Arsenic and other water-quality issues affecting groundwater, Indus Alluvial Plain, Pakistan.

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ABSTRACT

Groundwater beneath the alluvial plain of the Indus River, Pakistan, is reported to be widely polluted by arsenic (As) and to adversely affect human health. In 79 groundwaters reported here from the lower Indus River plain, in southern Sindh Province, concentrations of As exceeded the WHO guideline value of 10 µg/L in 38%, with 22% exceeding 50 µg/L, Pakistan's guideline value. The As pollution is caused by microbially-mediated reductive dissolution of sedimentary iron-oxyhydroxides in anoxic groundwaters; oxic groundwaters contain < 10 µg/L of As. In the upper Indus River plain, in Punjab Province, localised As pollution of groundwater occurs by alkali desorption as a consequence of ion-exchange in groundwater, possibly supplemented by the use for irrigation of groundwater that has suffered ion-exchange in the aquifer and so has values > 0 for residual sodium carbonate.

In the field area in southern Sindh, concentrations of Mn in groundwater exceed 0.4 mg/L in 11% of groundwaters, with a maximum of 0.7 mg/L, as a result of reduction of sedimentary manganese oxides. Other trace elements pose little or no threat to human health. Salinities in groundwaters range from fresh to saline (EC up to 6 mS/cm). High salinities result from local inputs of waste-water from unsewered sanitation, but mainly from evaporation/evapotranspiration of canal water and groundwater used for irrigation. The process does not concentrate As in the groundwater owing to sorption of As to soils. Ion-exchange exerts a control on concentrations of Na, Ca, and B, but not on As. High values of Cl/Br mass ratios (most » 288, the marine value) reflect the pervasive influence on groundwater of sewage-contaminated water from irrigation canals through seepage loss and deep percolation of irrigation water, with additional, well-specific, contributions from unsewered sanitation.

Keywords: arsenic, As, manganese, Mn, salinity, water quality, groundwater, Pakistan.

1. Introduction

The guideline value for the concentration of arsenic (As) in drinking water is given as 10 µg/L by the World Health Organization (WHO 2017). Concentrations of As in groundwater used for drinking from many of the World's deltaic and alluvial aquifers commonly exceed 10 µg/L as a result of natural mobilisation of As from aquifer sediments by mechanisms unconnected to mineralization or mining. The high concentrations adversely affect the health of millions of consumers who rely on groundwater for domestic supply, whilst also threatening agriculture by polluting soils with As in irrigation water pumped from such aquifers (see Ravenscroft *et al.* 2009 for a review).

Across Pakistan, many surveys have shown that concentrations of As in groundwater > 10 µg/L are common, whilst a small percentage exceed the provisional value for Pakistan of 50 µg/L (PEPA, 2008): such concentrations pose a risk to human health (Shrestha 2002; UNICEF 2004; Ahmad *et al.* 2004; PCRWR 2007, 2008, 2010; Haque *et al.* 2008). By 2004, 36% of the population of Sindh Province, and 20% of the population of Punjab, were estimated to be at risk from As in groundwater (Ahmad *et al.* 2004). Figures quoted by Rabanni *et al.* (2016) for a later national survey, reported in 2007, show that groundwater with > 10 µg/L As was tapped by 12 % of wells in Punjab and 11 % of wells in Sindh. Using population figures from the 2017 census (PBS 2017) and assuming 80% of the population drink groundwater, these figures extrapolate to some 11 million in Punjab and 4 million in Sindh at risk (we discount the national risk estimate of Podgorski *et al.* 2017 for reasons given in the supplementary information). More locally, a survey in Khairpur District, Sindh, allowed Rabanni *et al.* (2016) to estimate that 13 million of a putative 40 million (*i.e.* around 32%) of the population along the Indus River were at risk from groundwater with >10 µg/L As. No raw data are available to confirm the reports in any of the above.

That As pollution of groundwater in Pakistan is widespread has been confirmed by more than 40 local studies (Table S1). Unfortunately, only a few of these studies report raw data that substantiates the findings. Most of these studies were concerned with mapping the As pollution in order to quantify the risk posed to human health. Few have sought to identify the mechanism(s) of pollution, exceptions being Nickson *et al.* (2005) and Farooqi *et al.* (2007a,b) for Punjab, Naseem (2012) and Husain *et al.* (2012) for Sindh, and Ravenscroft (2007) basinwide. Remarks on mechanism by Podgorski *et al.* (2017) are discounted for reasons given in the supplementary information.

Aquifer development and remediation must be based on sound scientific understanding, so the mechanism of As pollution must be understood. The main aim of our study was to determine the mechanism of As pollution in groundwater in the Indus alluvial plain, Pakistan. Secondary aims were

to provide baseline compositions for groundwater in a region short of published data, determine the origin of high salinity in groundwater in southern Pakistan, and quantify the potential threat to human health and to agriculture posed by constituents in groundwater, particularly trace elements (*e.g.* Pb, B).

2. Study Area

2.1 Locality and climate

The study area is the region around Tando Allahyar, Sindh Province, between 10 and 40 km east northeast of Hyderabad and the Indus River (Fig. 1). It lies within the alluvial plain of the Indus River basin and is at an elevation of around 22 m with a total relief of no more than 5 m. The alluvial plain at the latitude of the study site is around 150 km wide as a result of repeated avulsion of the Indus River (Holmes 1968; Holmes and Western 1969; Inam *et al.* 2007).

The climate of southern Sindh is semi-arid to arid, with annual rainfall of around 125 mm occurring mostly during the months of July and August. Rare rainfall events result in up to 1100 mm of precipitation over days to weeks, such as occurred in 2011 and 2015 (ADB 2013). Annual pan evaporation is around 2000 mm. Daytime temperature often exceeds 46° C between May and August whilst minimum temperatures, which occur in December and January, rarely drop below a temperature of 2° C.

Across Sindh, irrigation underpins an economy based largely on arable and fruit farming. The soils of the Indus River plain are largely Calcisols (FAO, 2017) and typically would have a pH (water equilibrated) in the range 8.1 to 8.3 or lower (*e.g.* Ahmed *et al.* 2017).

2.2. Water Supply

Water for irrigation, industrial, and domestic use derives from the Indus River and from shallow alluvial aquifers. Indus River water is supplied through a network of unlined irrigation canals fed from the Indus River at the Sukker Barrage, some 240 km to the north (see the Supplementary Information, SI, and Azad *et al.* 2003; Fahlbusch *et al.* 2004; Inam *et al.* 2007). The barrage was completed in 1932 (Fig. 1 and Supplementary Information, Section S1). The availability of canal water for irrigation decreases from trunk to tail of the distribution system. Where canal supply is inadequate, groundwater is pumped to compensate and so comprises between 20% and 100 % of irrigation water, depending on proximity to canals (Mangrio *et al.* 2015; Qureshi *et al.* 2008).

Groundwater comes from wells that are typically < 70 m deep because groundwater below 90 m depth is mostly saline. Groundwater levels vary seasonally between 1 and 3 meters, decreasing in

October – April (the dry season). Abstraction for irrigation is through private wells with motorised pumps in boreholes typically 46 cm (18 inches) in diameter. Screens are either PVC and 3.9 – 4.6 m (13 – 15 feet) in length or iron and 3.0 – 3.6 m (10 – 12 feet) in length.

For personal and domestic use in urban areas, municipal piped water is supplemented in around 60% of household by groundwater from private hand-pumped wells. In rural parts of the study area, surface water is uncommon and there is no municipal water-supply, so groundwater is the principal or sole source of drinking water, delivered through wells fitted with hand pumps or, rarely, motor pumps. Private pumps are commonest near irrigation canals where seepage from canals (Rushton 2016) has raised the water table most, enabling cheap installation of wells at depth < 20 m. To serve the public, hand-pumped community wells tapping groundwater have been installed by government in rural and urban settings *e.g.* at road sides, and installed by community interests in mosques and shops. Hand-pumped wells are constructed with PVC or iron pipe and screen lengths are 1.5 – 3.0 m (5 – 10 feet).

2.3. The Alluvial Aquifer

In the study area, groundwater was sampled from depths ≤ 76 m, so all groundwater derives from the alluvial sediments of the Upper Tando Jam Formation (Fig. 2; Kazmi 1984). These are mostly fine sands with rare silt / clay interbeds, typically capped by floodplain silts and clays. The Upper Tando Jam Formation overlies a Lower Tando Jam Formation comprised of coarser sands, gravels, and interbedded clays (Kazmi and Jan 1997). The underlying Nasibar Formation comprises hard, multi-coloured, calcareous clays. The deposits fill an ancient erosional valley of the Indus River that was cut into the underlying Eocene basement of limestones, marly limestones, gypsiferous shales and ferruginous sandstones (Kureshy1977; Haq 1999) to depths relative to present ground level of over 200 m in its deepest parts within the study area. The valley fill of the Upper Tando Jam Formation postdates the last glacial maximum, is mostly of Holocene in age, and is derived mostly from the Himalaya (Holmes 1968; Haq 1999; Syvitski *et al.* 2013). In historic times, the Indus River flowed through, or just east of, the study area (Holmes 1968), so the uppermost alluvium, and its cover of fine-grained floodplain deposits, are possibly < 2000 years old in the study area.

2.4. Groundwater Recharge

Recharge by annual rainfall is modest and occurs mostly during the months of July and August. Rare recharge accompanies short-term inundation caused by exceptional rainfall events (ADB 2013). Most recharge occurs by seepage from the network of unlined irrigation canals across the area (Section

S1 of the SI; Azad *et al.* 2003; *cf.* Greenman *et al.*1967; Qureshi *et al.* 2008; Chandio *et al.* 2013) and deep percolation of river water used for irrigation. Such long-term irrigation has raised water tables across most of the Indus River plain from around 30 m depth in the 1900s to a level close to the surface by the 1960s in some areas (Greenman *et al.* 1967; Qureshi *et al.* 2008). As a consequence, waterlogging and salinization of soils is found now across some 25% of irrigated land in Punjab, and some 60% of irrigated land in Sindh (Qureshi *et al.* 2008).

Recharge by river flooding is largely prevented in the present day by levees that contains the present Indus River (ADB 2013; Syvitski and Brakenridge 2013). Nevertheless, exceptional flooding within the levees is relieved by diverting river water onto fields *via* the irrigation canals, so river flooding can lead to temporary inundation of the alluvial plain away from the Indus main channel (*e.g.* Fig. 7 of Deutsch and Ruggles, 1978).

The river Indus and its tributaries have repeatedly change course, even in historical times (Holmes 1968). As the climate of the Indus River plain has been arid to semi-arid since around 4 ka (Ansari and Vink 2007; Lamb 1995) the river would have been a losing stream and would have recharged groundwater. According to Panhwar (1964, quoted in Holmes 1969) these old river courses in Sindh Province, southern Pakistan, are still recognised as areas of fresher groundwater.

3. Sampling and Analytical Methods

Groundwaters were taken from 69 hand-pump wells up to 55 m depth and 10 motorised wells up to 76 m depth; for details and locations, see Fig. 1 and Table S2. Wells 1 – 35 were sampled in late February, 2015, and Wells 36 – 80 were sampled in early November, 2015. Water from trunk irrigation canals was also sampled on both occasions (Fig. 1, Table S2). Well depths were obtained from well-owners and ranged mostly from 9 to 55 metres below ground level (mbgl), with outliers of 5 and 76 metres. Well locations were determined with a hand-held GPS referenced to GTS84.

Wells were purged before sampling. Samples were collected in 13 ml polyethylene sample tubes directly from the pump outlet. When visibly turbid, samples were filtered through 0.45 µm polypropylene membrane filters to remove aquifer fines that might include As-bearing Fe-oxides. Comparisons by us and others *e.g.* Zheng *et al.* (2004), of non-turbid samples have shown that filtering introduces no noticeable artefact to chemical composition. Samples for cation analysis were acidified in the field to be 1% with respect to Analar© nitric acid; those for anion analysis were not acidified. Field measurements were made of temperature, pH, and Eh, using an Adwa AD-111 Multimeter. Calibration for Eh was by Zobel's solution.

Field measurements of turbidity were made with a HANNA HI93703-11 turbidity meter. Electrical conductivity was measured in the field with an Adwa ad-330 conductivity meter. Laboratory analysis for As, B, Br, and other trace elements was done by ICP-MS (Varian 820) using matrix-matched standards; precision and accuracy were ± 10% RSD. Analysis for Ca, Mg, Sr, Ba, Mn, Fe, P, Si, was done using ICP-AES (Varian 720) on the same dilutions used for ICP-MS and against matrix-matched; precision and accuracy are better than ± 5% RSD. For F, Cl, NO_3, and SO_4, analysis was done by ion chromatography within 2 weeks of collection; precision and accuracy are better than ± 3% RSD. Alkalinity given here is calculated from major ion balance. We calculate 'Residual Sodium Carbonate' (RSC) as [(Alkalinity) − (Ca + Mg)] in milli-equivalents per litre. All data are given in Table S2. Measurements of dissolved oxygen (DO_2) were compromised by pump aeration and are not reported. Elemental analysis was done at UCL excepting analysis for NH_4 which was done in the University of Karachi

For microbiological analysis, samples were collected in sterilized 200 ml plastic bottles and kept in the dark and at 4°C in an ice box for transportation to the laboratory. Within 24 hours of sampling, microbiological analysis was completed for total coliforms, faecal coliforms and *E. coli* using the multiple-tube fermentation technique (MPN). These assays was done in the Water Quality Laboratory of the Pakistan Council of Research in Water Resources, Karachi.

4. Results

4.1. Major Elements

Groundwaters from Tando Allahyar are fresh-to-brackish with values of EC ranging from 0.43 to 6.1 mS/cm. Groundwaters tend to freshen towards the canals, with values of EC > 2 mS/cm not being found within 500 m of any canal (Fig. 3) owing to seepage of fresh water from canals. Groundwater with EC < 2 mS/cm is found in occasional locations far from canals (Fig. 3; Table S2).

 For the major constituents (Na, K, Ca, Mg, Sr, Cl, SO_4, and HCO_3) there is little trend in groundwater composition with depth beyond a weak tendency for higher concentrations to occur between 10 and 30 mbgl (Fig. 4). The deepest well, No 44 at 76 m, is a motorised irrigation well in the middle of a field and its groundwater is amongst the freshest encountered. The lateral distributions of all dissolved constituents is heterogeneous and appear to have no clear pattern, so distributions are not shown for major elements.

The major cation is Na, with lesser amounts of Ca. Sodium concentrations range from 7 to 1,244 mg/L (Fig. 5). Many groundwaters plot along lines with Na/Cl mole-ratios of around 1. 2 or 5

(Fig. 5). Values of Na/Cl around 2 indicate evaporation of canal water, in which Na/Cl is 2 (Table S2). Values of Na/Cl $\approx$ 1 in groundwater (Fig. 5) show the effect of addition of NaCl in waste-water. Values > 2 suggest of ion-exchange. Values of Na/Cl are unrelated to depth, geographical location, or degree of urbanization; values close to 5 and close to 1 are found in groundwaters from wells in settings that are fully urban (*e.g.* Well 6) and fully rural (*e.g.* Well 26). Values of RSC for river-derived irrigation water in Tando Allahyar average –0.5 (Table S2). Values of RSC in groundwater range from −18 to +6.7, with two outliers of −29 and +11.

Ion-exchange removes Ca and adds Na (and B) to groundwater, so many in Tando Allahyar contain less Ca and more Na than expected from evaporative concentration (Figs. 5, 6a,b). Ion-exchange in groundwater is also seen in Punjab, Pakistan, (Fig. 6c, d). Concentrations of B range from 57 to 1,900 μg/L (Fig. 6b) and correlate well with concentration of Na because both are controlled by ion-exchange (this work; Nickson et al. 2005). Control of B by ion-exchange is common in soil waters (Goldberg 1993) and aquifers (Rowe 1999; Ravenscroft and McArthur 2004; refs therein).

The major anion is SO_4 accompanied by lesser amounts of Cl and HCO_3 (Table S2). Concentrations of SO_4 range from 11 to 1,900 mg/L with SO_4/Cl mass ratios mostly > 1 (Fig. 5; Table S2). In many groundwaters, the presence of H_2S was detected by smell on acidification, attesting to the presence of sulphate-reduction in the well and/or aquifer. Values of pH range from 6.9 to 8.1. Concentrations of F are < 0.75 mg/L in all wells and decrease with increase in concentrations of Ca (Table S2), as expected given the equilibrium solubility control on F exerted by CaF_2.

The Cl/Br in Tando Allahyar groundwaters show a range from 258 to 1140, with most being much higher than 300 (Fig. 7). Values of Cl/Br are unrelated to distance from canals or degree of urbanisation. The few values of Cl/Br that fall below the evaporation line are for groundwaters minimally affected, or affected not at all, by effluent inputs. Through the year, Cl/Br in canal water, which supplies all irrigation water, varies inversely with the varying volume of canal flow. Values for Rohri Canal water at low flow in February, 2015, were 584. Values of 439 to 567 were recorded for June 2016 in other canals, and 479 for the fully-flowing Jamrao Canal (Sample 83) that serves the east of the study area.

4.2. Redox-sensitive Species

Pump aeration compromised measurements of DO_2 concentrations. In their absence, we classify groundwaters as oxic or anoxic on values of Eh and the presence or absence of dissolved Fe, Mn, NH_4 and NO_3. Of the 79 groundwaters analysed, 41 are classified as oxic and are NO_3-bearing,

low in Fe and/or Mn and with a positive Eh (Table S2). Of oxic groundwater, only 2 contain $> 5\,\mu g/L$ As. A further 33 groundwaters are anoxic and contain NH_4, Fe, and/or Mn, < 0.2 mg/L of NO_3, and having negative Eh; of these, 30 contain As concentrations $> 10\,\mu g/L$ (Fig. 8a–f; Table S2). A further 5 groundwaters have equivocal signals on these grounds, either because the source well has a long screen that bridges redox zones, or because the well is defective and draws water from more than one level. Concentrations of V and U are inversely related to concentrations of As (Fig. S2 of Section S2).

Concentrations of NO_3 range from undetectable $(< 0.1$ mg/L) to 88 mg/L (Table S2). Groundwaters with > 10 mg/L NO_3 occur in both urban settings and in agricultural settings remote from human habitation. The NO_3 content of canal water was 3 mg/L in Feb 2015 and 0 mg/L in June 2016. Concentrations of NO_3 in the Indus River water at Hyderabad, in the years 1993 to 1995, are given by Dewani *et al.* (1997) as 3 to 6 mg/L NO_3.

The depth at which groundwater becomes anoxic differs from place-to-place. Anoxic groundwater do not occur at depths shallower than 9 m (Fig. 9). Oxic groundwaters are mostly < 25 m deep, with two outliers (Wells 5 and 19) in which NO_3 concentrations were > 40 mg/L. The severity of As pollution increases with depth in the aquifer to around 30 mbgl and decrease with depth thereafter (Fig. 9), as do the concentrations of dissolved Fe (Fig. 9). This trend is typical of the depth distributions of As and Fe in other As-polluted Asian deltas and alluvial settings *e.g.* the Bengal Basin (Karim *et al.* 1997; DPHE 1999; *et seq.*) and the Jianghan Plain, China (Gan *et al.* 2014).

The lateral distributions of all dissolved constituents is heterogeneous; those for As and Fe, shown in Fig. 10, are typical of all element distributions. Inherent spatial patterns in groundwater composition will, if present, be disguised by the interplay of the chemocline with well-depth: wells of different depths sample different parts of a chemocline that has a range of As and Fe concentrations, therefore disguising any real lateral pattern and making meaningless any attempt to contour the data. Real spatial patterns will be apparent only when all well depths are the same across a sampled area.

4.3 Trace elements

Concentrations of Mn in groundwater from Tando Allahyar exceed 0.4 mg/L in 11% of groundwaters, with a maximum of 0.7 mg/L, as a result of reduction of sedimentary manganese oxides. Concentrations of B, Cd, Cr, Cu, Ni, Se, Sb, are below WHO Guideline Values for drinking water, whilst WHO Guideline Values for Pb (10 µg/L) and U (30 µg/L) are found in 3% and 5% of well-water respectively. Concentrations of B reach 1.9 mg/L and so pose a potential threat to B-intolerant crops but not to human health. These results are discussed more in SI Section S4 and S5.

4.4. Microbiology

Of our 79 groundwaters, 54 are free of coliforms and 63 are free of faecal coliforms. Where coliform are present, their distribution shows only a tentative relation to depth, and no relation to other parameters, such as degree of urbanisation or proximity to canals. With regard to depth, where coliform-bearing wells are adjacent to coliform-free wells (Well pairs 78/79 and 66/67) groundwater from the shallower well has the higher coliform count (Table S2). Furthermore, in the three wells yielding coliform counts above 100 (Wells 4, 55, 66), the counts decrease with depth (Table S2). Groundwater from wells 55 and 66 also have Na/Cl close to 1 (0.78. 0.87 respectively; Table S2) and amongst the higher Cl/Br (671, 872 respectively). These results are discussed in SI Section S4.

5. Discussion of Arsenic

5.1. Mechanism of As pollution, Tando Allahyar

Pollution of water by As can be anthropogenic and derive from arsenical pesticides and herbicides, be caused in soil-water (not groundwater) by competitive-exchange with PO_4 from phosphate fertilizer, or derive from oxidation of gangue sulphides in mine-waste in spoil heaps and distributary channels. These anthropogenic mechanisms operate mostly in surface environments and are unlikely to affect groundwater, so discussion of them is given in the Supplementary Information Section S3.

