in the short- to medium-term. Contamination would have to be by advection from a high As portion of the aquifer and would be considerably retarded by adsorption (van Geen et al., 2008a,b). Advection of high nitrate water should, if anything, reduce rather than increase As concentrations given that any As in the solid phase supplied as sulfides appears to have been already oxidized based on the XAS data. This means every effort should be made to inform individual households in the region, starting with the entire Ravi floodplain, of the status of their well with respect to As using a field kit (van Geen et al., 2019). Test results are likely to remain valid for a considerable time. Unlike in Bangladesh, villages in the region have never been blanket tested for As and households are not aware about the severity of the problem and the health impacts of chronic exposure to As. While new wells continue to be installed throughout the region, the field kit could also be used in the Ravi floodplain to test sand cuttings for leachable As to target low As intervals. The massive deployment of fields kits for testing wells and sand cuttings could have a rapid impact on exposure and would be much less expensive than the limited number of centralized water supply schemes provided by the government (van Geen et al., 2019).

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gca.2020.03.003.

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