There are five natural mechanisms that pollute groundwater with arsenic. These are: volcanic/hydrothermal activity, oxidative weathering of arsenic-bearing sulphides, typically pyrite and arsenic pyrite; desorption of As from mineral surfaces at high pH (sometimes termed alkali desorption), reduction of sedimentary iron-oxyhydroxides, and evaporative concentration (Welch *et al.* 1988, 2000; DPHE 1999; Ravenscroft *et al.* 2009). Hydrothermal and volcanic activities are not present in the study area (Shuja 1988), so cannot contribute to As pollution. Weathering of sulphides gives rise to As pollution where oxygenated water intersects buried sulphide mineralisation (*e.g.* Schreiber *et al.* 2000) or pyrite-rich peatlands (Appleyard *et al.* 2006): no such mineralisation is reported in the study area. Furthermore, the As-polluted groundwaters in the study area are anoxic, not oxic, so this mechanism is ruled out. A positive correlation between As concentrations in groundwater and groundwater pH is diagnostic of the operation of alkali desorption (*e.g.* Robertson 1989; Farooqi *et al.* 2007b). Groundwaters in the study area show no correlation between pH and As concentration (see Section 5.6), so this mechanism cannot be responsible for As pollution in the study area. Concentrations of Cl are a conservative tracer of evaporative concentration, but the concentrations of

As and Cl show an inverse relation, with higher As concentrations occurring in the fresher groundwaters (Fig. 11). By default, the As pollution arises from the reductive dissolution of sedimentary Fe-oxyhydroxides.

For Fe-reduction to explain the As pollution, As-polluted groundwaters must contain little or no NO_3. (Nickson *et al.* 2000, McArthur *et al.* 2012) because NO_3 is reduced in preference to Fe-oxyhydroxides. In the field area, with few exceptions, concentrations of As above 10 µg/L occur only in anoxic groundwaters that contain < 0.2 mg/L of NO_3, have a low or negative Eh (*i.e.* are reduced), and contain dissolved Fe (Fig. 8, Table S2). Further proof of anoxia is that concentrations of the oxyanions V and U, which are insoluble under Fe-reducing conditions, are low when concentrations of Fe and As are high (Fig. S2; Table S2) as is found in groundwaters in the Bengal Basin (*c.f.* Hoque *et al.* 2014). Depth profiles of NO_3, NH_4, Fe, and Mn, show much scatter owing to local variations in aquifer properties and water supply. Nevertheless, and despite clear outliers, consumption of NO_3 is evident below 15m depth and NH_4, Fe, Mn increase downward to maxima around 20 to 30 m depth in general accord with the classic redox sequence in aquifers (Champ *et al.* 1979) and marine sediments (Froelich *et al.* 1979). Taken together, these indicators show that As and Fe have a common source and that As pollution in the groundwaters of Tando Allahyar arises from reduction of iron oxyhydroxides, as postulated by Naseem (2012).

5.2. Drivers of Fe-reduction, Tando Allahyar

Reductive dissolution of Fe-oxyhydroxides and accompanying release of As is a microbial process (Ahmann *et al.* 1997, Cummings *et al.* 1999; Islam *et al.* 2004) that has been widely invoked before to explain As pollution of anoxic groundwater in alluvial and deltaic aquifers both generically (Gulens *et al.* 1979; Korte and Fernando 1991) and in specific regions: the USA (Matisoff *et al.* 1982; Korte 1991; Kresse and Fazio 2003); the Bengal Basin (Nickson *et al.* 1998, 2000; DPHE 1999; van Geen *et al.* 2003 *et seq.*), Vietnam (Berg *et al.* 2001 *et seq.*), Cambodia (Rowland *et al.* 2007 *et seq.*), Italy (Baldantoni and Ferronato 1995; Rotiroti *et al.* 2014), and in many other regions (Ravenscroft *et al*. 2009). As the process is generic and not site specific it is no surprise that it occurs in the study area.

Reduction of iron oxyhydroxides is driven by microbial metabolism of organic matter (Gulens *et al.* 1979; Chapelle and Lovley 1992; Nealson 1997; Lovley 1997; Banfield *et al.* 1998; *et seq.*). Referring to the Fe-reduction mechanism, McArthur *et al.* (2001) stated that *"It is likely that any fluvial or deltaic basin that has hosted marshland and swamp* (i.e. organic matter) *will be prone to severe arsenic contamination of borehole water."* by Fe-reduction. This simple predictive model

applies to the Indus River plain. Within the basin, reduction will be driven by more than one source of organic matter (OM hereinafter), the relative importance of which will differ from place-to-place. Potential sources are:

1). Soils and, where present, floodplain silts and clays that form local-to-regional upper aquitards over channel sands, as appears to happen elsewhere (Mailloux *et al.* 2014; Kulkarni *et al.* 2017). Such deposits are thin and uncommon in the (mostly) unconfined aquifers of the upper Indus River plain in Punjab (Greenman *et al.* 1967) but are more likely to be present in the lower Indus River plain in Sindh owing to gentler slopes and the more meandering nature of the river in the south compared to the north.

2). Surface point-sources, such as rubbish dumps *e.g.* in markets (Naseem 2012);

3). The far-field of pit latrines (McArthur *et al.* 2012);

4) Canal water. Canals are sumps for waste-water (e.g. sewage, effluent from sugar mills) that supplements OM in Indus River source-water. Where river-bank infiltration is exploited for public supply, reduction in the aquifer commonly occurs (Farnsworth and Herring 2011), so loss of canal water by seepage, and its use for irrigation, are therefore potential sources of OM to groundwater.

5). Subsurface occurrences. Sediments laid down during the Holocene Humid Period (approximately 10 to 4 ka in Pakistan; Ansari and Vink 2007; Lamb 1995) would have incorporated more OM than those laid down in the subsequent arid period from 4ka to today. Sedimentation during the arid period would nevertheless have incorporated OM from vegetation growing along frequently-avulsing rivers and in abandoned channels and cut-off meanders.

Such OM might occur as discrete deposits *e.g.* peat (McArthur *et al.* 2001; Ravenscroft *et al.* 2001), or dispersed in sediments, possibly as mineral-associated OM, as is found in soils (see the review by Kögel-Knabner *et al.* 2008), that might easily be mobilised (Neumann *et al.* 2014). The concentration of OM in sediments increases as grain size decreases, so OM in fine-sediment fills of abandoned palaeo-channels is a potential source (Saha and Sahu 2015; Desbarats *et al.* 2014, 2017; Donselaar *et al.* 2017). This potential is clear from the complex pattern of channel migration present in the lower Indus River plain as a result of repeated river avulsion (Inam *et al.* 2007; Holmes 1968; Holmes and Western 1969).

5.3. Relation of As to Fe and PO₄

In groundwaters polluted by As through reduction of Fe-oxyhydroxide, the correlation of Fe and As is often poor, whilst correlations between Fe and PO_4, or As and PO_4, may be better (McArthur *et al*. 2001, 2004 *et seq.*). This is the case for groundwaters from Tando Allahyar (Fig. 12). A poor

correlation between As and Fe in groundwater might imply that reduction of iron oxyhydroxides does not cause As pollution (*e.g.* van Geen *et al.* 2004). Such reasoning overlooks the role, during and after Fe-reduction, of secondary processes that can degrade the relation between dissolved As and dissolved Fe, even where both result from reductive dissolution of Fe-oxyhydroxides. Firstly, as reduction progresses, the As liberated may be resorbed to unreacted Fe-oxyhydroxides (Welch *et al.* 2000; McArthur *et al.* 2004). Secondly, As is accommodated into diagenetic pyrite (McArthur 1978; Belzile and Lebel 1986; Moore *et al.* 1988; Rittle *et al.* 1995; Chakraborti *et. al.* 2001; Lowers *et al.* 2007), so loss of As from groundwater to pyrite has often been invoked as the mechanism that degrades expected As-Fe correlation or explains the lack of As in some high-Fe groundwater (*e.g.* Kress and Fazio 2003; Kirk *et al.* 2004). In Tando Allahyar, many groundwaters, both arsenical and otherwise, smelled of H_2S on acidification, so the mechanism may be reducing As concentrations in some groundwaters.

Iron alone may be removed into siderite or mixed-valence hydroxycarbonates (green rust) which sorb As (Jönsson and Sherman 2008). Iron and As may be removed into symplesite (Johnston and Singer 2007). Iron and PO_4 may be removed into vivianite (Rothe *et al.* 2016), which structurally incorporates As (Mori and Ito 1950; Muehe *et al.* 2016) and can also sorb As (Islam *et al.* 2005). Furthermore, (Smith *et al.* 2017) showed that As and PO_4 may be removed from groundwater onto freshly-precipitated Fe-oxyhydroxides through anoxic oxidation of Fe(II) by NO_3. In the formation of these diagenetic (secondary) phases As, Fe, and PO_4, will be incorporated into the secondary phase in a ratio different from that in groundwater, thereby degrading inter-element relationships that might exist in groundwater as a result of Fe-reduction in the absence of secondary minerals.

In addition, alluvial/deltaic sediments are lithological heterogeneous and have a range of Fe/As ratios in diagenetically-available Fe-oxyhydroxides, so their dissolution imparts variable Fe/As ratios to groundwater, so degrading As-Fe relationships. Finally, groundwaters in alluvial aquifers are usually chemically stratified. Wells at different depths sample different parts of a chemocline, so data aggregated across wells mix chemical signatures from a range of depths and so a range of redox environments. Given the above, it is surprising that any As-bearing groundwaters show a relationship of As to Fe, as was noted by McArthur *et al.* (2004).

5.4. Mitigation of As pollution by NO_3

Concentrations of NO_3 in river water, lake water, and groundwater are typically low (typically < 2 mg/L) in the absence of leguminous plants or anthropogenic contamination because NO_3 is either rapidly utilised by plants or reduced, usually to N_2 gas, as a result of microbial activity. Data in

Livingstone (1963) suggests concentrations of NO_3 in rivers would be < 1 mg/L in the absence of human influence, and this likely would be the case for the Indus River in its natural state. In fact, concentrations of NO_3 recorded by Dewani *et al.* (1997) for Indus River water were < 6 mg/L and canal water analysed for this study have concentrations ≤ 3 mg/L (Table 1). The likely source of this NO_3 is sewage effluent disposed of by discharge into the Indus River and to canals.

Concentrations of NO_3 up to 88 mg/L are found in the groundwaters of Tando Allahyar (Table S2, Figs. 8, 9) with 16% of groundwaters containing > 10 mg/L NO_3. The NO_3 is anthropogenic and derives from unsewered sanitation, over-application of NO_3-bearing fertilizer, and from irrigation water in which NO_3 is derived from sewage effluent; with evaporative concentration factors typically up to 10, evaporation of irrigation water would typically yield up to 30 mg/L in the absence of nitrate-reduction in soils and aquifers of the region.

In the presence of NO_3, its reduction is preferred over Fe-reduction. Addition of NO_3 to Fe-bearing waters permits anoxic oxidation of dissolved Fe(II) by NO_3, a process that precipitates iron oxide and removes As, and PO_4 from groundwater by sorption (Smith *et al.* 2017). With few exceptions, likely resulting from mixed waters in the well, NO_3 and As are mutually exclusive in solution. Fig. 8a). The propensity of the groundwaters in the study area to be reducing and so As polluted is thus negated locally by the presence of some high concentrations of NO_3. We hypothesis that reduced groundwater, and so As pollution, was more widespread in the past before the impact of anthropogenic NO_3 was manifest. By distributing NO_3 into the environment, human activity in Sindh appears to have lessened the severity and extent of natural pollution by As. It follows that agricultural practice, particularly inputs of nitrogenous fertilizers, should be examined when assessing the potential for As pollution in other parts of the Indus Basin or elsewhere.

5.5. Evaporation concentrates As?

Evaporative concentration of conservative salts (*e.g.* Cl) by factors up to 10 are common in groundwaters in the study area (Fig. 5). Salinization of soils by evaporative concentration of salts potentially increases concentrations of As in recharge and so in groundwater. Canal waters contain 2 – 5 µg/L As, so a potential 20 to 50 µg/L As might occur through this route. In fact, concentration of As are unrelated to Cl concentrations (Fig. 11), which suggests that As is not significantly concentrated during evaporation. Furthermore, the relation of As to Cl is inverse in groundwaters from Punjab (Fig. 11). This is not surprising, as evaporation occurs under oxic surface conditions. The As in irrigation water and groundwater used for irrigation is sorbed to sediments in the soil zone and the unsaturated

zone in both Punjab (Nickson et al. 2005) and elsewhere (Evans *et al.* 1979; van der Graaf *et al.* 2002) and does not pass into the aquifer. This is not surprising, as soils across the Indus River plain are Calcisols (FAO 2017) and so buffered by calcite to a pH of around 8.0 ± 0.3 (Ahmed *et al*. 2017) , and so insufficiently high (i.e. > 8.5) to drive alkali desorption and so leach As into infiltrating waters. The potential for As to accumulate in irrigated soils of the Indus River plain is therefore clear and should be investigated in view of its potential for adversely affecting crops (McLaughlin *et al.* 1999; Meharg and Hartley-Whitaker 2002; *et seq.*).

5.6. Comparison of groundwater As, Punjab and Sindh

In the field area, reductive dissolution of sedimentary iron oxyhydroxides causes As pollution. In Muzaffargarh District, central Indus Plain, Nickson *et al.* (2005) showed that As pollution in some groundwaters < 30 m deep arose from the same cause, but those authors were tentative about the mechanism of As release to other groundwaters. More recently, Rabanni et al. (2016) appeared to show, albeit without supporting data, that As pollution in Khairpur District, Sindh Province, increased in the direction of the River Indus: the trend is consistent with the As pollution being caused by Fe-reduction. In contrast, for the central Indus Plain around Lahore, Farooqi *et al.* (2007a,b) and Sultana *et al.* (2014) provided good evidence that high pH drives desorption of As from sediments and so As pollution (*cf.* Robertson 1989; Welch *et al.* 2000; the alkali-desorption of Ravenscroft *et al*. 2009). Ravenscroft (2007) ascribed this mechanism to most of the Indus River plain whilst including a component of hydrothermal As.

Key indicators of these two mechanisms are compared in Fig. 13 for groundwaters from near Lahore, in Punjab, central Pakistan, and Tando Allahyar in Sindh, south-east Pakistan. Firstly, in groundwaters from Lahore, alkali desorption causes a strong positive correlation between pH and As concentrations. Such a correlation is absent from Tando Allahyar groundwaters. Secondly, As and Fe are mutually exclusive in groundwaters from Lahore, but are positively correlated, albeit weakly, in groundwaters from Tando Allahyar. Finally, NO_3 inhibits reductive dissolution of Fe-oxyhydroxides but does not inhibit alkali desorption; As-polluted groundwaters from Lahore contain much NO_3 whereas As-polluted groundwaters from Tando Allahyar contain little or none. From the discussion above it is clear that the different mechanisms of As release to groundwater can exist in the same drainage basin: alkali desorption occurs around Lahore, and reductive dissolution occurs around Muzaffargarh and Tando Allahyar, and probably in Khairpur District.

It is often assumed that natural As pollution results from a single cause in any one drainage basin. This assumption is incorrect, as we show, and as others have shown before us. Nimick (1998) showed that As pollution of groundwater in the lower valley of the Madison River, Montana, USA, had three sources: hydrothermal activity in Yellowstone Nation Park, leaching of volcaniclastic sediments, and reduction of iron oxyhydroxides. Appleyard *et al.* (2006) showed that As pollution in groundwater near Perth, Australia, resulted both from reduction of iron oxyhydroxides in deeper groundwaters and, in shallow groundwaters, from oxidation of diagenetic As-bearing pyrite in wetland peats exposed to oxidation as the water-table was lowered through over-abstraction of groundwater.

5.7. The Driver of Alkali-desorption

Across the Indus River plain, both Fe-reduction and alkali desorption have been shown to drive As pollution. We hypothesise that the underlying condition driving As pollution across the Indus River plain is Fe-reduction caused by groundwater anoxia driven by subsurface organic matter. This natural condition has been heavily modified not only by addition of NO_3 but also by long-term, pervasive, irrigation (see section 2.4). A by-product of the modifications is As pollution driven by alkali desorption. The modified state is considered below.

Arsenic pollution by alkali desorption is caused by high pH in groundwater. The causes of high pH are silicate hydrolysis, ion exchange of Ca in groundwater for Na on mineral surfaces, and evaporation of water with alkalinity in excess of (Ca+Mg), the last typically viewed as water with RSC > 0 (Eaton 1950; van Beek and van Breeman 1973; van Breemen 1983; Robertson 1989; Schlottmann *et al.* 1998; Kortelainen and Karhu 2009). Silicate hydrolysis consumes H^+ ion, so raising pH. Loss of Ca by ion-exchange drives further dissolution of calcite, increases concentrations of carbonate and bicarbonate, and so increases pH whilst shifting RSC from < 0 to > 0. Evaporation of groundwater with RSC > 0 drives it to precipitate calcite and so increases RSC, thereby increasing pH. Each process may operating independently or they may work in conjunction.

Beneath the Indus River plain, pH in groundwater is increased by ion-exchange of Ca in solution for Na on mineral surfaces. It may also be increased by evaporative concentration of groundwater (*not* river water) used for irrigation in which ion-exchange has shifted RSC from < 0 to > 0. Evidence for ion-exchange is strong and is seen in the groundwaters of Tando Allahyar (Fig. 6a,b) and those from Punjab reported by Nickson *et al.* (2005; Fig. 6d). In both cases, the exchange has been insufficient to raise pH to the degree required (pH > 8.5) to cause noticeably As pollution *via* alkali desorption. More extreme ion-exchange occurs in As-polluted groundwaters near Lahore in Punjab

(Farooqi *et al.* 2007a,b) where it has reduced Ca concentrations in some groundwaters to concentrations so low (< 10 mg/L; Fig. 6c) that equilibrium dissolution of fluorite generates F pollution (*ibid*): it is therefore not surprising that pH has risen above 8.5 and As pollution appeared as a result of alkali desorption. We speculate that one reason the aquifers have such a high ion-exchange capacity is because the part exploited for water supply is usually shallow and was, until widespread irrigation raised the water table, part of the unsaturated zone.

Where the supply of canal water is inadequate, groundwater is used for irrigation. Where that groundwater is depleted in Ca through ion-exchange, its RSC will be > 0. Values of RSC are > 0 in 93% of 147 groundwaters reported by Farooqi *et al.* (2007b) from around Lahore, Punjab, in most of which As concentrations increase with increase in pH (Fig. 13). Kelleners and Chaudhry (1998) noted positive RSC in groundwater from more than half of 400 tubewells located on the left bank of the Sutlej River in Punjab. They also noted increases in RSC in shallow groundwater in Punjab over a ten-year period and quote Beg and Lone (1992) as having note similar increases elsewhere in Punjab over a similar period. Of groundwaters reported on by Nickson *et al.* (2005) for Punjab, 68% have RSC > 0, although pH has remained ≤ 8.3.

Evaporation of groundwater with RSC > 0 tends to increase pH, although buffering by soils may moderate this process (Condom *et al.* 1999). It is therefore possible that the use of groundwaters with RSC > 0 may enhance As pollution in one or both of two ways. Firstly, it might return low-Ca water to the aquifer through deep percolation, thereby allowing further ion-exchange to drive Ca concentrations to abnormally low concentrations, and pH and As to abnormally high values. Secondly, evaporation in soils might precipitate calcite and so increase RSC and pH, thereby raising pH and mobilizing As. The latter seems unlikely because, were that happening, As concentrations would be more directly related to Cl concentrations than they are; they are unrelated or inversely related (Fig. 11). Notwithstanding that, if this process occurs, groundwater pH and As pollution will be most severe in those areas that have been irrigated the longest with groundwater with RSC > 0. This hypotheses can be tested.

It is important to note that high pH in groundwater in Pakistan cannot not result from evaporative concentration of *river water* used for irrigation. Values of RSC for the rivers suppling irrigation water (Indus, Chenab, Jhelum, Ravi, Sutlej) range from −0.3 to −0.7 (Karim and Veizer 2000). A value of −0.4 is given by Condom *et al.* (1999) for irrigation waters derived from rivers of Punjab. Values for river-derived irrigation water in Tando Allahyar average –0.5 (Table S2).

The co-occurrence of As and F in unusual concentrations is explained by ion-exchange; such co-occurrence is a chemical signature for alkali desorption as a mechanism driving As pollution. The co-occurrence can be used to distinguish alkali desorption from Fe-reduction *in the field* because Fe-reduction is not accompanied by F. A field-test for As accompanied by a pH measurement would be a condition necessary to suggest alkali desorption, with final confirmation coming from high F determined by ion-specific electrode in the field.

5.8. Prognosis for As pollution

We hypothesise that the reason alkali desorption causes As pollution in parts of Punjab but has not yet been seen to do so in Tando Allahyar or, by implication the lower Indus plain, is because of the different irrigation histories of these two areas. The rise in the water table has occurred slowly from decades of deep percolation of irrigation water and seepage from irrigation canals. This rise occurred in the Punjab by the 1960s (Greenman *et al.* 1967, Qureshi *et al.* 2003; 2008), some 90 years after intensive, industrial-scale, perennial irrigation with river water began in the 1860s (Wescoat 1991). The rise in water tables was possible in the lower Indus plain only after the completion in 1932 of the Sukkur Barrage and attendant irrigation canals (*e.g.* Rohri Canal, Fig. 1; Table 1 of Alam *et al.* 2007). We suggest that groundwater rise in Sindh lagged that in Punjab so that, in Sindh, ion-exchange in the previously unsaturated zone, and evaporative concentration of high-RSC groundwater, developed later, and has had less time to drive alkalization than it has in Punjab.

If this hypothesis is correct, the present attenuation of Fe-reduction and As pollution being caused by anthropogenic NO_3, especially in Sindh, will eventually be reversed in localities where groundwater with RSC > 0 is used for irrigation. Use of such groundwater will increase pH and drive the development of alkali desorption, causing As pollution to reappear. Values of RSC are > 0 in 19 out of 79 of our groundwaters. Values range up to 10 but as yet show no relation to concentrations of As because pH remains ≤ 8.1.

Rising water tables and evaporation of shallow groundwater has caused waterlogging, and/or salinity and/or sodicity, to affect a substantial proportion of groundwater beneath the Indus plain (Qureshi *et al.* 2008). Irrigation with groundwater accounts for a substantial, district-dependent, fraction of irrigation in Pakistan today. According to Qureshi et al. (2008, p5), some 70% of tubewells used for irrigation pump saline or sodic groundwater, albeit only a small fraction of sodic groundwaters are currently alkalized. The potential for pH to increase further in the longer term is clear and monitoring of As pollution should bear this in mind.

Our hypotheses needs to be tested because they are based on little data. Firstly, the proportion of groundwater with RSC > 0 is poorly documented in available literature. Secondly, the relation of As pollution to groundwater with RSC > 0 has been documented in one place only (Farooqi *et al.* 2007a,b). Thirdly, Muhammed *et al.* (2008) imply that pH in some soils in Punjab may reach pH > 9 under rain-fed agriculture, although that high-pH may result from raised water tables and ion-exchange. Finally, sodic soils may be remediated by dressing with gypsum (Qadir and Oster 2004). This may clean the soil but its effect on pH is not clear. It may lower pH by decreasing RSC, or raise pH and exacerbate As pollution by promoting additional ion-exchange between Ca in solution and Na on mineral surfaces: the connection, if any, between gypsum use and As pollution must be assessed.

Notwithstanding that, if we are correct, other areas of the world under irrigation with waters in which RSC > 0 may be at risk of developing As pollution by alkali desorption. Such regions may include the irrigated plains of the Ganges, Nile and Niger rivers (Jobbágy *et al.* 2017).

6. Discussion of other parameters.

6.1. Origin of Salinity

The Indus River flowed through the study area in historic times (Holmes 1968), so the fresher water at depth may be river water remnant from those times. Notwithstanding such fresher lenses, saline groundwater at depth appears to be widespread in the Indus basin of Pakistan (*e.g.* Greenman *et al.* 1967 *et seq.*). With a shoreline during the last glacial maximum around 18 ka reaching at least as far inland as the study area (Abbasi 1962; Kazmi 1984; Holmes 1968; Giosan *et al.* 2006), and with the study area only some 20 m above current sea level at present, contributions to salinity from brackish water of marine origin appear possible. We have tested this possibility.

The chemistry of our groundwaters appears to rule out any contribution having been made by seawater or by brackish water of marine origin. Major element ratios depart greatly from those characteristic of seawater; *e.g.* SO_4/Cl mass ratios in groundwaters are > 0.75, and mostly much higher, compared with a value of 0.14 in seawater (Fig. 5). Similarly, most Cl/Br ratios (Fig. 7) are much higher than 288, the value for seawater. Most groundwaters plot along evaporation lines that originate at canal (Indus River) water (Fig. 5).

High-salinity waters arise through evaporation and evapotranspiration. Concentration factors up to 10 are common in the study area (Fig. 5) as a result. The 10 groundwaters with higher salinities (Fig. 5; EC > 3 mS/cm in Table S2) require apparent evaporation factors up to 40 to account for their ECs. Such high salinities probably reflect the repetitive movement of groundwater through the cycle of

abstraction for irrigation, evaporation, deep percolation, and re-abstraction for irrigation. Nevertheless, of the 10, only 3 are from wells in fields away from any building; the others are close to single buildings or in small housing compounds where salinity may be increased through a local input of waste-water.

6.2. Impact of sewage and waste-water

Values of Cl/Br mass ratio in recharging derived from rain are typically < 200 and decrease with increasing distance from coastlines *i.e.* marine influences (Davis *et al.* 1998, 2004; Short *et al.* 2017). Where groundwater is contaminated by seawater intrusion, groundwater Cl/Br plot along a mixing line between the recharge end-member and the marine value of 288. Values above the marine mixing-line reveal contamination from waste-water in sewage (Vengosh and Pankratov 1998; Davis *et al.* 1998, 2004; Katz *et al.* 2011; Panno *et al.* 2006; Alcalá and Custodio 2008; McArthur *et al.* 2012).

High values of Cl/Br in groundwater are pervasive across the field area. The high Cl/Br values appear to reflect the use of canal water for irrigation. Canal water has high Cl/Br because of the waste water, including sewage, received from towns along the 240 km route of the trunk irrigation canals serving the study area (Fig. 1). Groundwaters also spread along the Cl axis of Fig 5, showing that evaporation has strongly affected infiltrating irrigation waters; evaporation increases Cl concentrations but leaves Cl/Br unchanged. Finally, some high Cl/Br may occur from the local addition to groundwater of waste-water from unsewered sanitation, which is common in the study area (Husain 2008); evidence of such local effluent inputs come from the random presence of Na/Cl mole ratios around 1 (Fig. 5), which reflect contamination with NaCl (common salt) used for cooking, which would enter groundwater mostly in urine.

7. Conclusions

1. Pollution of groundwater by As in the alluvial aquifers of the Indus River plain, Pakistan, is primarily caused by microbial reduction of sedimentary iron oxyhydroxides, driven by the microbial oxidation of organic matter.

2. Over-application of NO_3-bearing fertilizer and unsewered sanitation add NO_3 to groundwater and suppresses Fe-reduction and As pollution: anthropogenic action has thus reduced As pollution.

3. Across the Indus River plain, ion-exchange removes Ca and adds Na (and B) to groundwater.

4. In groundwaters beneath the Indus plain of Punjab, extreme ion-exchange has increased pH to values > 8.5 and caused As pollution from alkali desorption.

5. Arsenic pollution from alkali desorption may be exacerbated by long term irrigation with alkalized groundwater *i.e.* groundwater with residual sodium carbonate (RSC) > 0.

6. As increasing anthropogenic NO_3 reduces As pollution from Fe-reduction, use of alkalized groundwater with RSC > 0 may replace it with As pollution from alkali desorption.

7. Groundwater salinity results from evaporation and evapotranspiration of canal water and ground water used for irrigation, and not from marine incursion. Evaporation factors range up to 40 but most are ≤ 10.

8. High Cl/Br mass ratio (258 – 1140) prove pervasive contamination of groundwater with sewage effluent in canal water and from point-sources of unsewered sanitation.

9. Apart from As, trace-elements in well water pose little (Pb, U) or no (Sb, Cd, Cr, Cu, Ni, Se) threat to human health and only a modest, well-specific, threat to crops (B, Mo).

Acknowledgements

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Arsenic in groundwater, and other water-quality issues, Indus Alluvial Plain, Pakistan.

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Supplementary Information

S.1. Irrigation in Pakistan.

To quote from Prathapar *et al.* (2005), *"The Indus Basin Irrigation System (IBIS) of Pakistan, home to more than 140 million people and 2 million farms, is the largest contiguous irrigation system in the world. Within the IBIS, approximately 16 million ha of land receives 172 BCM of high quality (approximately 200 ppm) river water per annum.*

The main parts of the distributary network in Sindh Province, southern Pakistan, are shown in Fig. S1, based on maps of SIDA, the Sindh Irrigation and Drainage Authority, Pakistan: see http://sida.org.pk/gisweb.aspx?id=2 and links therefrom. See Fig. 1 of the main text for the distribution of irrigation canals in the study area of Tando Allahyar
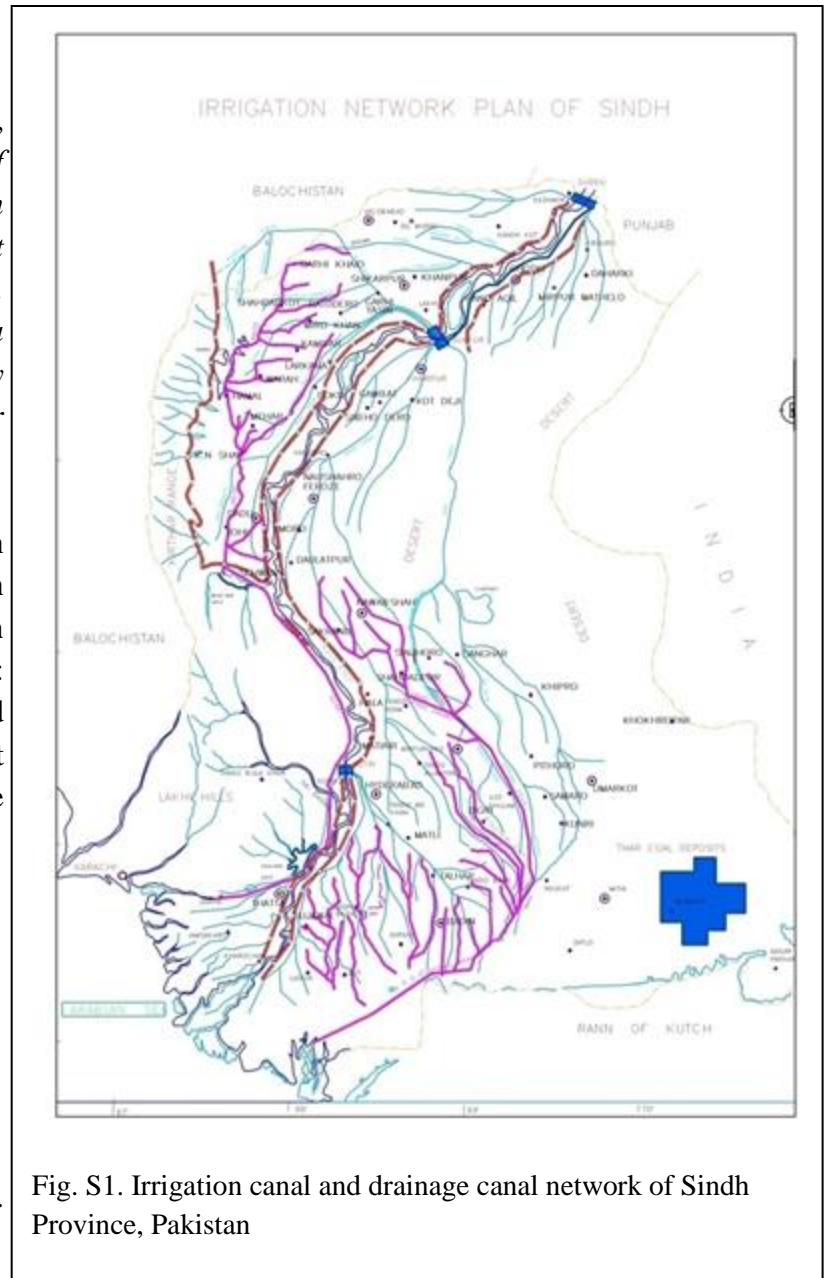
Fig. S1. Irrigation canal and drainage canal network of Sindh Province, Pakistan

S.2. Redox, V, and U.

The inter-element relations between many redox species that are shown in Fig. 8, and the depth profiles of Fig. 9, document the existence of reduction at depth. Further proof of anoxia at depth, and of redox control of trace elements, comes from the relation of As to U and V, briefly discussed in Section 5.1 of the main text. These relations are shown in Fig. S2.
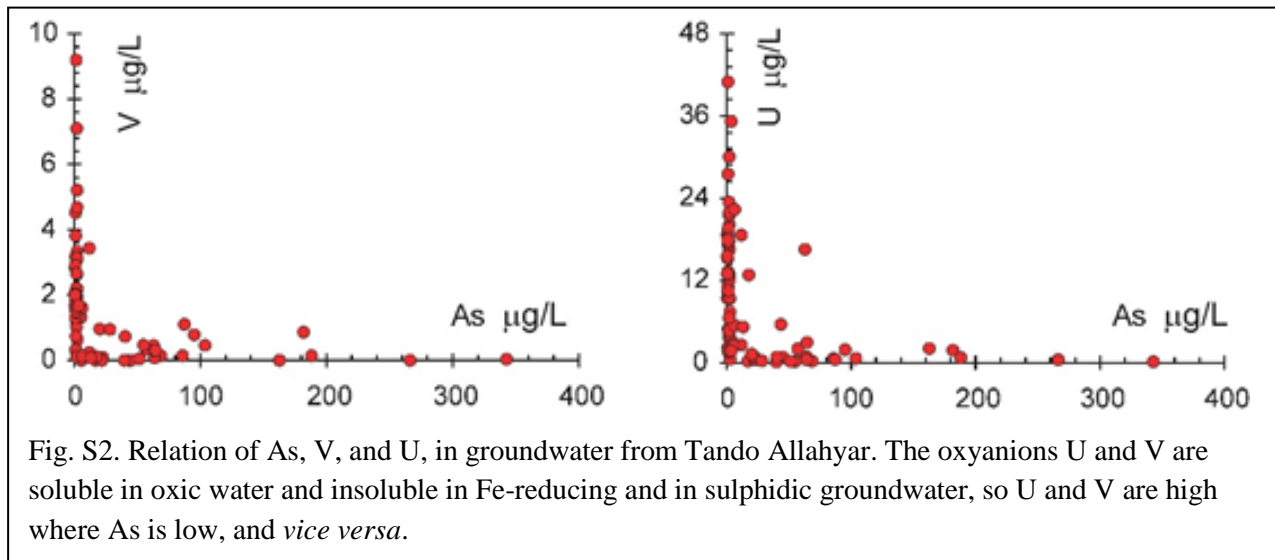
Fig. S2. Relation of As, V, and U, in groundwater from Tando Allahyar. The oxyanions U and V are soluble in oxic water and insoluble in Fe-reducing and in sulphidic groundwater, so U and V are high where As is low, and *vice versa*.

S.3. Other mechanisms of As pollution

Farooqi, Masuda & Firdous (2007), Farooqi, Masuda, Kusakabe *et al.* (2007) and Farooqi *et al.* (2009) report the source of arsenic in the Lahore area to be, in part, emissions from brick-kilns. In the Tando Allahyar area, the most As-polluted groundwaters are from Well 73, with 266 µg/L, and well 76, with 343 µg/L. These wells are within 200 and 1,000 m respectively of brick-kilns. Other wells equally near or nearer to kilns (74, 75) have only 40 and 52 µg/L respectively. The loose association of brick-kilns and As-pollution in the area is considered to be coincidental.

Pollution by As of soil-water, but not groundwater, can be caused by application of As-bearing fertilizer that causes elevated concentrations of As in soil and so in shallow leachates (Hartley *et al.* 2013). Pollution by As may also be caused in *soil-water* by competitive exchange of PO_4 from fertilizer for As if phosphate fertilizer is applied to soils contaminated by As from arsenical pesticides and defoliants (Davenport and Peryea 1991). No demonstrations are known to us of As-pollution of groundwater arising from either mechanism or from the use of phosphate fertilizers on soils to which arsenical agents have not been applied. Sulphide mining does not occur in the study area, so weathering of spoil heaps is not causing As-pollution. We therefore discount such mechanism as a cause of As-pollution in the study area.

S.4. Compliance with WHO and Irrigation-Water Standards

Here, we discuss the degree to which groundwaters from Tando Allahyar conform to WHO Guidelines for Drinking Water Quality (WHO 2017) and standards for the quality of irrigation water (Table S3).

1. Arsenic; in 38% of groundwaters, concentrations of As exceeds the WHO Guideline Value (GV) of 10 µg/L (WHO 2017) with 22% exceeding 50 µg/L, the guideline value set in Pakistan (PEPA 2008). For our domestic and community wells, the average number of users is 130 (median 50). These users will supply a greater number of family members with drinking water. The risk to health is clear as most of the wells reported on here are domestic or community hand-pumped wells.

2. Boron; in drinking water, B is may be hazardous at concentrations exceeding 2.4 mg/L (WHO 2017). Concentrations of boron in the groundwaters around Tando Allahyar are mostly in the range 0.4 to 1.9 mg/L. The snapshot concentrations we report here should therefore be investigated further over an extended time period at frequent sampling intervals in order not to alias any short-term signal.

3. Bismuth, cobalt, molybdenum, vanadium; no guideline value has been set by the World Health Organisation (WHO 2017) for these elements in drinking water. The maximum concentration recommended for irrigation water is 10 µg/L (Table S2). In 16% of groundwaters, concentrations of Mo exceed 10 µg/L with the maximum concentration being 66 µg/L, so groundwater in the study area present only a minor hazard to agriculture. Concentrations of Co and V (Table S2) are below recommended values for irrigation water of 50 and 100 µg/L respectively (Table S2).

4. Antimony, barium, cadmium, chromium, copper, lead, nickel, selenium, and uranium; the elements Cr, Cu, and Ni, commonly enter drinking water from well and pump fittings, such as components plated with chrome or nickel, Cu piping and washers. None are present in concentrations of concern either for human health or agriculture. Of the other elements, none apart from Pb and U in a few groundwaters only exceed WHO GV (WHO 2017) and most concentrations are much lower. Only Pb and U pose any threat to consumers and that threat is low. For U, only 2 groundwaters exceed the WHO GV of 30 µg/L; the maximum is 41 µg/L. Concentrations of Pb exceed the WHO GV of 10 µg/L in only 4 groundwaters, the maximum being 15 µg/L. In solution, Pb is quickly scavenged by particles, so detectable Pb concentrations likely derive from components of the well and pump (*e.g.* Pb piping, washers, solder). The concentrations found here should not be extrapolated to imply potential contamination or pollution of the aquifer by Pb.

5. Manganese; a guideline value for Mn in drinking water of 0.4 mg/L was abandoned by WHO for its 2011 guideline values (WHO 2017) on the grounds that 0.4 mg/L was "well above concentrations of manganese normally found in drinking-water", a statement that was plainly erroneous (see McArthur *et al.* 2012). In the study area, 9 groundwaters (11%) exceed 0.4 mg/L of Mn.

6. *Nitrate*: WHO GV is 50 mg/L NO_3. One exceedance - Well 58, with 88 mg/L. Little immediate threat from NO_3 pollution is therefore present in the study area. The nitrate derives from anthropogenic sources, so the present situation is no guidance to future risk other than to suggest that it is increasing with the passage of time.

7. Iodine: There is no WHO GV for this element. The concentrations of total-I in groundwaters range from < 1 to 60 µg/L. In only 6 groundwaters (8%) are concentrations ≥ 40 µg/L, a concentration sufficient to supply a useful fraction of the recommended daily intake for humans of 90 – 150 µg/day, depending on maturity and gender, and 250 µg/day during pregnancy and lactation (IGN 2016a). In 60% of groundwaters, concentrations of total iodine are <10 µg/L and so cannot contribute usefully to daily intake or to alleviate serious iodine-deficiency in Sindh Province (IGN 2016b). By extrapolation groundwater cannot be relied upon as a useful source of iodine in Sindh Province.

8. Fluoride: WHO GV (WHO 2017) appropriate to Pakistan is 0.75 mg/L. No exceedances.

9. Coliforms: the WHO GV (WHO 2017, p149) is zero coliform bacteria per 100ml of sample. Most well waters contain no coliform bacteria. Nevertheless, several wells yielding groundwaters with high coliform counts (*e.g.* Wells 20, 21) are found and are remote from habitation, hinting that irrigation canal water is a bacterial source or that the aquifer is patchily contaminated by coliforms as a result of the use of irrigation water containing pathogens. Nevertheless, we cannot conclude that the aquifer is itself contaminated with coliform or faecal bacteria.

Firstly, in sand aquifers, coliform bacteria are rapidly attenuated and typically travel only a few metres (*e.g.* Harvey *et al.* 1989; Carre and Dufils, 1991; Weiss *et al.* 2005; Hijnen *et al.* 2005; Knappett *et al.* 2012a; Ravenscroft *et al.* 2017). Secondly, bacterial analysis of well waters has poor repeatability so repeat analysis are essential before concluding that coliforms inhabit the aquifer. Multiple sampling throughout the year is required to confirm such a conjecture, as coliform bacteria concentrations in shallow wells in alluvial aquifers may vary seasonally in phase with antecedent rainfall (Knappett *et al.* 2012b; van Geen *et al.* 2011). Thirdly, rapid vertical flow of water down the annulus of a wells in which seals are poor can cause bacterial contamination of a well (Rudolph *et al.* 1998; Knappett *et al.* 2012b; Ravenscroft *et al.* 2017). Finally, once introduced into a well, coliform bacteria e.g. *E. coli*, may persist for many months (Parr and Caldwell 1933; Ferguson *et al.* 2011).

S.5. Hazards to Crops

1. Sodium adsorption ratio: one of many measures of the suitability of water for irrigation is its sodium adsorption ratio, SAR, defined as Na / $\sqrt{}$ (Ca + Mg), expressed in milliequivalents per litre. Of the 79 groundwaters from Tando Allahyar reported on here, 17% have an SAR > 6, a value that poses a threat to the long-term sustainability of soil quality. A further 59% have SAR < 3, a value unlikely to generate long-term problems.

2. Residual sodium carbonate (RSC). This measure provides an indication of the potential for soils to become alkaline through precipitation of sepiolite, and precipitation of calcite with loss of CO_2 gas, carbonic acid and so increase in pH. RSC = (CO_3+HCO_3)-(Ca + Mg) where values are milliequivalents /L. Values of RSC correlate positively with pH. Values of RSC exceed 0 in 33% of groundwaters from Tando Allahyar. Positive values indicate a risk of alkalinisation and sodification of soils and groundwater.

Fig. S3. RSC v pH for Tando Allahyar groundwaters. Symbols as for Figs. 5,6, of main text. Black filled circles denote samples that have undergone most ion-exchange in the aquifer; yellow filled squares are samples that have had salt (NaCl) added from septage *via* any of several routes.

3. Boron: concentrations of boron in the groundwaters around Tando Allahyar are mostly in the range 0.4 to 1.9 mg/L (Table S2). Boron in irrigation water may be a hazard to crops, the range of tolerable B concentrations being narrow for many, such as B-intolerant lemon, mango, banana, wheat, sugar cane and some vegetables (Table S3; Maas 1986, 1990; Gupta 1993; Leyshon and Jame 1993; Yau and Ryan 2008).

Table S1. Compilation of publications on groundwater in the Indus Basin. Entries in green contain the data on which the papers are based.

Table S1. Concentrations of arsenic together with other trace and minor elements in groundwater of Pakistan as of August, 2017.

Sampling location	Province	Note	Number	Fe mg/L	Mn mg/L	Cu mg/L	Zn mg/L	As µg/L	Cd µg/L	Cr µg/L	Ni µg/L	Pb µg/L	Reference	Ref No.
Punjab														
Lahore city	Punjab		16	0.8	-	< dl – 1.5	< dl – 1.9	13 – 83	-	< dl – 1	-	< dl – 1200	Abbas et al. (2015)	1
Lahore city	Punjab	1	48	0.01 – 2.3	-	-	-	25 – 72	-	-	-	0.3 – 7.1	Akhter et al. (2010)	2
Matiari and Khairpur	Punjab	3, 8	94	-	-	-	-	0 – 250	-	-	-	-	Arain et al. (2007)	3
Lahore and Sheikhopura	Punjab	1	56	-	-	-	-	5 – 80	-	-	-	-	Bibi et al. (2015)	4
Lahore, Kalalanwala, Kasur	Punjab		24	-	-	-	-	32 –1900	-	-	-	-	Farooqi et al. (2007a)	5
Eastern Punjab	Punjab	1	147	< dl – 2.8	-	-	-	1 – 2400	-	-	-	-	Farooqi et al. (2007b)	6
Lahore	Punjab	10	5	0.0001 – 0.27	0.006 – 0.11	0.01 - 10.5	-	5.3 - 36	-	-	-	-	Iftekhar et al. (2016)	7
Rahim Yar Khan	Punjab	3, 5	121	0.009 – 1.9	0.001 – 0.4	< d.l – 1.1	-	6 – 118	-	-	< dl – 81	-	Mahar et al. (2015)	8
Dera Ghazi Khan	Punjab		32	-	-	-	-	0.4 – 29	-	-	-	-	Malana and Khosa (2011)	9
Multan	Punjab		3	0.07 – 2.7	0.06 – 1.0	-	-	88 – 905	-	-	-	-	Nickson et al. (2005)	10
Muzaffargarh	Punjab		46	< dl – 1.7	< dl – 0.7	-	-	1 – 184	-	-	-	-	Nickson et al. (2005)	10
Villages in industrial areas, Sheikhupura	Punjab	1, 5	235	-	0.26 – 0.3	0.07 – 0.2	-	< dl – 390	360 – 380	-	-	-	Qazi et al. (2014)	11
Rahim Yar Khan District; Tehsil Rahim Yar Khan and Tehsil Khanpur	Punjab	1	55					<5 – 107					Qurat-ul-Ain et al. (2016)	12
Six villages, Districts Kasur, Sahiwal, Bahawalpur, Rahim Yar Khan	Punjab	1	228					0.5 – 3090					Rasheed et al. (2017)	13
Dur Pur and Jallah Jeem, Tehsil Mailsi	Punjab		52	0.02 – 0.31	0.001 – 0.05	-	-	6 – 507	-	-	-	-	Rasool et al. (2015)	14
Near Sargana and Mailsi City	Punjab	1	44	.002 - 0.05	0.001 – 0.09	-	-	11 - 828	-	-	-	-	Rasool et al. (2016a)	15
Near Sargana and Mailsi City	Punjab		44	0.05 - 3.3	0.001- 0.09	0.002 - 0.27	0.011 - 4.9	12 - 812	34 - 111	13 - 64	11 – 97	10 - 230	Rasool et al. (2016b)	16
Dur Pur and Jallah Jeem, near Sargana and Mailsi City	Punjab	1	44	0.07 – 2.0	0.002 - 0.04	0.002 - 0.14	0.016 - 4.4	13 – 395	28 – 111	12 – 61	11 – 81	20 – 160	Rasool et al. (2016c)	17
Near Sargana and Mailsi City	Punjab	1	44	0.001 - 0.3	0.002 - 0.1	-	-	12 – 449	-	-	-	-	Rasool et al. (2017)	18
Vehari District	Punjab	1	156					0.4 - 132					Shahid et al. (2017)	19
Chichawatni, Vehari, Rahim Yar Khan	Punjab	1	62	0.1 – 2.0	0.004 – 0.8	0.001 – 0.2	0.01 – 2.0	1.5 – 201	< dl – 0.6	0.3 – 2	1 – 20	0.5 – 20	Shakoor et al. (2015)	20
Fringing plains of Chenab, Sutlej, and Indus rivers	Punjab	1	123	0.09 - 1.93	0.01 - 0.78	-	-	1.2 - 206	-	-	-	-	Shakoor et al. (2018)	21
Manga Mandi, Shamki Bhattian, Kalalanwala, Nr lahore	Punjab	1, 2, 9	30	-	-	-	-	< dl – 525	-	-	-	-	Sultana et al. (2014)	22
Old Khana, Lahore	Punjab	5	10	-	-	-	-	25 – 200	-	-	-	-	Taskeen et al. (2009)	23
Bahawalpur	Punjab	1, 5	620	-	-	-	-	3 – 101	-	-	-	-	Toor and Tahir (2009)	24
R. Y. Khan	Punjab	1, 5	580	-	-	-	-	3 – 103	-	-	-	-	Toor and Tahir (2009)	24
Multan	Punjab	1, 5	590	-	-	-	-	2 – 107	-	-	-	-	Toor and Tahir (2009)	24
D. G. Khan	Punjab	1, 5	304	-	-	-	-	5 – 83	-	-	-	-	Toor and Tahir (2009)	24
Jhang	Punjab	1, 5	595	-	-	-	-	< dl – 48	-	-	-	-	Toor and Tahir (2009)	24
Leiah	Punjab	1, 5	198	-	-	-	-	4 – 62	-	-	-	-	Toor and Tahir (2009)	24
Manwali	Punjab	1, 5	301	-	-	-	-	< dl – 37	-	-	-	-	Toor and Tahir (2009)	24
Muzaffargarh	Punjab	1, 5	398	-	-	-	-	2 – 45	-	-	-	-	Toor and Tahir (2009)	24
Rajanpur	Punjab	1, 5	172	-	-	-	-	4 – 39	-	-	-	-	Toor and Tahir (2009)	24
T. T. Singh	Punjab	1, 5	388	-	-	-	-	2 – 30	-	-	-	-	Toor and Tahir (2009)	24
Sargodha	Punjab	1, 5	401	-	-	-	-	0 – 28	-	-	-	-	Toor and Tahir (2009)	24
Lahore District	Punjab	1	100					2 - 111					Waqas et al. (2017)	25
Sindh														
Tando Allayar, Tando Jam	Sindh		80	< dl – 16	< dl – 0.7	< dl – 0.11	-	< dl – 343	< dl – 0.2	< dl – 4.8	< d.l. – 2.3	< d.l. – 15	This work	26
Keti Bundar, Shah Bundar, Thata	Sindh	1, 3	56	0.03 – 0.6	0.21 – 1.0	0.001 – 0.03	0.54 – 1.7	5 – 5	-	10 – 170	490 – 1940	5 – 410	Alamgir et al. (2016)	27
Thar coalfield, aquifer 1	Sindh	1	5	0.20 – 0.37	-	-	-	81 – 107	-	-	-	-	Ali et al. (2015)	28
Thar coalfield, aquifer 2	Sindh	1	5	0.13 – 0.26	-	-	-	35 – 57	-	-	-	-	Ali et al. (2015)	28
Thar coalfield, aquifer 3	Sindh	1	5	0.11 – 0.14	-	-	-	28 – 39	-	-	-	-	Ali et al. (2015)	28
Manchar Lake region	Sindh	1, 3, 4, 5	1994	-	-	-	-	23 – 96	-	-	-	-	Arain et al. (2009)	29
Jamshoro	Sindh	1, 2, 3, 5	153	0.09 – 4.3	-	-	-	13 – 106	-	-	-	-	Baig et al. (2009)	30
Khairpur Mir	Sindh	1, 3, 4, 5	360	0.3 – 3.8	-	-	-	9 – 361	-	-	-	-	Baig et al. (2010)	31
Gambat and Thari Mirwah, Khairpur Mir	Sindh	1, 3, 4, 5	550	-	-	-	-	15 – 362	-	-	-	-	Baig et al. (2011)	32
Jamshoro	Sindh	1, 3, 4, 5	160	0.09 – 4.3	-	-	-	13 – 106	-	-	-	-	Baig et al. (2012)	33
Sukkur,	Sindh	1, 3, 4, 5	50	-	-	-	-	25 – 93	-	-	-	-	Baig et al. (2016)	34
Naushehro Firoze	Sindh	1, 3, 4, 5	50	-	-	-	-	18 – 49	-	-	-	-	Baig et al. (2016)	34
Nawab Shah	Sindh	1, 3, 4, 5	50	-	-	-	-	50 – 84	-	-	-	-	Baig et al. (2016)	34
Dadu	Sindh	1, 3, 4, 5	50	-	-	-	-	62 – 335	-	-	-	-	Baig et al. (2016)	34
Chachro and Diplo, Tharparkar	Sindh	1, 2, 5, 11	not given	0.09 - 0.38	-	-	-	6 – 4330	-	-	-	-	Brahman et al. (2013a).	35
Mithi and Nagaparkar, Tharparkar	Sindh	1, 2, 5, 11	not given	0.07 – 0.29	-	-	-	76 – 3960	-	-	-	-	Brahman et al. (2013b).	36
Tharparkar	Sindh	1, 3, 5	200	-	-	-	-	523 – 2350	-	-	-	-	Brahman et al. (2016)	37
Khairpur Mir	Sindh	1, 3, 5	180	-	-	-	-	26 – 45	-	-	-	-	Brahman et al. (2016)	37
Badin	Sindh	5	16	0.01 – 0.04				0 – 10					Husain (2008)	38
Jamshoro	Sindh	5	9	0.01 – 0.08				0					Husain (2008)	38
Thatta	Sindh	5	31	0.02 – 0.83				0 – 200					Husain (2008)	38
Tando Allahyar	Sindh	5	20	0.02 – 4.8				0 – 300					Husain (2008)	38
Tando Mohammad Khan	Sindh	5	19	0.02 – 4.4				0 – 500					Husain (2008)	38
Hyderabad	Sindh	5	21	0.02 – 7.8				0 – 60					Husain (2008)	38
Matiari	Sindh	5	18	0.01 – 2.6				0 – 200					Husain (2008)	38
Nagar Parkar	Sindh	5	23	0.01 – 0.07				0 – 60					Husain (2008)	38
Nawab Shah	Sindh	5	25	0.02 – 1.2				0 – 60					Husain (2008)	38
Tando Allayar, Tando Mohammad Khan	Sindh	5, 8	20	0.02 – 4.8	-	-	-	<10 – 500	-	-	-	-	Husain et al. (2012)	39
Tharpakar	Sindh	5, 8	20	-	-	-	-	< dl – 60	-	-	-	-	Husain et al. (2012)	39
Manchar Lake	Sindh	1, 2, 5	not given	-	-	-	-	48 – 74	-	-	-	-	Kazi et al. (2009)	40
Tando Muhammad Khan	Sindh	3, 8	24	-	-	-	-	10 – 300	-	-	-	-	Khan et al. (2014)	41
Tando Allahyar	Sindh	1, 3, 8	175	0.014 – 1.4	0.002 – 0.7	0.07 – 0.09	-	0 – 300	1 – 17	-	12 – 95	-	Majidano et al. (2010)	42
Tando Allayar, Tando Mohammad Khan	Sindh		41	0.04 – 4.8	-	-	-	<10 – 500	-	-	-	-	Naseem (2012)	43
Khairpur	Sindh	1, 3, 5, 7	2517	-	-	-	-	≤ 350	-	-	-	-	Rabbani et al. (2017)	44
Municipal Karachi	Sindh	1, 5, 6, 7	not given	-	-	0.09	4	80	40	340	500	2000	Rahman et al. (1997)	45
Across Sindh Province	Sindh	1	218	0–1				0–250					Shahab et al. (2016)	46
Matiari, Hala	Sindh	1, 5, 8	85	-	-	-	-	5 – 250	-	-	-	-	Uqaili et al. (2012)	47
Coastal Sindh Province	Sindh	1, 5	not given					1 – 84					Zubair et al. (2014)	48

Notes

Green entries have data per well, rather than summary data

dl = detection limit, which differs from paper-to-paper	Green entries have data per well, rather than summary data	
1. Summary data only, or no data, given	2. Composites of individual wells; no individual well-data given	
3. Appear not to have been acidified on collection, so suspect.	4. Evaporative concentration in lab; may have suffered Fe precipitation	5. Lacks details of collection and/or analysis
6. Minimum not given.	7. Maximum only given	8. Field testing data for As
9. Reported as mg/L but may be mg/L.	10. Table 3 and Table 5 conflict., Table 5 used	11. Data suspect

Table S2. Chemical composition of groundwater, canal water, and river water, from Tando Allahyar.

Sample N	Type	Name of site	Long. East Datum	Lat. North Datum	Type of sample	No of Users	No of Users	Date Inst.	Height mad	Depth mbgl	Sceen Length	Temp °C	pH units	Eh mv	EC µS/cm
CANAL WATERS															
Out of Field Area															
IR1	River	Indus River below Kotri Barrage.	68.31194	25.44250	Surface water	min	max		36			20.4	8.7		612
IR2	River	Indus River below Kotri Barrage.	68.31222	25.44000	Surface water				6			19.8	8.4		811
IR3	River	Indus River below Kotri Barrage.	68.31222	25.44000	Surface water				5			21.3	8.6		606
TAS-86	Canal	Channal Canal, Hala Naka	68.40306	25.39167	Flowing										365
TAS-87	Canal	Channal Canal, Hala Naka, Gangra Mori	68.40556	25.38722	Flowing										361
TAS-88	Canal	Phulelli Canal	68.40389	25.38583	Flowing										379
TAS-89	Canal	Gangra Mori	68.40083	25.38361	Flowing										381
In Field Area, fed from Sukher Barrage															
IR4	Canal	Distributary canal from Kotri Barrage	68.33333	25.43944	Surface water				46			20.4	8.4		620
IR5	Canal	Sukhur Barrage distributary.	68.58528	25.44500	Surface water				47			19.3	8.7		414
TAS-81	Canal	Naseer Wah Canal	68.67861	25.53000	Stagnent										355
TAS-82	Canal	Naseer Wah canal, near Mehran Suger Mill	68.71694	25.48889	Stagnent										356
TAS-84	Canal	Naseer Wah Canal near Juman Shah Dargah	68.73139	25.46972	Stagnent										418
TAS-83	Canal	Jamrao Canal, Sultan Abad	68.90250	25.50250	Flowing										251
TAS-85	Canal	Kisana Mori Canal (Rohri Barrage)	68.58500	25.44389	Stagnent										336
GROUNDWATERS															
TA1	Agricultural field	Machi Hotel.	68.60167	25.44556	Hand pump	300		2014	23	21.3		26.5	7.8		510
TA2	Agricultural field	Kernal Sharaf Bhatti farm.	68.62278	25.45028	Hand pump	200		2014	23	15.2		27.5	7.9		565
TA3	Community well	Obho Stop	68.66833	25.45583	Hand pump	0	not drunk	2013	24	54.9		25.3	7.6		4100
TA4	domestic well	Tando Allah Yar-Nasar Pur Road	68.69778	25.47500	Hand pump	50	60		19	42.7		27.0	7.7		1129
TA5	domestic well	Syed Ali CNG Station	68.71528	25.47833	Electric pump	0	rarely drunk	2007	21	48.8		25.5	7.5		4660
TA6	Community well	Tando Adam Road	68.72111	25.46917	Hand pump	200		1965	23	15.2		25.6	7.7		1160
TA7	domestic well	Baloch Coloney	68.73000	25.46972	Hand pump	200		2014	24	9.1		24.9	7.7		773
TA8	domestic well	Pathan Coloney Hyderabad Road	68.69694	25.46139	Hand pump	100		2011	21	21.3		27.0	7.8		1071
TA9	Agricultural field	Tajpur Road	68.59333	25.45028	Hand pump	10	20	1990	23	12.2		24.1	7.5		1725
TA10	domestic well	Kot Wali Muhammad	68.59222	25.46528	Hand pump	15		2014	21	13.7		25.6	7.5		1637
TA11	Agricultural field	Mango Garden	68.60000	25.45889	Hand pump	50		2006	22	9.1		23.8	7.9		861
TA12	Agricultural field	Barami Road, Nasar Pur	68.61528	25.46583	Hand pump	20	30	2014	23	18.3		24.0	7.6		904
TA13	Agricultural field	Brohi Mori, Nasar Pur Road	68.61722	25.47722	Hand pump	300		2014	25	18.3		22.6	7.4		1447
TA14	Agricultural field	Alam Brohi Goth	68.62417	25.50417	Hand pump	300		2012	22	21.3		25.7	7.5		1479
TA15	Community well	Nasarpur City	68.61889	25.51667	Hand pump	500		2010	23	51.8		26.3	8.0		544
TA16	Agricultural field	Nasarpur	68.63333	25.50972	Hand pump				24	21.3		26.0	7.8		2550
TA17	Agricultural field	Nasarpur Road	68.64889	25.50194	Hand pump	600		2014	22	48.8		24.2	7.6		4500
TA18	Agricultural field	Nasarpur Road-Tando Allahyar Road.	68.66139	25.49444	Hand pump			2013	21	45.7		24.0	7.8		543
TA19	domestic well	Asim Agriculture Farm	68.66806	25.52278	Hand pump	80	90	2008	23	30.5		24.5	7.6		1082
TA20	Agricultural field	Tando Somro	68.67694	25.53444	Hand pump				21	30.5		24.6	7.8		1446
TA21	Agricultural field	Tando Somro	68.68611	25.53694	Hand pump	50	60	2007	21	24.4		23.3	7.7		1669
TA22	domestic well	Tando Somro	68.69111	25.53417	Hand pump				23			26.3	7.8		1841
TA23	Agricultural field	Tando Somro Stop	68.70778	25.53417	Hand pump			2012	24	18.3		24.7	7.6		6140
TA24	Agricultural field	Tando Somro Shiakh	68.70972	25.52694	Hand pump	100		2013	22	21.3		24.2	8.1		429
TA25	Community well	Shahpur Rizvi Ali Nawaz Shah.	68.71167	25.51500	Hand pump	10			22			26.5	7.7		1496
TA26	Agricultural field	Police Post Syed Izat Shah Rizvi	68.71444	25.50083	Hand pump	50	60		22	18.3		24.5	8.1		506
TA27	Agricultural field	Menzoor Punjabi.	68.72472	25.48083	Hand pump				21	18.3		24.7	7.4		865
TA28	Agricultural field	Saleem Punjabi Bypass.	68.73167	25.47694	Hand pump	80	90	2010	18	18.3		24.3	7.6		1053
TA29	Community well	Quater Stop.	68.77167	25.47833	Hand pump	500		2010	21	18.3		24.9	7.6		818
TA30	Agricultural field	Mirpur Road.	68.78389	25.48028	Hand pump	500		2011	23	24.4		26.3	7.6		731
TA31	Agricultural field	Qamaro Sharif.	68.80111	25.48306	Hand pump	100		2011	21	15.2		25.7	7.7		1525
TA32	Agricultural field	Haji Ali Ghulam Dhal farm.	68.83389	25.48833	Hand pump				20	19.8		25.6	7.6		1719
TA33	Community well	Mirpur Road.	68.84778	25.49000	Hand pump	200		2009	20	15.2		24.6	7.7		925
TA34	Agricultural field	Sultan Abad	68.87222	25.49528	Hand pump				18	15.2		26.6	7.7		5270
TA35	Agricultural field	Bhatlu Stop.	68.82333	25.48639	Hand pump	500		2006	20	13.7		24.6	8.1		1025
TA36	Community well	Racke stop, Dedar Halipota, by roadside	68.46611	25.41056	Hand pump	55		2013	23	4.6	N/A		7.2	86	1935
TA37	Community well	DCO office TA	68.70333	25.47139	Hand pump	100		2014	22	18.3	N/A		7.4	-77	3580
TA38	Community well	DCO office TA	68.70361	25.47083	Electric pump	150		2000	22	30.5	N/A		7.5	-50	2080
TA39	domestic well	Misri Gujarwal	68.68833	25.47361	Hand pump	nfd		2012	24	24.4	N/A		7.1	63	2970
TA40	Agricultural field	Nasar pur Road, Haji Naeem Jarwar	68.69222	25.47917	Hand pump	5		2012	23	18.3	N/A		6.9	29	1937
TA41	domestic well	Khair M Jarwar	68.67722	25.48361	Hand pump	9		2014	22	48.8	N/A		7.4	-35	909
TA42	Agricultural field	Haji Ghulam Kakepota	68.63528	25.50056	Hand pump	50		2015	24	54.9	N/A		7.5	-205	747
TA43	domestic well	Haji Ghulam Kakepota	68.63528	25.50139	Hand pump	50		2011	24	30.5	N/A		7.5	-55	477
TA44	domestic well	Yousafani Farm	68.61444	25.46528	Irrigation well			1990	23	76.2	60		7.4	-71	1065
TA45	domestic well	Khan Pur Union Council Tajpur	68.59167	25.46083	Electric pump	10		2013	22	21.3	40		7.2	163	1831
TA46	domestic well	Khan Pur	68.59167	25.46083	Hand pump	10		2011	22	12.2	N/A		7.4	-11	1868
TA48	domestic well	Khan Pur	68.59139	25.46139	Hand pump	8		2014	22	12.2	N/A		7.3	40	2230
TA49	domestic well	Khan Pur	68.59111	25.46139	Hand pump	5		2005	22	12.2	N/A		7.4	75	1769
TA50	domestic well	Khan Pur	68.59139	25.46111	Hand pump	7		2005	22	15.2	5		7.4	123	2050
TA51	domestic well	Khan Pur, Imam Bargah Faqqer Wali Muhamm	68.59083	25.46611	Hand pump	20		2014	23	12.2	N/A		7.5	-7	1183
TA52	domestic well	Saen Faqqe Wali Muhammed Kot, Taj Pur	68.59056	25.46556	Hand pump	15		1985	22	12.2	N/A		7.5	-51	1405
TA53	domestic well	Saen Faqqe Wali Muhammed Kot, Taj Pur	68.59056	25.46556	Electric pump	15		2003	22	18.3	10		7.4	54	1797
TA54	domestic well	Saen Faqqe Wali Muhammed Kot, Taj Pur	68.59056	25.46556	Hand pump	20		2000	22	15.2	5		7.4	90	1166
TA55	domestic well	Saen Faqqe Wali Muhammed Kot, Taj Pur	68.59028	25.46583	Hand pump	20		2005	23	15.2	5		7.5	120	1269
TA56	Community well	Deghanee Buzdar	68.65250	25.43750	Hand pump		n/a	1995	21	18.3	5		7.6	-31	1538
TA57	domestic well	Deghanee Buzdar, Otaq	68.65333	25.42972	Hand pump	200		2005	22	12.2	5		7.5	63	848
TA58	Agricultural field	Deghanee Buzdar	68.65250	25.42389	Hand pump	100		2011	21	21.3	5		7.3	136	1686
TA59	Community well	Deghanee Buzdar	68.65167	25.42417	Hand pump	50		2006	21	21.3	5		7.4	-74	1432
TA60	domestic well	Deghanee Buzdar	68.65528	25.42528	Electric pump	7		2012	21	54.9	N/A		7.7	12	1244
TA61	domestic well	Deghanee Buzdar	68.65583	25.42472	Hand pump	7		2012	21	24.4	10		7.7	-96	1120
TA62	domestic well	Goth Baloch Shah, Nasar pur Road	68.69861	25.47611	Hand pump	12		2003	20	51.8	10		7.6	-100	885
TA63	domestic well	Goth Baloch Shah, Nasar pur Road	68.69833	25.47639	Hand pump	50		2013	22	45.7	N/A		7.6	-86	1325
TA64	Community well	Dy Amri, Nasarpur Road	68.68028	25.48611	Hand pump	50		2015	21	18.3	5		7.8	-329	774
TA65	Community well	Mooj Khan, Nasarpur road	68.65417	25.50000	Hand pump	100		N/A	22	18.3	N/A		7.9	-112	487
TA66	Community well	Nasarpur City, Dada Juman Shah	68.61861	25.51583	Hand pump	60		1990	23	24.4	20		7.9	-168	705
TA67	Community well	Nasarpur City, Dada Juman Shah	68.61861	25.51583	Electric pump	60		2013	23	54.9	N/A		7.8	-20	829
TA68	domestic well	Nasarpur City,	68.61806	25.51583	Electric pump	13		2000	23	33.5	20		8.0	19	612
TA69	Community well	Tandojam Graveyard, Moosa Kathian road	68.52972	25.43889	Hand pump	20		2013	23	18.3	5		7.4		1915
TA70	Agricultural field	Moosa Kathian road	68.53139	25.46139	Hand pump			2011	22	15.2	5		7.7	-83	3300
TA71	Community well	Govt secondary school Moosa Kathian	68.53000	25.46222	Electric pump	500		2011	23	30.5	10		7.4	58	3820
TA72	Community well	Govt secondary school Moosa Kathian	68.53000	25.46222	Hand pump	500		2014	23	24.4	15		7.6	-26	2730
TA73	Community well	Shahpur road, police check post	68.53222	25.47444	Hand pump	200		2008	22	30.5	8		7.7	-134	1486
TA74	Community well	Shahpur road, Sheedi faqeer	68.53389	25.47722	Hand pump	300		1995	21	24.4	10		7.6	-110	1355
TA75	Community well	Shahpur road, Dargah syed talib shah	68.53833	25.48556	Hand pump	100		2011	22	24.4	8		7.9	-156	1121
TA76	Community well	Goth Mochano Onar, Mosque	68.53472	25.48694	Hand pump		not drunk	N/A	26	30.5	N/A		7.3	-119	5020
TA77	Community well	Shahpur road, Allahsand chowk	68.54639	25.50167	Hand pump	300		2015	23	15.2	N/A		7.5	-18	1779
TA78	domestic well	Shahpur road, Qazi Faqeer Muhammed	68.54917	25.50972	Hand pump	50		2014	23	21.3	5		7.6	-172	1003
TA79	domestic well	Shahpur road, Qazi Faqeer Muhammed	68.54917	25.50972	Electric pump	12		2015	23	25.9	10		7.6	-33	1177
TA80	Agricultural field	Shahpur road	68.55194	25.54000	Hand pump			N/A	24	N/A	N/A		7.9	-3	452

Table S2 *ctd*. Chemical composition of waters from Tando Allahyar

Table S2 ctd. Parameters for surface and groundwaters from Tando Allahyar																	
Sample N	Na	K	Ca	Mg	Ba	Sr	Fe	Mn	NH$_4$	PO4	H$_4$SiO$_4$	F	Cl	NO$_3$	SO$_4$	HCO3	RSC
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mEq/L
CANAL WATERS																	
Out of Field Area																	
IR1	74	5.8	49	17	2.2	0.51	0.028	0.00	0.00	0.13	7.9	0.2	69	3.3	91	208	-0.5
IR2	100	6.3	55	23	2.3	0.61	0.020	0.03	0.00	0.02	8.4	0.3	106	3.2	125	218	-1.1
IR3	70	5.7	47	17	2.5	0.47	0.028	0.01	0.00	0.10	8.2	0.3	69	3.3	87	191	-0.6
IR4	67	6.6	47	17	0.1	0.46	0.012	0.00	0.00	0.06	7.8		69	3.2	87	172	-0.9
TAS-86	29	2.9	28	8	2.4	0.28	0.010	0.00		0.00	10.7		29	1.0	47	100	-0.4
TAS-87	24	3.9	28	8	0.2	0.27	0.010	0.00		0.00	10.9		28	1.2	47	77	-0.8
TAS-88	27	4.1	28	8	0.3	0.27	0.007	0.00		0.00	13.0		31	1.2	49	80	-0.8
TAS-89	30	3.2	29	9	2.4	0.30	0.007	0.02		0.00	11.0	0.5	32	1.1	51	99	-0.6
In Field Area																	
IR5	29	4.7	43	12	0.1	0.35	0.006	0.00	0.14	0.05	7.6	0.2	22	3.0	50	173	-0.3
TAS-81	21	6.3	29	10	0.1	0.31	0.023	0.01		0.00	10.0		18	0.0	46	114	-0.4
TAS-82	27	7.4	20	9	0.2	0.27	0.033	0.00		0.04	6.6		24	0.0	51	85	-0.3
TAS-84	22	6.4	40	11	0.1	0.37	0.018	0.01		0.00	12.7		18	0.0	38	167	-0.2
TAS-83	10	3.4	27	6	0.2	0.22	0.017	0.00		0.00	10.7		7	0.0	28	97	-0.3
TAS-85	21	4.2	33	8	2.4	0.30	0.090	0.01		0.02	9.9	0.3	14	0.0	38	133	-0.1
GROUNDWATERS																	
TA1	30	2.7	60	16	0.1	0.4	0.2	0.00	0.00	0.15	23	0.3	23	0.0	44	253	-0.1
TA2	30	4.9	69	14	0.1	0.4	0.0	0.08	0.00	0.10	21	0.3	44	6.0	67	200	-1.3
TA3	679	6.2	132	155	0.0	2.4	2.9	0.29	0.21	0.26	37	0.2	602	0.0	1328	277	-14.8
TA4	62	6.4	111	52	0.1	1.5	1.4	0.16	0.43	0.18	44	0.5	86	0.0	182	399	-3.3
TA5	868	8.2	168	118	0.1	2.0	0.0	0.41	0.00	0.31	40	0.3	729	43.9	1019	828	-4.5
TA6	217	10.3	46	16	0.1	0.5	0.1	0.04	0.01	0.18	35	0.4	73	1.4	130	521	4.9
TA7	59	4.7	54	40	0.1	0.9	0.4	0.18	0.00	0.14	40	0.6	37	0.0	72	378	0.2
TA8	148	5.3	60	41	0.0	1.0	0.7	0.01	0.55	0.28	38	0.3	63	0.0	159	481	1.5
TA9	225	7.9	147	56	0.2	1.0	1.3	0.33	0.20	0.35	35	0.3	167	0.2	324	641	-1.4
TA10	175	8.3	156	54	0.1	0.9	0.6	0.11	0.39	0.17	34	0.3	200	0.0	302	495	-4.1
TA11	90	5.5	76	27	0.1	0.7	0.1	0.10	0.00	0.07	28	0.2	33	18.1	94	423	0.9
TA12	46	5.9	105	38	0.1	0.9	0.1	0.29	0.00	0.11	29	0.2	38	3.4	90	462	-0.8
TA13	106	7.2	156	64	0.2	1.2	1.5	0.11	0.01	0.08	31	0.1	141	15.5	224	548	-4.0
TA14	136	7.4	160	42	0.1	1.1	1.6	0.58	0.53	0.11	38	0.2	145	0.0	242	522	-2.9
TA15	24	4.5	55	22	0.2	0.8	0.2	0.09	0.26	0.13	31	0.2	36	0.0	47	231	-0.8
TA16	339	7.6	163	52	0.1	1.1	0.7	0.33	0.36	0.19	33	0.1	431	0.0	500	297	-7.5
TA17	705	4.7	91	119	0.1	2.6	0.3	0.16	0.00	0.24	28	0.2	343	0.0	1290	527	-5.7
TA18	54	4.2	41	16	0.1	0.5	0.3	0.02	0.22	0.07	40	0.5	15	0.0	20	303	1.6
TA19	104	8.3	79	48	0.1	1.1	0.2	0.09	0.00	0.10	41		40	45.5	118	505	0.4
TA20	313	4.4	36	31	0.0	0.7	0.1	0.04	0.19	0.20	41		85	0.0	224	670	6.7
TA21	329	12.3	56	46	0.1	1.2	0.2	0.05	0.00	0.16	41	0.4	102	10.8	300	726	5.3
TA22	475	6.3	27	31	0.0	0.7	0.1	0.01	0.17	0.13	43	0.2	155	0.0	270	899	10.8
TA23	1326	11.2	104	151	0.0	2.4	0.7	0.10	0.00	0.29	48	0.0	810	0.0	1901	807	-4.4
TA24	29	4.6	38	12	0.1	0.7	0.1	0.01	0.10	0.01	24	0.3	16	0.0	41	183	0.1
TA25	238	7.6	74	52	0.1	1.3	0.1	0.03	0.07	0.15	43		177	0.0	303	438	-0.8
TA26	58	4.4	33	17	0.0	0.4	0.3	0.02	0.02	0.09	33		20	0.0	45	249	1.1
TA27	46	15.5	98	35	0.1	2.2	0.1	0.01	0.00	0.07	34	0.4	51	28.1	86	397	-1.3
TA28	110	8.4	66	51	0.1	1.3	0.3	0.00	0.00	0.13	35	0.4	74	19.6	127	454	0.0
TA29	48	4.8	92	35	0.1	0.7	0.3	0.09	0.00	0.04	33	0.4	23	12.7	73	445	-0.2
TA30	41	5.9	98	20	0.1	0.7	0.7	0.03	0.12	0.04	33	0.2	38	0.0	89	340	-1.0
TA31	273	5.2	74	47	0.0	1.0	0.1	0.05	0.00	0.14	41		93	0.0	424	491	0.5
TA32	208	9.4	157	58	0.1	1.8	0.5	0.03	0.00	0.13	38	0.2	202	1.7	395	487	-4.6
TA33	64	6.3	108	32	0.1	0.9	0.1	0.07	0.00	0.04	31	0.4	67	17.9	91	420	-1.1
TA34	835	19.4	191	157	0.0	3.9	0.1	0.44	0.26	0.18	32	0.3	1244	0.0	939	285	-17.8
TA35	180	4.6	36	30	0.1	0.6	0.1	0.03	0.00	0.11	31	0.5	64	0.9	141	452	3.2
TA36	187	10.1	186	49	0.1	1.0	0.9	0.04	0.05	0.14	34	0.1	169	0.3	535	360	-7.4
TA37	562	9.1	130	93	0.0	1.9	0.9	0.16	0.57	0.21	47	0.1	322	0.2	967	595	-4.4
TA38	292	6.7	93	54	0.3	1.2	0.3	0.15	0.38	0.18	44	0.2	209	0.1	413	461	-1.6
TA39	242	12.1	298	107	0.2	3.4	0.4	0.12	0.02	0.06	49	0.2	376	2.5	788	460	-16.1
TA40	345	16.2	397	144	0.2	3.2	0.3	0.03	0.42	0.00	35		485	0.2	952	833	-18.0
TA41	129	3.2	38	25	0.1	0.7	0.0	0.03	0.47	0.00	43	0.3	51	0.1	103	369	2.1
TA42	63	3.7	67	15	0.1	0.6	0.1	0.12	0.54	0.12	44	0.2	45	0.1	81	275	-0.1
TA43	26	3.0	56	13	0.1	0.5	0.1	0.13	0.03	0.00	42	0.3	7.3	0.0	18	273	0.6
TA44	66	5.7	106	35	0.3	1.2	0.8	0.17	0.55	0.08	42	0.2	64	0.2	116	432	-1.1
TA45	122	10.9	179	67	0.1	1.4	0.0	0.34	0.02	0.00	34	0.1	181	13.7	289	532	-5.7
TA46	166	15.6	161	60	0.1	1.5	0.2	0.49	0.43	0.00	38	0.1	126	7.6	338	606	-3.0
TA48	176	35.7	133	78	0.1	1.8	0.5	0.70	0.09	0.12	40	0.1	197	28.9	300	574	-3.6
TA49	159	11.3	117	51	0.0	1.5	0.3	0.16	0.50	0.00	42	0.2	145	5.7	261	467	-2.4
TA50	198	57.8	125	66	0.1	1.6	0.1	0.51	0.00	0.14	42	0.2	184	17.2	233	702	-0.2
TA51	98	7.1	119	25	0.2	0.8	0.1	0.26	0.33	0.11	39	0.2	103	0.1	117	437	-0.8
TA52	123	9.8	131	34	0.1	0.8	1.0	0.41	0.45	0.02	31	0.1	129	0.2	150	503	-1.1
TA53	155	37.5	131	60	0.2	1.1	0.1	0.22	0.62	0.17	33		183	0.3	210	587	-1.8
TA54	102	10.7	102	31	0.1	0.8	0.1	0.23	0.00	0.00	32	0.1	63	0.6	124	490	0.4
TA55	95	9.9	133	35	0.1	0.8	0.1	0.09	0.00	0.08	32	0.2	121	6.4	143	451	-2.1
TA56	223	6.9	97	33	0.2	0.9	0.4	0.13	0.64	0.06	43	0.4	85	8.2	239	611	2.5
TA57	40	5.5	77	50	0.1	0.8	0.0	0.17	0.00	0.09	34	0.1	23	2.0	74	466	-0.3
TA58	157	9.4	139	59	0.1	1.4	0.1	0.01	0.00	0.00	36	0.2	198	88.1	167	516	-3.4
TA59	80	7.5	172	47	0.1	1.4	3.7	0.57	1.73	0.00	43	0.2	148	0.1	181	513	-4.0
TA60	67	6.5	150	38	0.1	1.1	0.1	0.18	1.30	0.12	40	0.2	118	0.1	245	326	-5.3
TA61	70	6.5	129	28	0.2	1.2	1.1	0.21	1.60	0.21	41	0.0	98	0.2	174	348	-3.0
TA62	49	7.1	92	34	0.1	1.1	1.4	0.18	0.75	0.09	47	0.4	68	0.0	75	386	-1.1
TA63	93	7.8	138	53	0.1	1.6	1.7	0.18	0.42	0.10	48	0.3	119	0.0	261	414	-4.5
TA64	93	3.9	41	24	0.1	0.7	0.1	0.08	0.68	0.19	43	0.0	42	0.0	85	318	1.2
TA65	42	4.6	38	16	0.1	0.6	0.3	0.11	0.24	0.09	41	0.3	13	0.0	11	281	1.4
TA66	46	6.1	68	21	0.1	1.1	1.8	0.06	0.47	0.00	42	0.2	53	0.0	74	264	-0.8
TA67	62	7.4	79	24	0.1	1.3	0.3	0.11	0.09	0.09	43	0.2	77	0.0	91	290	-1.2
TA68	44	5.7	53	17	0.1	0.8	0.0	0.05	0.16	0.10	39	0.3	39	0.0	63	222	-0.4
TA69	182	9.2	178	77	0.0	2.0	3.7	0.35	0.53	0.07	47	0.3	288	0.0	413	416	-8.4
TA70	615	7.5	67	58	0.0	1.6	1.0	0.21	0.45	0.01	41	0.4	492	0.0	669	451	-0.8
TA71	489	9.4	217	126	0.1	3.4	0.1	0.42	0.70	0.10	45	0.1	615	0.2	939	358	-15.3
TA72	293	7.6	165	97	0.0	2.3	1.3	0.33	1.14	0.00	45	0.1	401	0.0	627	302	-11.3
TA73	133	6.9	147	50	0.2	1.5	4.0	0.20	1.58	0.46	45	0.3	174	0.0	236	479	-3.6
TA74	140	5.7	117	40	0.1	1.3	2.3	0.23	1.24	0.13	42	0.1	156	0.0	224	396	-2.6
TA75	111	5.3	110	27	0.1	0.7	4.8	0.28	0.91	0.11	39	0.2	72	0.0	181	436	-0.6
TA76	501	10.2	404	218	0.1	4.2	16.1	0.53	1.58	0.76	42	0.1	1034	0.0	1084	558	-28.9
TA77	219	7.7	143	51	0.0	1.1	0.4	0.16	0.43	0.08	38	0.2	250	1.9	397	351	-5.6
TA78	81	5.5	99	33	0.1	1.2	8.9	0.22	1.53	0.06	42	0.3	85	0.0	134	394	-1.1
TA79	121	5.8	108	33	0.2	1.2	0.3	0.24	1.29	0.03	44	0.2	90	0.0	150	481	-0.2
TA80	23	2.8	52	10	0.1	0.3	0.2	0.04	0.45	0.12	21	0.2	43	3.0	59	125	-1.4

Table 1 ctd. Parameters for surface and groundwaters from Tando Allahyar

Sample No	As	Br	I	B	V	Cr	Co	Ni	Cu	Mo	Se	Cd	Sb	Pb	Bi	Total Colifs (MPN)	Fecal Colifs (MPN)	E.Coli E.Coli (cfu)
	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	/100ml	/100ml	/100ml
CANAL WATERS																		
Out of Field Area																		
IR1	2	91	3	1316	1.6	0.2	0.1	1.0	3.0	2.9	0.4	0.1	0.3	1.1	0.0	90	21	1
IR2	2	133	8	1297	1.4	0.7	0.1	0.9	2.8	3.1	1.0	0.2	0.5	0.7	0.0	110	40	9
IR3	2	92	4	1353	1.6	0.1	0.1	1.1	3.2	3.0	0.5	0.1	0.5	0.8	0.1	0	0	0
TAS-86	2	37	5	1111	1.7	0.4	0.0	0.4	1.5	2.4	0.4	-0.1	1.3	0.3	0.1			
TAS-87	2	30	4	155	1.6	0.7	0.0	0.4	0.6	2.3	0.2	-0.1	1.6	0.2	-0.1			
TAS-88	2	32	4	199	2.0	0.4	0.0	0.2	0.9	2.2	-0.3	-0.2	1.1	0.2	-0.1			
TAS-89	2	39	6	998	1.8	0.8	0.0	0.4	1.1	2.3	0.1	-0.1	1.0	0.2	0.0			
In Field Area, fed from Sukher Barrage																		
IR4	2	80	5	212	1.5	0.1	0.1	0.4	1.9	3.4	0.8	0.1	0.3	0.4	0.3	70	33	2
IR5	2	38	1	168	1.4	0.1	0.0	0.3	0.9	2.9	0.6	0.0	0.3	0.3	0.2	90	26	4
TAS-81	4	34	3	105	1.3	1.0	0.1	1.0	4.5	2.6	0.8	0.0	1.2	0.8	0.1			
TAS-82	4	42	3	187	2.5	0.5	0.1	0.7	3.6	2.6	0.1	-0.1	1.1	0.6	0.0			
TAS-84	5	39	15	123	2.5	1.1	0.1	0.7	1.9	3.0	0.1	-0.1	1.4	0.4	0.1			
TAS-83	2	15	1	158	1.8	0.6	0.0	0.2	1.5	2.1	0.3	-0.1	1.2	0.4	0.0			
TAS-85	3	31	2	1049	1.6	0.5	0.1	1.0	3.8	2.4	0.4	0.0	1.2	0.8	0.1			
GROUNDWATERS																		
TA1	2.0	66	6	86	1.9	0.4	0.2	0.7	1	4	0.0	0.1	0.1	0.5	0.1	0	0	0
TA2	5	59	3	179	1.3	0.1	0.0	0.3	0	4	0.1	0.0	0.1	0.2	0.0	23	0	0
TA3	17	873	6	606	0.0	0.9	0.0	0.1	3	6	1.3	0.1	0.0	0.0	0.0	11	0	0
TA4	86	193	10	188	0.1	0.0	0.0	0.4	0	5	0.0	0.0	0.1	0.5	0.2	110	70	5
TA5	2	970	8	1196	2.0	0.3	0.2	0.0	5	14	4.4	0.1	0.0	0.0	0.0	27	0	0
TA6	1	107	4	448	2.8	0.2	0.1	0.2	0	17	0.6	0.0	0.1	0.3	0.0	0	0	0
TA7	1	115	29	236	2.1	0.2	0.1	0.3	1	11	0.0	0.1	0.1	0.3	0.0	0	0	0
TA8	69	123	19	306	0.1	0.4	0.1	0.2	0	6	0.4	0.0	0.0	0.7	0.1	34	12	0
TA9	63	302	18	626	0.5	0.2	0.2	0.4	0	4	0.0	0.0	0.1	0.3	0.1	0	0	0
TA10	2	390	21	330	1.2	0.4	0.2	0.6	0	3	0.0	0.0	0.1	0.0	0.0	40	7	0
TA11	1	58	2	302	2.0	0.2	0.1	0.2	0	4	0.0	0.1	0.1	0.2	0.1	0	0	0
TA12	2	63	0	262	1.6	0.1	0.1	0.3	0	3	1.2	0.0	0.1	0.2	0.0	50	0	0
TA13	3	203	1	350	2.2	1.3	0.2	0.8	1	5	0.0	0.0	0.1	0.2	0.1			0
TA14	44	296	12	355	0.0	2.0	0.3	2.3	0	2	0.3	0.0	0.2	6.2	0.0	80	22	2
TA15	64	69	4	174	0.1	0.1	0.0	0.1	4	2	0.0	0.0	0.0	0.8	0.0	0	0	0
TA16	45	671	26	616	0.0	0.0	0.2	0.4	0	8	0.4	0.0	0.0	0.2	0.3	0	0	0
TA17	4	910	60	827	0.1	1.3	0.0	0.4	0	32	0.4	0.0	0.0	0.0	0.0	40	8	0
TA18	3	37	5	240	0.1	0.4	0.1	0.1	0	7	0.0	0.0	0.0	2.1	0.0	0	0	0
TA19	1	91	3	465	4.5	0.3	0.1	0.3	27	19	2.6	0.0	0.0	3.3	0.0	0	0	0
TA20	1	124	63	771	0.3	0.3	0.0	0.4	14	66	0.0	0.1	0.1	15	0.0	60	12	0
TA21	2	163	7	672	9.2	0.8	0.1	0.3	3	48	2.1	0.1	0.1	1.0	0.0	80	33	0
TA22	2	261	30	480	7.1	1.1	0.0	0.1	6	22	0.4	0.0	0.0	0.6	0.0	0	0	0
TA23	2	851	44	1553	5.2	1.8	0.0	0.3	14	18	4.2	0.0	0.0	0.0	0.3	0	0	0
TA24	2	36	2	166	1.0	0.2	0.1	0.2	4	6	0.0	0.0	0.0	0.7	0.0	0	0	0
TA25	2	311	4	326	3.3	1.0	0.1	0.5	14	6	0.0	0.0	0.1	1.3	0.0	0	0	0
TA26	2	39	9	255	2.0	0.4	0.1	0.2	1	25	0.0	0.1	0.0	0.5	0.0	34	0	0
TA27	1	87	8	208	1.9	0.3	0.1	0.4	7	3	0.4	0.1	0.1	1.0	0.1	0	0	0
TA28	1	132	5	269	3.2	1.8	0.0	0.3	3	3	0.5	0.0	0.0	0.5	0.1	50	21	0
TA29	1	50	1	262	1.7	0.3	0.0	0.0	2	5	0.9	0.1	0.0	0.7	0.0	0	0	0
TA30	1	63	3	165	1.3	0.0	0.0	0.0	0	3	0.0	0.1	0.0	0.2	0.1	70	26	3
TA31	2	242	40	393	2.6	0.5	0.1	0.1	0	12	0.4	0.1	0.1	0.1	0.0	0	0	0
TA32	2	300	10	406	3.1	1.8	0.2	1.4	100	2	0.3	0.1	0.3	6.3	0.0	60	17	0
TA33	1	94	5	232	2.1	0.1	0.0	0.0	5	1	0.1	0.0	0.0	0.7	0.0	0	0	0
TA34	3	1348	64	473	0.6	2.0	0.1	0.1	15	6	5.0	0.0	0.0	0.0	0.1	0	0	0
TA35	2	72	6	566	3.1	0.3	0.1	0.1	0	33	0.6	0.0	0.0	0.3	0.1	0	0	0
TA36	1	221	30	617	2.9	3.4	0.2	0.3	8	2	1.6	0.1	0.2	1.9	0.1	0	0	0
TA37	182	666	9	1268	0.9	3.4	0.1	0.2	3	8	2.2	0.1	0.1	1.2	0.0	0	0	0
TA38	95	350	18	602	0.8	1.7	0.1	0.2	4	9	2.9	0.2	0.2	0.3	0.7	17	14	3
TA39	2	1456	24	358	4.7	0.5	0.4	0.1	2	4	10.8	0.0	0.1	1.1	0.8	0	0	0
TA40	1	896	5	1904	1.7	0.0	0.3	0.7	1	2	0.9	0.0	0.1	0.1	0.0	22	0	0
TA41	23	98	12	340	0.1	3.9	0.0	0.2	0	6	0.5	0.0	0.0	0.0	0.0	0	0	0
TA 42	22	111	8	115	0.0	1.4	0.1	0.1	17	4	0.1	0.0	0.0	3.3	0.0	13	0	0
TA43	20	21	6	82	1.0	0.0	0.1	0.4	0	8	0.6	0.0	0.0	0.3	0.1	34	26	5
TA44	57	86	4	172	0.3	3.1	0.0	0.0	0	3	0.2	0.0	0.0	0.0	0.0	0	0	0
TA45	2	230	6	286	0.3	1.9	0.2	0.0	0	3	1.0	0.0	0.1	0.1	0.0	0	0	0
TA46	2	169	16	384	1.5	0.9	0.3	0.0	1	4	1.9	0.0	0.1	0.2	0.6	0	0	0
TA48	6	379	15	432	1.6	2.6	0.4	0.6	63	4	2.9	0.2	0.2	14.2	0.0	0	0	0
TA 49	2	280	17	334	2.1	4.8	0.2	0.2	4	4	1.5	0.0	0.1	0.2	0.0	0	0	0
TA50	12	314	27	514	3.4	1.1	0.3	0.2	64	4	2.2	0.0	0.1	2.2	0.1	0	0	0
TA51	12	203	23	184	0.2	2.8	0.1	0.0	4	3	0.7	0.0	0.1	0.4	0.0	8	0	0
TA52	18	202	16	288	0.1	3.6	0.1	0.0	0	3	1.0	0.0	0.1	0.3	0.2	0	0	0
TA53	2	282	38	436	2.7	0.0	0.3	0.2	1	2	1.0	0.0	0.2	0.1	1.1	0	0	0
TA54	2	128	19	249	2.2	0.2	0.1	0.2	23	3	0.3	0.0	0.1	1.4	0.0	0	0	0
TA55	1	181	23	215	2.0	2.9	0.2	0.0	7	3	0.1	0.0	0.1	1.5	0.0	900	220	26
TA56	1	186	2	730	3.8	4.4	0.1	0.1	0	11	3.8	0.0	0.1	0.1	0.0	0	0	0
TA57	1	35	1	156	1.5	0.0	0.0	0.1	0	4	2.6	0.0	0.0	0.0	0.0	0	0	0
TA58	1	281	5	278	1.7	3.3	0.0	0.1	2	2	3.6	0.1	0.1	0.1	0.0	0	0	0
TA59	163	183	4	258	0.0	3.0	0.1	0.0	0	3	1.1	0.0	0.2	0.2	0.0	0	0	0
TA60	104	250	8	157	0.5	0.9	0.1	0.0	0	4	0.0	0.0	0.3	0.4	1.3	0	0	0
TA61	188	330	7	152	0.1	2.7	0.2	0.0	0	7	0.4	0.0	0.3	0.5	0.0	0	0	0
TA62	55	87	8	161	0.5	0.0	0.1	0.5	49	3	0.2	0.0	0.1	5.9	0.1	33	0	0
TA63	64	190	9	171	0.3	0.0	0.0	0.0	0	3	0.0	0.0	0.1	0.1	0.1	0	0	0
TA64	87	61	7	269	1.1	0.0	0.1	1.3	1	5	0.6	0.0	0.5	6.0	0.2	0	0	0
TA65	28	26	5	120	0.9	0.0	0.0	0.2	26	5	0.3	0.0	0.1	2.4	0.0	0	0	0
TA66	1	60	11	122	0.3	0.0	0.0	0.1	0	3	0.2	0.0	0.0	0.0	0.1	300	80	7
TA67	6	84	9	142	0.0	1.4	0.2	0.2	0	3	0.0	0.0	0.2	0.0	0.0	0	0	0
TA68	2	39	3	103	0.1	1.9	0.0	0.1	0	3	0.5	0.0	0.1	13.5	0.0	0	0	0
TA69	1	629	8	346	0.7	3.6	0.3	0.1	0	5	1.9	0.1	0.3	0.4	0.1	0	0	0
TA70	6	759	13	670	0.1	0.8	0.0	0.3	64	4	0.8	0.0	0.2	6.4	0.0	0	0	0
TA71	2	901	49	515	1.6	0.7	0.1	0.1	1	5	1.7	0.0	0.4	1.7	0.2	0	0	0
TA72	13	529	21	374	0.1	1.2	0.0	0.0	0	4	0.5	0.0	0.2	1.1	0.2	0	0	0
TA73	266	323	12	257	0.0	2.8	0.1	0.0	0	5	1.7	0.0	0.2	0.4	0.0	0	0	0
TA74	40	233	18	281	0.0	0.0	0.1	0.0	0	7	1.2	0.0	0.4	0.2	1.0	0	0	0
TA75	52	127	3	262	0.0	1.1	0.1	0.0	0	5	0.3	0.0	0.1	2.4	0.0	70	21	0
TA76	343	1637	8	944	0.0	0.0	0.0	0.1	1	4	1.2	0.0	0.2	0.3	0.0	0	0	0
TA77	1	385	6	474	2.0	2.6	0.2	0.3	0	3	3.7	0.2	0.3	1.9	0.2	0	0	0
TA78	40	180	8	190	0.7	0.0	0.1	1.1	110	4	0.8	0.0	0.5	10.5	0.2	0	0	0
TA79	65	180	6	257	0.3	0.4	0.1	0.0	0	9	1.2	0.0	0.3	0.1	0.0	27	13	3
TA80	4	38	2	57	1.7	0.6	0.1	0.3	0	2	1.3	0.0	0.4	1.9	0.0	0	0	0

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Table S3. Recommended maximum concentrations of listed elements for irrigation water (from http://www.fao.org/docrep/003/T0234E/T0234E06.htm#tab21; boron, B, from Ayers and Westcote 1985). The maximum concentrations listed are based on an application rate of water that is consistent with good irrigation practice (10,000 m^3 per hectare per year). For higher application rates the maximum concentrations should be adjusted downward. No adjustment need be made for application rates less than 10,000 m^3 per hectare per year. The values given are for water used on a continuous basis at one site.

Element	Maximum (mg/l)	Remarks
As	0.10	Toxicity to plants varies widely, ranging from 12 mg/l for Sudan grass to less than 0.05 mg/l for rice.
B	< 0.5 to <15	Sensitivity to B ranges from "very sensitive" (< 0.5 mg/L) for lemon, to "very tolerant" for cotton and asparagus (6–15 mg/L).
Cd	0.01	Toxic to beans, beets and turnips at concentrations as low as 0.1 mg/l in nutrient solutions. Conservative limits recommended due to its potential for accumulation in plants and soils to concentrations that may be harmful to humans.
Co	0.05	Toxic to tomato plants at 0.1 mg/l in nutrient solution. Tends to be inactivated by neutral and alkaline soils.
Cr	0.10	Not generally recognized as an essential growth element. Conservative limits recommended due to lack of knowledge on its toxicity to plants.
Cu	0.20	Toxic to a number of plants at 0.1 to 1.0 mg/l in nutrient solutions.
F	1.0	Inactivated by neutral and alkaline soils.
Fe	5.0	Not toxic to plants in aerated soils, but can contribute to soil acidification and loss of availability of essential phosphorus and molybdenum. Overhead sprinkling may result in unsightly deposits on plants, equipment and buildings.
Mn	0.20	Toxic to a number of crops at a few-tenths to a few mg/l, but usually only in acid soils.
Mo	0.01	Not toxic to plants at normal concentrations in soil and water. Can be toxic to livestock if forage is grown in soils with high concentrations of available molybdenum.
Ni	0.20	Toxic to a number of plants at 0.5 mg/l to 1.0 mg/l; reduced toxicity at neutral or alkaline pH.
Pb	5.0	Can inhibit plant cell growth at very high concentrations.
Se	0.02	Toxic to plants at concentrations ≥ 0.025 mg/l and toxic to livestock if forage is grown in soils with relatively high levels of added selenium. An essential element to animals but in very low concentrations.
V	0.10	Toxic to many plants at relatively low concentrations.

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S.6. Podgorski *et al.* 2017.

On the basis of more than 1000 groundwaters sampled across Pakistan and analysed for arsenic (As), Podgorski *et al.* (*Sci Adv.* 3, 2017; P17 hereinafter) quantify the risk to health of the population exposed through drinking groundwater and propose two mechanisms for the generation of that pollution. Given the importance of the issue, the findings of P17 need to be robust. The evidence that they are not is given below.

Previous Surveying

To assess hazard, P17 used "*population figures… calculated using census data from 2010 (Ref 55)...*". Pakistan held a census in 1998 and again in 2017 (PBS 2017). Citing a paper as questionable as their own, P17 state that "*a lack of resources in the country has prevented the comprehensive evaluation of arsenic in groundwater*". This comment misrepresents reality. A nationwide survey of As pollution of groundwater in Pakistan was done between 1999 and 2004 with UN support. The project analysed groundwater from around 20,000 wells across Pakistan (Ahmad *et al.* 2004). Table 3 of Ahmad *et al.* (2004) is given as Table S6.1. It reported that groundwater from 36% of wells in Punjab, and 20 % of wells in Sindh, contained > 10 µg/L of As. Rabbani *et al.* (2016) quote figures for a later national survey, that reported in 2007, whereby 12 % of wells in Punjab and 11 % of wells in Sindh gave water with > 10 µg/L As, figures close to those given by field data in Table S6.1. Despite discrepancies, related to methodology, the widespread nature of As-pollution in Pakistan was clear at that time. Since then, over 45 published papers have sought to further the knowledge of As pollution in Pakistan's groundwater (Table S1).

Table 3. Results of National Level Survey for Arsenic Contamination.						
Province	Total Samples (No.)		>10 ppb (%age)		>50 ppb (%age)	
	Field	Lab	Field	Lab	Field	Lab
Balochistan	619	71	1.30	1.40	0.0	0
NWFP	1560	156	0.30	22.0	0.0	0.6
Punjab	4315	428	12.2	36.0	0.60	9.0
Sindh	2218	193	11.0	26.0	1.40	10
Total	8712	848	9.0	28.0	0.70	7.0

Table S6.1. Table 3 of Ahmad *et al.* (2004); summary data from a national survey of As pollution in Pakistan, 1999 to 2004. Differences between field and laboratory data do not disguise the presence of a widespread problem.

Punjab has 110 million inhabitants, Sindh has 48 million (PBS 2017). Assuming 80% of them drink groundwater, the figures quotes by Rabbani et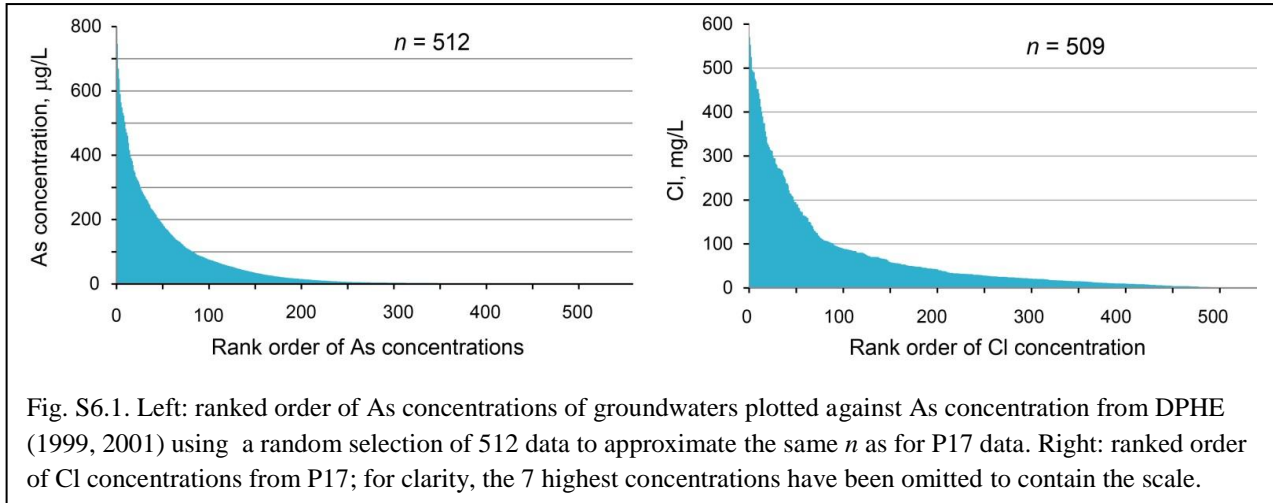 al. 2016 for the 2007 survey extrapolate to 11 million in Punjab and 4 million in Sindh at risk. Equivalent risk calculated from Table S6.1 are 33 million for Punjab and 10 million in Sindh. P17 conclude that 50 – 60 million people are at risk from using groundwater with > 10 µg/L As. Why are P17's estimates so much higher?

The differences arise from incorrect data, inappropriate methodology, and from misinterpretation of the results from the use of each. We discuss each issue below, starting with data. We consider not just data for As but data more widely because flawed data in other areas adds to the weight of evidence that the As data are suspect.

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Data

Arsenic data

P17 states that their groundwaters were analysed for As by ICP-MS. There is no mention in P17 of field-test data. The considerations below show that field data for As (of unknown accuracy) may have been included, undeclared, in P17. If so, the method description given in P17 is misleading.

Fig. S6.1. Left: ranked order of As concentrations of groundwaters plotted against As concentration from DPHE (1999, 2001) using a random selection of 512 data to approximate the same *n* as for P17 data. Right: ranked order of Cl concentrations from P17; for clarity, the 7 highest concentrations have been omitted to contain the scale.

When hydrochemical data are numerous and plotted in ranked order, smooth curves result *e.g.* As concentrations from the National Survey of Arsenic Contamination in Bangladesh (DPHE 1999, 2001; Fig. S6.1 left); Cl data of P17 (Fig. S6.1 right). In contrast, the As data of P17 show plateaus (*e.g.* A in Fig. S6.2 right) because, in 30% of samples, As concentrations are exact multiples of 50 µg/L: for 43% of samples, they are exact multiples of 5 µg/L As. Specifically, the step-up at 'A' on Fig. S6.2 indicates over-representation values of 100 µg/L As.

Fig. S6.2. Ranked order of As concentrations of groundwaters given by P17 plotted against As concentration.
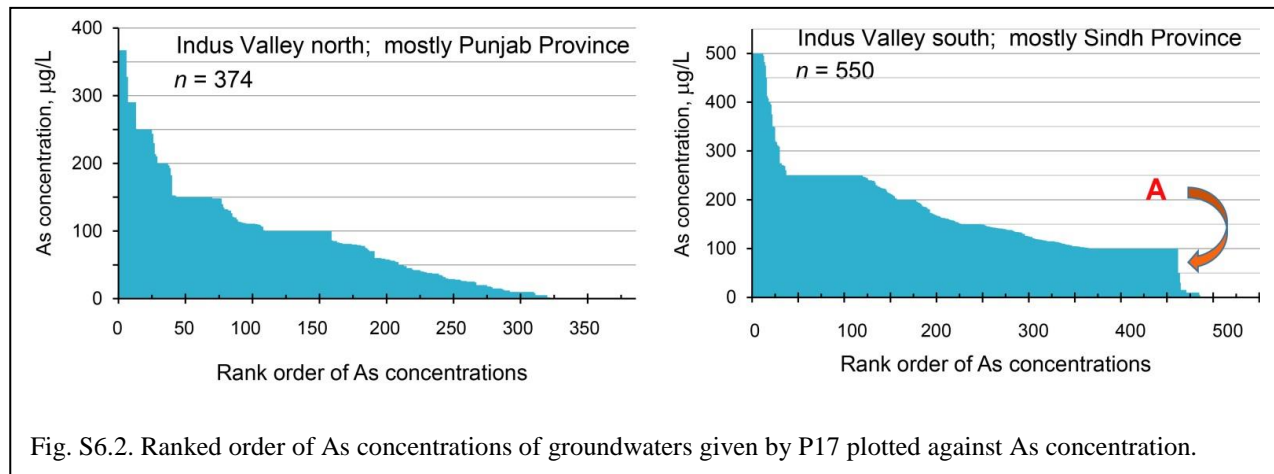
Problems exist also with laboratory data. In P17, 6 groundwaters are reported to contain 367.2 µg/L As, 6 more are 290.2 µg/L, 6 more are 110.56 µg/L, and 6 more are 148.34 µg/L. The probability of each coincidence is vanishingly small. These 24 samples have 23 different GPS locations.

The above suggest that the As data is unreliable both in the critical interval of 0 to 10 µg/L As and at higher concentrations where As concentrations well above critical levels may have appeared to P17 to obviated the need for laboratory confirmation.

The numerous data at multiples of 50 µg/L and 5 µg/L in P17 suggests that the field-test method used was based on the Gutzeit reaction. The method can falsely report H_2S as As. Where H_2S is uncommon, precautions against H_2S may be dispensed with because avoidance itself can cause false positives from acetate contamination (van Geen *et al.* 2005a: these authors found 21 % of wells > 50 µg/L were misclassified – see van Geen *et al.* 2005b).

Most of P17's groundwaters come from cities (Lahore, Islamabad, Karachi, Multan) or towns (Fig. S6.3), suggesting that urbanisation is driving As-pollution. Beneath urban areas, leaking sewers and unsewered sanitation create reducing conditions that promote reduction of both Fe-oxides and SO_4.

Dadu: 27 wells, 38 As data, 37 > 100 ppb As

Matiari: 15 wells, 15 As data 14 > 100 ppb As

Gambat: 35 wells, 40 As data, 39 > 100 ppb As

Mirpur Bathoro: 37 wells, 62 As data, all 100, 250, or 500 ppb

Fig S6.3. Arsenic concentrations in some wells of P17. Maps from Google Earth; altitude of view, 1 km. Yellow scale-bars are 200 m. Well positions are shown by yellow circles. For Mirpur Bathoro, all As concentrations are either 100, or 250, or 500 µg/L.

In the high-SO_4 groundwaters of the Indus River basin, H_2S is therefore likely to be a serious problem for As field-testing and may be one reason for the high number of groundwaters > 10 µg/L reported in P17. The problem affects data for Sindh more than data for Punjab (Fig. S6.2).

Fluoride

Fluoride in groundwater above 1.5 mg/L is a hazard to health, although a value of 0.75 may be used if appropriate to local circumstance (WHO 2017). To scope this hazard, P17 give a map (their Fig. S6.4) of F concentrations. The observations below question the validity of at least some of the F data and so on its hazard map for F. The severity of hazard given in P17 thus appears questionable.

In groundwater, concentrations of F are controlled by equilibrium with fluorite and apatite; as concentrations of Ca increase, those of F decrease (our Fig. S6.4 upper). These trends are absent from the data of P17 (Fig. S6.4 lower) despite some F concentrations exceed equilibrium concentrations for fluorite, which is ≤ 2 mg/L of F at 100 mg/L Ca, and usually much less. One sample of P17 contains 988 mg/L of Ca and 2.11 mg/L of F and is oversaturated by a factor > 10.

The F data were obtained using ion-chromatography. Some groundwaters contain substances that interfere with the F peak in ion-chromatograms and so give falsely high values for F unless peak shape is closely monitored the interference seen and corrected for.

Fig. S6.4. Relation of Ca to F in groundwaters. Upper left, data from this paper for Sindh. Upper right data of McArthur *et al.* (2018) for Kolkata, West Bengal. Lower left, data of P17 for Punjab Province. Lower right, data of P17 for Sindh Provinces.

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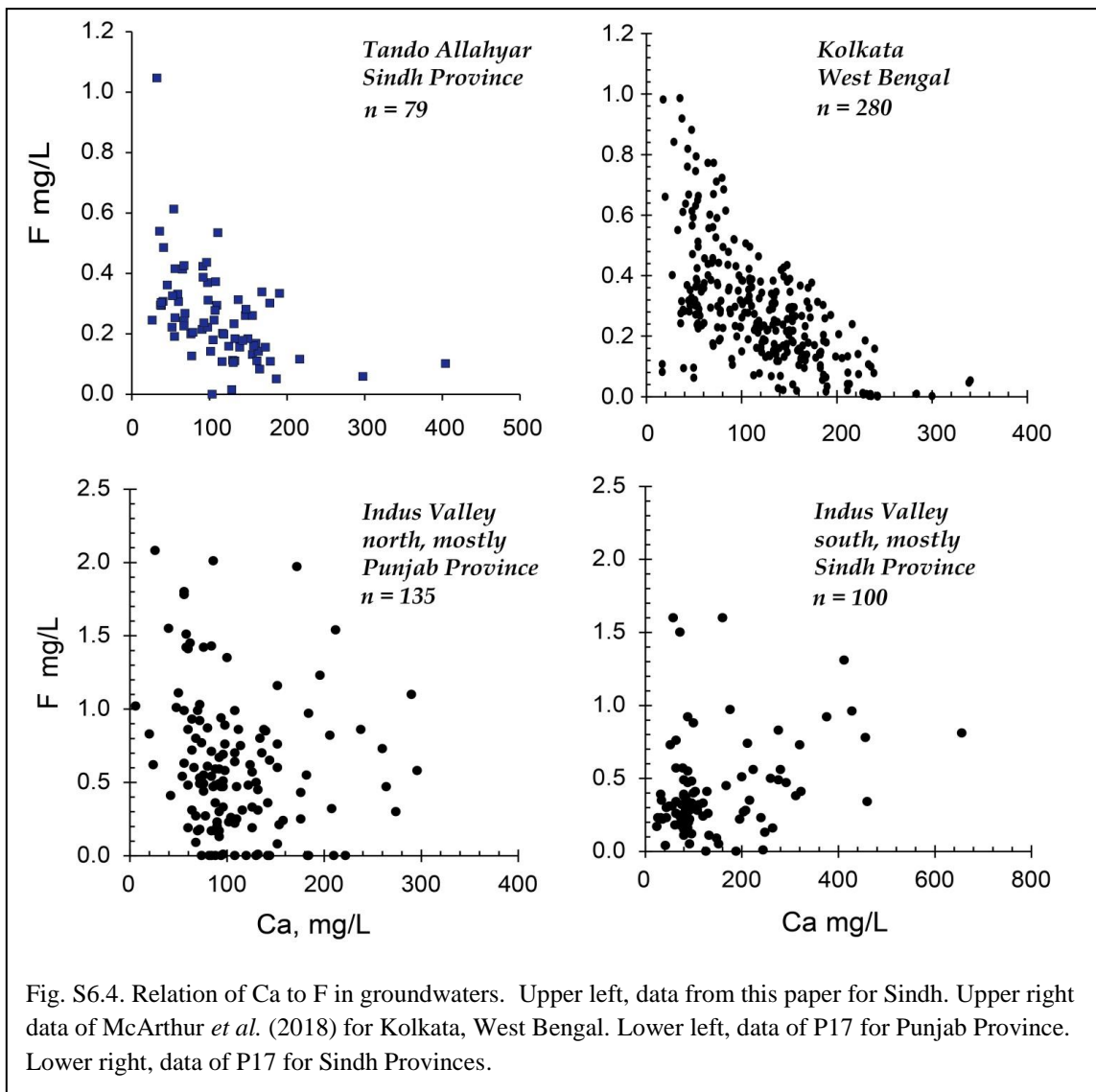
GPS Co-ordinates

Some well locations are questionable (Table S6.2) and undermine confidence in the data generally. Most such locations are in Balochistan, where the barren land between well-sites makes oddities easily seen. Of the 13% of questionable Balochistan locations (BU in Table S6.2), most GPS are given to > 3 d.p., allowing location to better than 100 m (4 d.p. = 10 m resolution, 5 d.p. = 1 m resolution). Wells can be found atop barren mountains, in river beds, and on scree-slopes, all far from habitation. Elsewhere in Pakistan, questionable locations, if present, are harder to spot, except where a well is located in the middle of an airport runway, or 4 km offshore, or in the middle of a reservoir.

Table S6.2. Oddly sited wells.

McA No	Latitude	Longitude	McA No	Latitude	Longitude	McA No	Latitude	Longitude	McA No	Latitude	Longitude
A1	69.24150	31.80540	Bu13	68.81245	31.45698	Bu86	69.12750	30.95000	P369	70.92887	28.42116
A3	71.45520	35.52500	Bu19	68.84196	31.13854	Bu91	69.75413	31.95680	P370	70.92887	28.42116
AK5	74.07700	33.94880	Bu30	63.50722	26.17472	K1	73.61090	35.84100	S53	67.57681	24.05480
Ba2	73.32000	36.35000	Bu34	67.09411	28.06870	K6	70.36000	32.40000	S67	68.26083	24.26339
Ba9	76.21000	35.28000	Bu35	65.21595	26.39771	K39	72.68270	34.56480	S73	67.62190	24.35500
Ba11	75.55000	34.68000	Bu37	65.55294	28.02084	K45	73.13496	34.85580	S90	69.07765	25.68680
Ba13	74.82800	35.04900	Bu44	65.66580	26.30950	K54	72.04681	35.16550	S133	68.26085	24.72752
Ba15	74.86530	36.31000	Bu57	67.31240	29.45290	K62	72.15250	36.16590	S188	68.90026	27.67508
Ba16	74.05000	35.25000	Bu60	67.18945	29.40874	K64	72.31193	36.29317	S575	68.97999	28.06035
Ba17	74.05000	35.25000	Bu63	67.18945	29.40870	K69	70.95482	32.65240	T1	69.66760	31.81330
Bu2	67.07250	27.76070	Bu65	68.33390	31.01403	P88	72.96390	32.71240	T3	71.28742	34.02110
Bu3	64.59230	25.36436	Bu76	66.90349	28.56510	P103	73.70000	32.80000	T6	71.49510	34.49450
Bu10	67.18945	29.40874	Bu82	68.89649	29.25249	P321	71.46099	30.44893	T7	71.47743	34.56549
Bu112	63.22310	26.65401	Bu84	67.28479	30.91238	P334	70.92887	28.42116			

Wells P 334, P369 and 370, with identical GPS, similar depths (35, 35, 50 m) and similar As concentrations (146, 156, 178 µg/L As), are located in a desert 2 km from the nearest (abandoned) sign of habitation. An unusual alignment of wells is seen in Fig. S6.5.

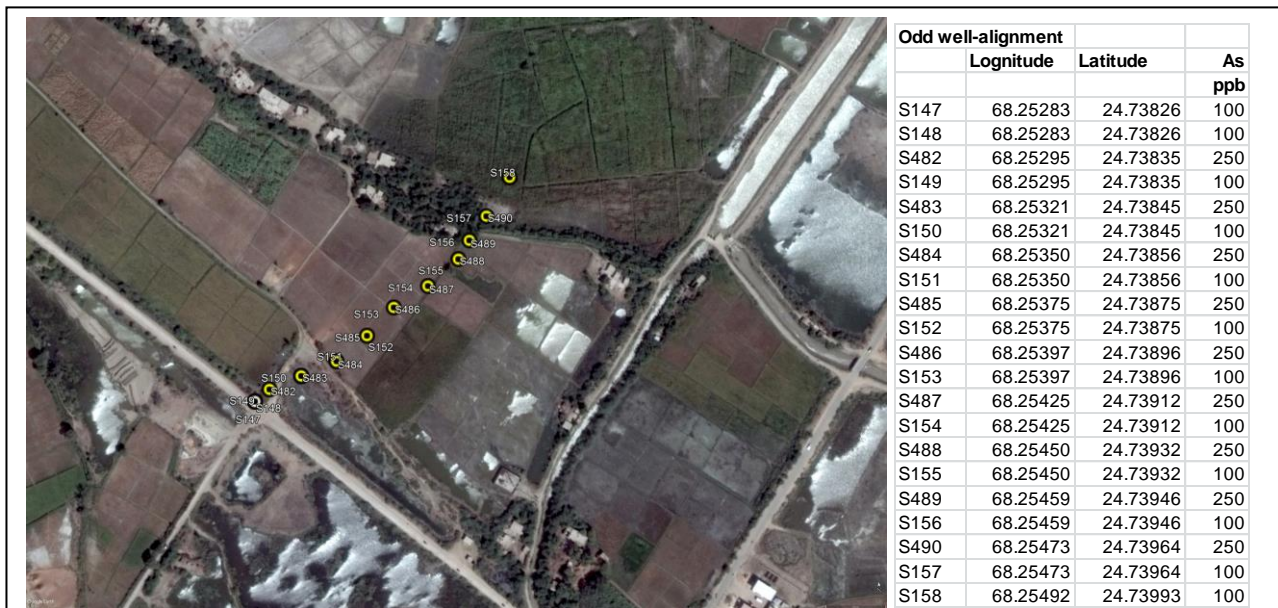| Odd well-alignment			
	Lognitude	Latitude	As ppb
S147	68.25283	24.73826	100
S148	68.25283	24.73826	100
S482	68.25295	24.73835	250
S149	68.25295	24.73835	100
S483	68.25321	24.73845	250
S150	68.25321	24.73845	100
S484	68.25350	24.73856	250
S151	68.25350	24.73856	100
S485	68.25375	24.73875	250
S152	68.25375	24.73875	100
S486	68.25397	24.73896	250
S153	68.25397	24.73896	100
S487	68.25425	24.73912	250
S154	68.25425	24.73912	100
S488	68.25450	24.73932	250
S155	68.25450	24.73932	100
S489	68.25459	24.73946	250
S156	68.25459	24.73946	100
S490	68.25473	24.73964	250
S157	68.25473	24.73964	100
S158	68.25492	24.73993	100

Fig. S6.5. Location map and GPS co-ordinates for a string of wells across a field. Analysis for all but one are duplicated. The wells do not fall along a lineament (road, pathway, canal); the distribution demands explanation.

Temperature

The temperature of groundwater tapped by a well reflects closely the mean annual-average air temperature at the well-site. For example, Nickson *et al.* (2005) reported temperatures of 27.5 ± 2.1 ° C (2s.d.) for 47 well-waters from in and around Multan, Punjab. For 35 groundwaters from wells in and around Tando Allahyar, Sindh Province, this paper reports temperatures of 25.3 ± 2.3 (2.s.d.).

The mean annual air temperature in Punjab and Sindh is between 20 to 30 °C, the range allowing for inter- and intra-regional variation. Mean annual air temperatures hide seasonal ranges. These are from around 10° C in winter to around 40° C in summer, although temperatures can range outside these values. Temperatures of groundwaters reported by P17 range from 15° to 35° C across the northern Indus Valley (Punjab; mean 22.7 ± 8.8) and 13° to 35° C across the southern Indus Valley plain (Sindh; mean 21.8 ± 15.0). The wide range of temperatures recorded in the groundwaters of P17 suggest that some wells were not adequately purged before sampling and that the groundwater reflects local, seasonal, temperature in the upper well-pipe at the time of sampling. What effect this might have on data collected is unknown, other than that it may compromise its quality. It is notable that the range of temperatures given in P17 is greater for Sindh than for Punjab.

Methodology

Statistical binning and correlations

Page 3 of P17 states that the predictor variables retained in their final hazard model for As are, with their Pearson correlation coefficients: "*fluvisols (0.704), Holocene fluvial sediments (not given), slope (not given), soil organic carbon (-0.778), and soil pH* (*0.977*). To calculate the correlation coefficients, P17 binned their data. No justification is given for binning data which can, and in P17's case did, introduce artefacts and false correlations, as Wainer *et al.* (2006) highlight in an article aptly named as "*Finding what is not there through the unfortunate binning of results: the Mendel Effec*t".

All the coefficients lack meaning because they are artefacts of binning (Wainer *et al.* 2006). In the next section, we show the effect of binning by using the example of 'soil-pH' (Fig. S6.6 upper), as it is the highest correlation coefficient used in P17's model and so influences it strongly. The exposition based on soil-pH applies to all predictor variables of P17. In addition, the coefficients for 'fluvisols' and 'soil organic carbon' are erroneous because the binned data on which they are based is not distributed normally *i.e.* it is skewed by outlier data (*cf.* Fig. S6.7 in the next section).

Sturges' Rule

P17 invoke Sturges' Rule (1926) to select bin-width for their data. This procedure brings problems. Firstly, Sturges' rule was formulated to choose bin-widths for histograms, which is not what P17 plot. Secondly, to quote Hyndman (1995) "*The problem with Sturges' rule is that its derivation is wrong. It is a rule which no longer deserves a place in statistics textbooks or as a default in statistical computer packages.*". More appropriate ways of choosing class-intervals *for histograms* are given by Scott (1979) and Freedman and Diaconis (1981), and summarised by Hyndman (1995). Use of Sturges' rule divides P17's As data into 11 bins. Use of Scott's rule results in 32 bins.

Estimated Soil-pH

The hazard model developed by P17 for As relies heavily upon the high correlation coefficient ($r = 0.977$, Fig. S6.6 upper) found in binned data between the proportion of groundwaters containing As > 10 µg/L and 'soil-pH'. The values of 'soil-pH' are estimated from remote-sensing data (Hengl *et al.* 2014). The value 0.977 is surprisingly high given that 1) the soil-pH data is accurate only to ± 1.5 pH units (Fig. 8 of Hengl *et al.* 2014) and, 2) that the model of Hengl *et al.* (2014) for predicting soil-pH does to with an accuracy of only about 51% *i.e.* the predicted soil-pH explains only 51% of the variation in test data.

The updated model of Hengl *et al.* (2017) explain 83% of variation in soil-pH. Using the updated estimates, the relation seen between 'estimated soil-pH' and As exceedance remains high ($r = 0.80$, Fig. S6.6 middle), but means little because the data are skewed by the outlier at pH 7.3. In fact, it means as little as does the correlation coefficient of 0.77 for 'binned Fe' against As exceedances (Fig. S6.7), derived from the data of P17, that is also skewed by an outlier and which we do *not* invoke as evidence that Fe-reduction causes As pollution across Pakistan.

The correlation coefficient of 0.977 is an artefact of data handling (Wainer *et al.* 2006) and arises from the aggregation of data from different regions (Fig. S6.8). To show this, we binned and plotted, using the method of P17, data from Bangladesh, the Punjab of Pakistan, and
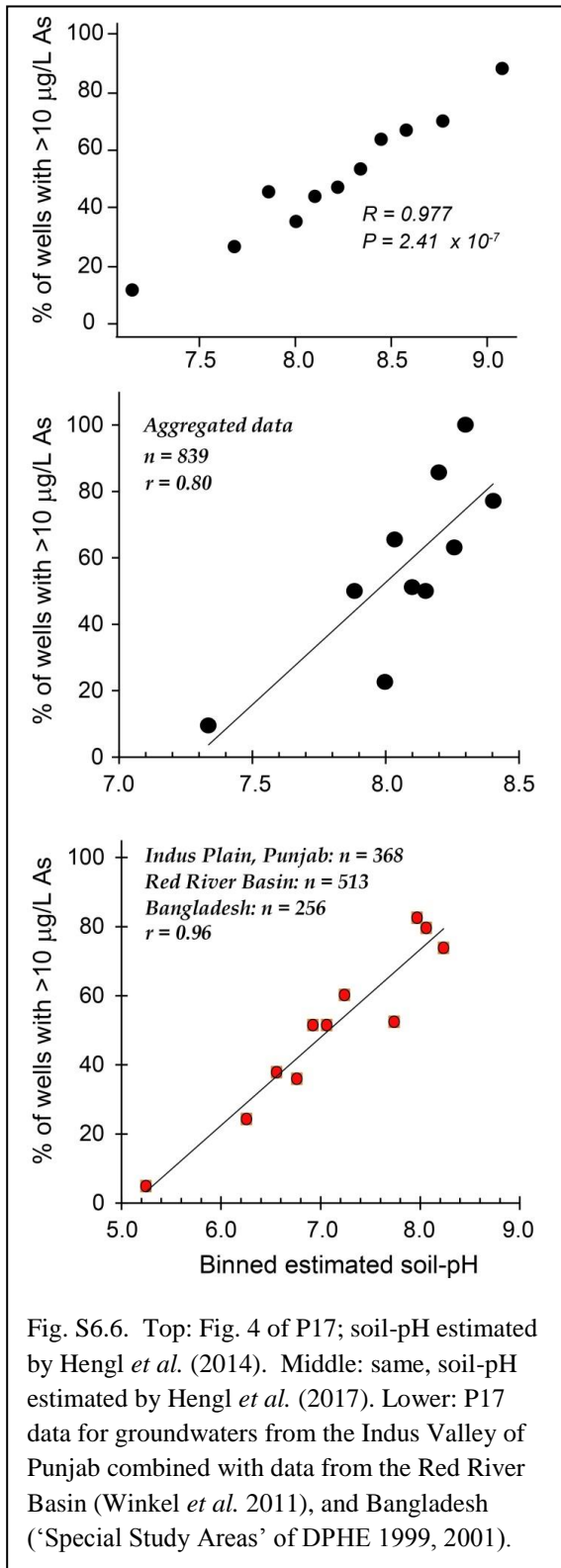
Fig. S6.6. Top: Fig. 4 of P17; soil-pH estimated by Hengl *et al.* (2014). Middle: same, soil-pH estimated by Hengl *et al.* (2017). Lower: P17 data for groundwaters from the Indus Valley of Punjab combined with data from the Red River Basin (Winkel *et al.* 2011), and Bangladesh ('Special Study Areas' of DPHE 1999, 2001).
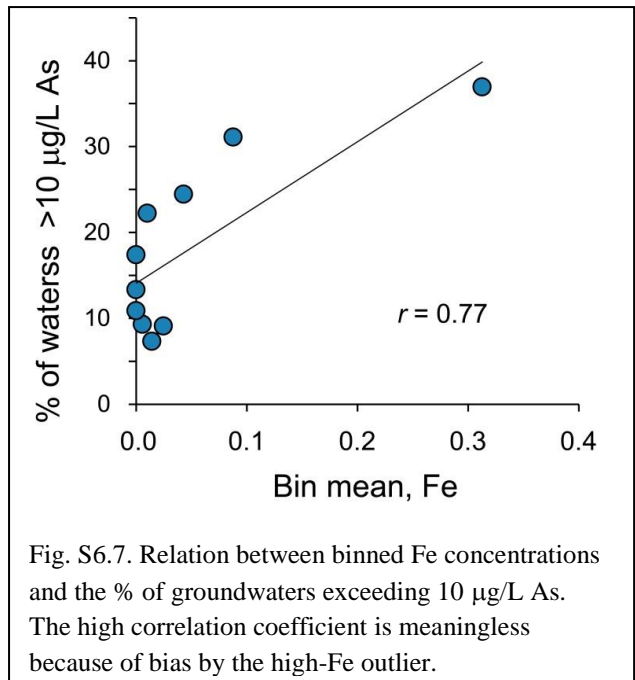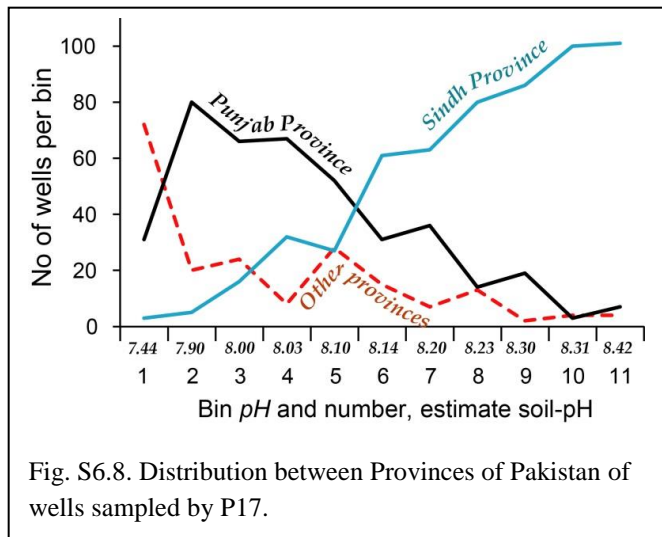

Fig. S6.7. Relation between binned Fe concentrations and the % of groundwaters exceeding 10 µg/L As. The high correlation coefficient is meaningless because of bias by the high-Fe outlier.

the Red River Basin of Vietnam . The data show a correlation coefficient of 0.96, or 0.93 if the outlier at pH < 6 is omitted (Fig. S6.6 bottom). To incorporate that coefficient into a hazard model for any region would clearly be wrong. To use such a model to infer that alkali-desorption causes As pollution in Bangladesh and Vietnam would be equally wrong because in those regions the mechanism of As-pollution is Fe-oxide reduction (Nickson *et al.* 1998, 2000; Berg *et al.* 2001; Postma *et al.* 2007, *et seq.*).

Fig. S6.8. Distribution between Provinces of Pakistan of wells sampled by P17.

Were the relation between As exceedance and 'estimated soil-pH' (Fig. S6.6 upper) to be real, it would be seen in each subset of the data. The relation is absent (*r* = 0.09) in data from the Indus Valley in Punjab (Fig. S6.9 left), where it might be expected because As-pollution by alkali desorption has been shown to occur in As hotspots to the SW of Lahore (Farooqi *et al.* 2007) from where some samples of P17 derive. The relation between As exceedance and 'estimated soil-pH' is higher (*r* = 0.5) for the Indus Valley in Sindh (Fig. S6.9 right), where alkali desorption has not been shown to occur. The robustness of the value of 0.5 is questionable. No value of *r* is robust if it changes markedly on exclusion of < 10% of the data (here, one data point, arrowed in Fig. S6.9 right), as happens here; the value of the correlation coefficient, *r*, is 0.16 without the outlier.
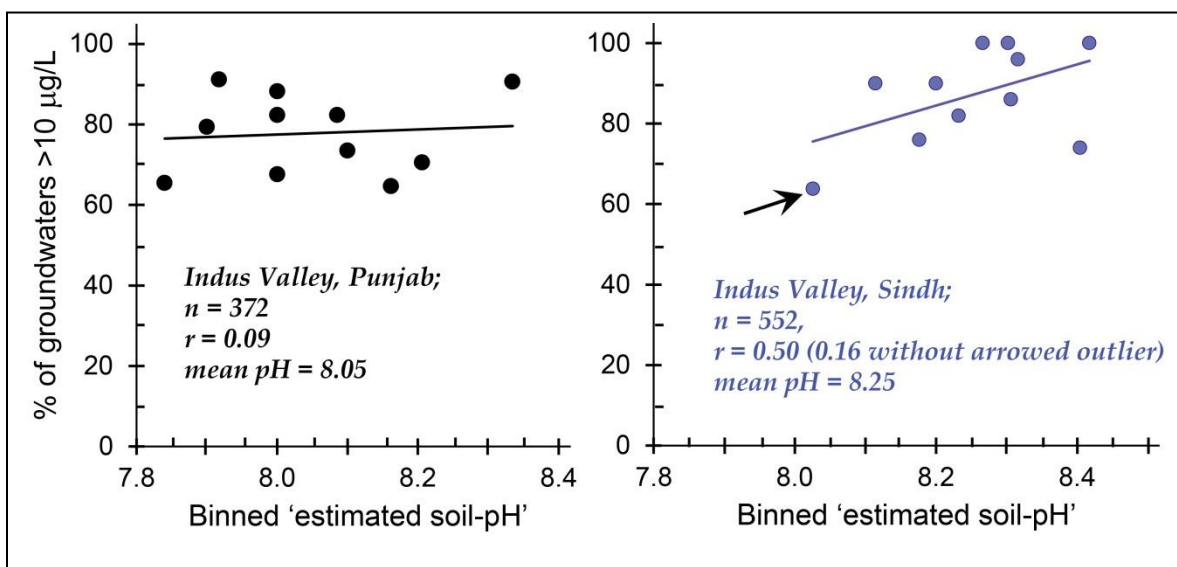
The main regions of Pakistan are the Indus River plain, which is flat and is almost exclusively in Punjab and Sindh Provinces; Balochistan, which has rugged topography; and other provinces (Baltistan, Azad-Kashmir, and Kyber-Pakhtun), which are mountainous. Punjab and Sindh can be differentiated into upper and lower Indus Valley, with different rainfall, average temperature, and mean 'estimated soil-pH' (8.05 *v* 8.25 respectively; Fig. S6.9 and 10). These values from Hengl *et al.*

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(2017) are strongly influenced by the annual amount of precipitation received and by surface reflectivity, which is influenced in turn by precipitation. The difference in 'estimated soil-pH' between Punjab and Sindh probably reflects those facts and may not be real. Across the Indus River valley, the pH of most soils is likely to be buffered to around 8.0 ± 0.3 by the calcareous nature of the soils, which are Calcisols (FAO 2017), although local variations to both higher and lower pH will occur (*e.g.* Ahmed *et al.* 2017; Saeed Khan and Rafiq, 1987).

Pollution of groundwater by As in the Indus River plain is common and has been known to be widespread since, at the latest, 2004 (previous text and Table S1). Other regions have mostly low-As groundwater. For groundwaters of P17 that came from outside the Indus River plain (Fig. S6.9 lower), As concentrations are > 10 µg/L in only 21 (8%) and 8 of those are questionable because they come from questionable locations (Table S6.2). Of the remainder, most are from alluvial sediments in valley bottom close to rivers, where As-pollution will be driven by Fe-reduction.

Fig. S6.10. Distribution of estimated soil-pH (Hengl *et al.* 2017) and As concentrations in groundwater for the three regions of Pakistan.

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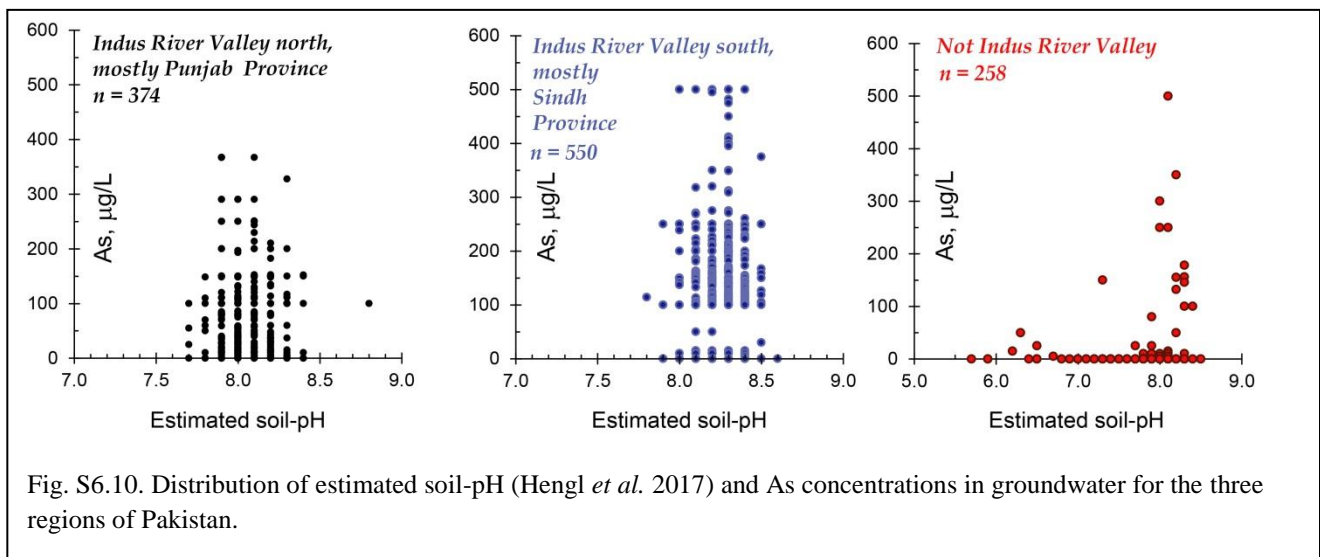
% irrigation

Page 3 of P17 states that the predictor variables retained in their final hazard model for As are "*fluvisols, Holocene fluvial sediments, slope, soil organic carbon, and soil pH*." The predictor variable '% irrigated area' was not used in the hazard-prediction model despite its high correlation with As exceedance (Fig. S6.11). The relation shown in Fig. S6.11 is induced by the same process that gave a false correlation between soil-pH and As exceedance - mixing data from different physiographic regions (*cf.* Wainer *et al.* 2006). False correlation is something the authors acknowledge: they concede that the relation *"could simply be a coincidence…."*, yet figure it as important and discuss it.

P17 do not justify including in the hazard model the strong and coincidental correlation between 'estimated soil-pH' and As exceedance whilst excluding from their model the equally strong and coincidental correlation ($r = 0.967$) between '% irrigated area' and As exceedance.

Many locations quoted in P17 have no data on '% irrigated area' which is inferred to derive from Version 5 of the 'Global Map of Irrigation Areas' (FAO 2013) (FAO 2013). Where data is available

Figure S6.11. Reproduction of that part of Fig. S8 of P17 that shows the relation between '% irrigation' and As exceedance.

from the web-site quoted, values of '% irrigated area' fall into the 7 intervals (bins) given in Table S6.3. Yet there are 11 intervals (bins) in the figure of P17 (reproduced here as Fig. S6.11). It is not clear how the 7 bins of FAO (which did not include zero) have been converted to 11 bins, including zero, of P17 (Table S6.3).
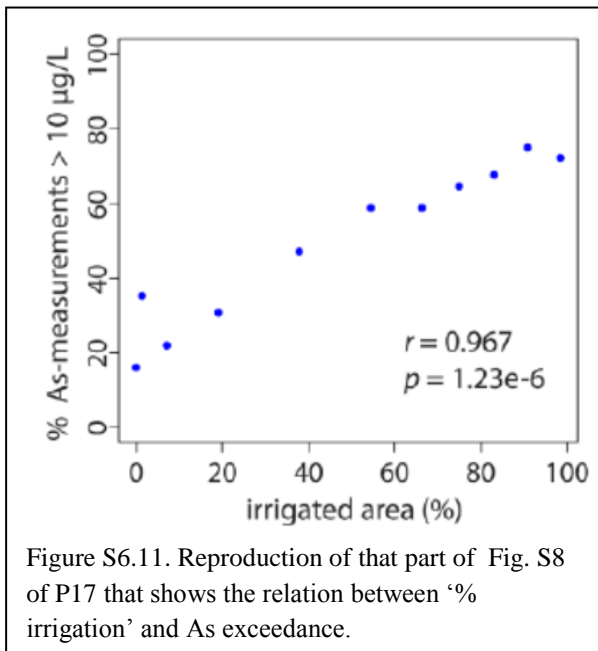
Table S6.3. Classification intervals for % irrigation data.

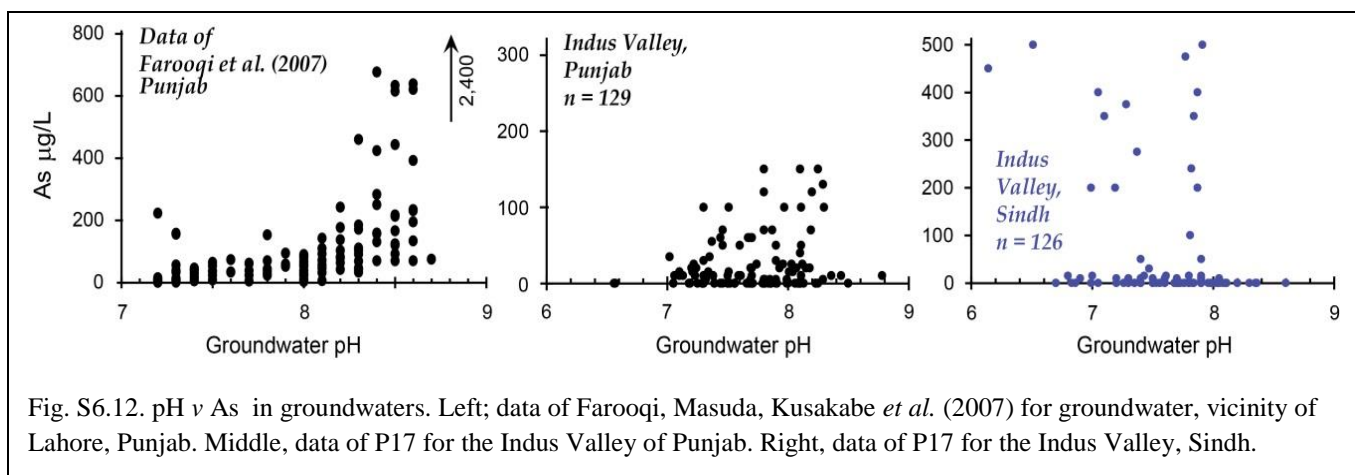| FAO Interval	1	2	3	4	5	6	7
FAO Interval range %	1 – 5	5 – 10	10 – 20	20 – 35	35 – 50	50 – 75	75 – 100
FAO Interval centre %	2.5	7.5	15.0	27.5	42.5	62.5	87.5
P17 bin (centre?) %	0, 1.8	7	19	38	54	66,75	83,89,98

P17 discuss '% irrigated area' without defining the term. The web-site quoted as FAO (2013) gives the % of an area *equipped for* irrigation (not necessarily irrigated) for the year 2005 in 5 arc-minutes which, at the latitude of Pakistan, is equal to a pixel size of 7.6 x 9.0 km *i.e.* 68 km^2. Being overwhelmingly in urban areas, individual wells have commands between 10 and 200 m; *i.e.* commands extend halfway to the next well (not the next well sampled by P17); commands are thus less than 4% of the pixel area and mostly a great deal less. The proxy '% irrigated area' is thus inappropriate because *inter alia* it is inappropriate in scale.

# Mechanism of Pollution

Alkali desorption

P17 predict that alkali desorption (and lesser evaporative concentration) cause As pollution across the Indus River plain. Ravenscroft (2007), not cited by P17, also predicted alkali desorption as important as a pollution mechanism in the Indus Valley – see *www.gapmaps.org* and, for more detail, see *http://www.gapmaps.wiki/index.php?title=UNICEF_arsenic_prediction_models*. P17's reiteration of Ravenscroft's prediction is, however, contradicted by their own data, as they acknowledge. Yet it is retained in P17 as a main conclusion, so we explore the matter further.

The diagnostic feature of alkali desorption is that as pH increases, so do concentrations of As, and that high As occurs only above pH 8.5. In P17's data, groundwater As concentrations show little relation to groundwater pH (Fig. S6.12 middle and right), as P17 acknowledge, although a few

Fig. S6.12. pH *v* As in groundwaters. Left; data of Farooqi, Masuda, Kusakabe *et al.* (2007) for groundwater, vicinity of Lahore, Punjab. Middle, data of P17 for the Indus Valley of Punjab. Right, data of P17 for the Indus Valley, Sindh.
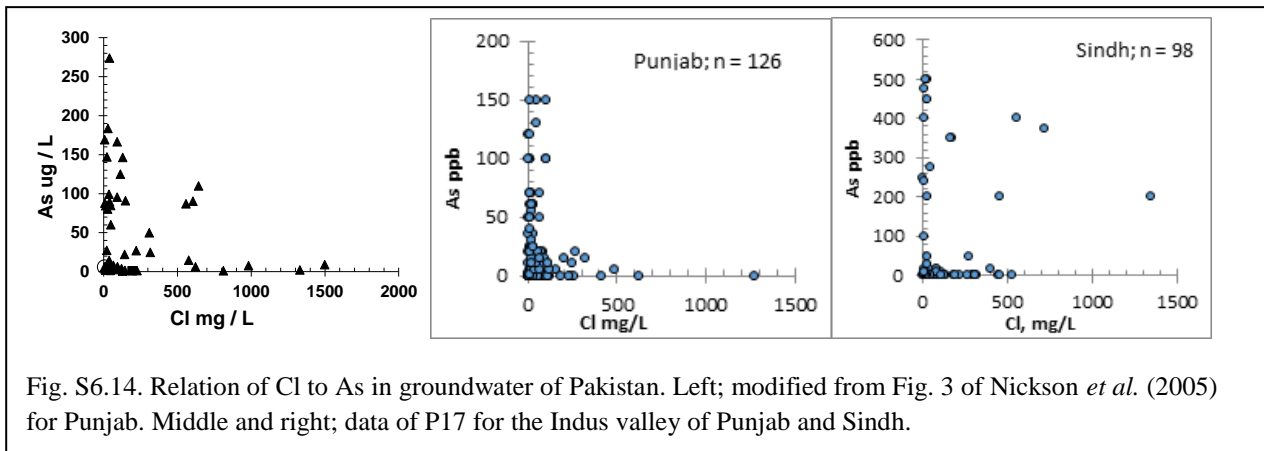
wells in Punjab polluted by alkali desorption doubtless occur in P17's data, given the number of wells they sampled in areas where alkali desorption operates (Farooqi *et al.* 2007). Furthermore, few of P17's groundwater have a pH above 8.3 (Fig.S6.12) and so are mostly too low for concentrations of As > 10 µg/L to arise from alkali desorption. Groundwater pH is also independent of soil-pH in the data of P17 (Fig. S6.13).

It follows from the data of P17 that alkali desorption does not explain As pollution across Pakistan, as they contend. Here it is worth noting that As-pollution from Fe-reduction was shown to occur in Punjab by Nickson *et al.* (2005). P17 argue that high-pH in soils causes desorption of As from soils and that the As is carried down the profile to pollute groundwater. Such a mechanism requires a replenishable source of As in order to work (none is identified). It is an unlikely mass balance; As in groundwater in an aquifer tens of metres in thickness must all be derived from the soil zone, which is < 1 m thick. Such a mechanism requires a high-pH to occur both in soils and in groundwater and it is manifestly absent in most groundwaters that contain > 10 µg/L of As.

Fig. S6.13. Groundwater pH plotted against 'soil-pH' for data of P17.
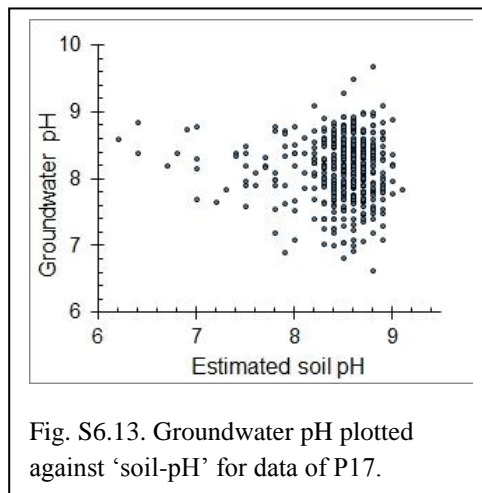
Evaporative concentration

P17 suppose that evaporative concentration might contribute to As-pollution of groundwater in Pakistan, citing such suggestions by Brahman *et al.* (2013) and Rasool *et al.* (2016). Brahman *et al.* (2013) give only as summary data; it appears unreliable and should not be used to support any geochemical proposition. Their sample C-4, for example, has a pH of 10.1 and an HCO_3/CO_3 ratio of around 3; the ratio should be $<< 1$ given the high salinity of the groundwaters, in which pK_2 for carbonic acid would be between 9 and 10. The concentrations of Ca is 406 mg/L, yet 'Ca hardness' is 45 mg/L and F is 43 mg/L and are clearly erroneous. The data of Rasool *et al.* (2016) for eastern Punjab show that As concentrations decrease as Cl concentrations increase, as does the data of Nickson *et al.* (2005) for central Punjab, Pakistan (Fig. S6.14 left). The data of P17 for Punjab (Fig, S6.14 middle) show an inverse relation, which is also may be (poorly) discernible and with much scatter, in the data for Sindh (Fig. 6.14. right).

Fig. S6.14. Relation of Cl to As in groundwater of Pakistan. Left; modified from Fig. 3 of Nickson *et al.* (2005) for Punjab. Middle and right; data of P17 for the Indus valley of Punjab and Sindh.

Possibly excepting the Sindh data of P17, these observations show that when As is high Cl is low and *vice versa*, so evaporative concentration does not concentrate As in Pakistan's groundwater. This is not a surprise; Nickson *et al.* (2005) addressed this issue thus "*An important observation is that As is not conservative in solution (Fig. 3); many waters contain between 10 and 100 times less As than expected from evaporative concentration of end-members (water from the TP Link Canal or Chenab River)...*", because As is sorbed to soils and removed from groundwater during evaporative processes.

Fe-reduction

According to P17, high concentrations of NO_3 in groundwater may be suppressing As pollution in some pockets of the Indus River plain where it might arise from Fe-reduction. Such an observation is correct generically, but its application using the data of P17 is flawed because the concentrations of NO_3 they report are unreliable. They state that "*NO_3 was determined spectrophotometrically using an ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu, model UV 1601) at a wavelength of 220 nm.*". Dissolved organic matter sorbs at 220 nm (Edwards *et al.* 2006). The NO_3 measurements in P17 have not been corrected for absorption by DOM and so may be too high. A correction applied by measuring sorbance at 275 nm, where NO_3 does not absorb, is inadequate because the degree of sorption by DOM increases as wavelength decreases. The NO_3 measurements of P17 would therefore be suspect even had they been adjusted for DOM absorption at 275 nm.

Conclusion

Further analysis of P17's results could not be undertaken because 5 requests for the primary data on predictor variables made to the corresponding authors of P17, and a similar request to the editor of the journal in which P17 is published (*Science Advances*), failed to secure the raw data for P17's predictor variables. The publication policy of *Science Advances* can be found at *http://advances.sciencemag.org/content/editorial-policies* under the heading '**Publication Policies:** Data and Materials Availability after Publication'.

Nevertheless, even without close analysis of that primary data, the discussion here raises doubts about the reliability of the data and methodology in P17 and show that its hazard model for As is unreliable. The prevalence of As-pollution found by P17 is probably a result of the incorporation into their data of between 30 and 43% of field-test data that reported concentrations of As (as arsine) plus H_2S. The conclusion of P17 that widespread As-pollution across the Indus River plain results from alkali desorption is incorrect.

Finally, it should be noted that more than 40 articles (Table S1) have been published on the As-pollution across the Indus River Valley, in addition to government-supported surveys. Most, including Podgorski *et al.* (2017) and all government-supported surveys, do not contain the data on which the claims in them are based. Had each of the papers in Table S1 contained the data on which they are based (well position, depth, As concentration, date of sampling) there would, by now, be a good body of data useful for predicting the hazard across the Indus River plain that arises from As-pollution.

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