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## Waste-water impacts on groundwater: Cl/Br ratios and implications for arsenic pollution of groundwater in the Bengal Basin and Red River Basin, Vietnam

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### HIGHLIGHTS

- ▶ Groundwater in the Bengal Basin is widely polluted by domestic waste-water.
- ▶ The impact on groundwater can be quantified using Cl/Br mass ratios.
- ▶ Both NO<sub>3</sub> and SO<sub>4</sub> in groundwater are sourced from waste-water.
- ▶ Pollution of groundwater by arsenic is decreased adjacent to sources of waste-water.
- ▶ Distally from its source, waste-water may exacerbate As-pollution of groundwater.

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### ABSTRACT

Across West Bengal and Bangladesh, concentrations of Cl in much groundwater exceed the natural, upper limit of 10 mg/L. The Cl/Br mass ratios in groundwaters range up to 2500 and scatter along mixing lines between waste-water and dilute groundwater, with many falling near the mean end-member value for waste-water of 1561 at 126 mg/L Cl. Values of Cl/Br exceed the seawater ratio of 288 in uncommon NO<sub>3</sub>-bearing groundwaters, and in those containing measurable amounts of salt-corrected SO<sub>4</sub> (SO<sub>4</sub> corrected for marine salt). The data show that shallow groundwater tapped by tube-wells in the Bengal Basin has been widely contaminated by waste-water derived from pit latrines, septic tanks, and other methods of sanitary disposal, although reducing conditions in the aquifers have removed most evidence of NO<sub>3</sub> additions from these sources, and much evidence of their additions of SO<sub>4</sub>. In groundwaters from wells in palaeo-channel settings, end-member modelling shows that >25% of wells yield water that comprises ≥10% of waste-water. In palaeo-interfluvial settings, only wells at the margins of the palaeo-interfluvial sequence contain detectable waste water. Settings are identifiable by well-colour survey, owner information, water composition, and drilling.

Values of Cl/Br and faecal coliform counts are both inversely related to concentrations of pollutant As in groundwater, suggesting that waste-water contributions to groundwater in the near-field of septic-tanks and pit-latrines (within 30 m) suppress the mechanism of As-pollution and lessen the prevalence and severity of As pollution. In the far-field of such sources, organic matter in waste-water may increase groundwater pollution by As.

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### 1. Introduction

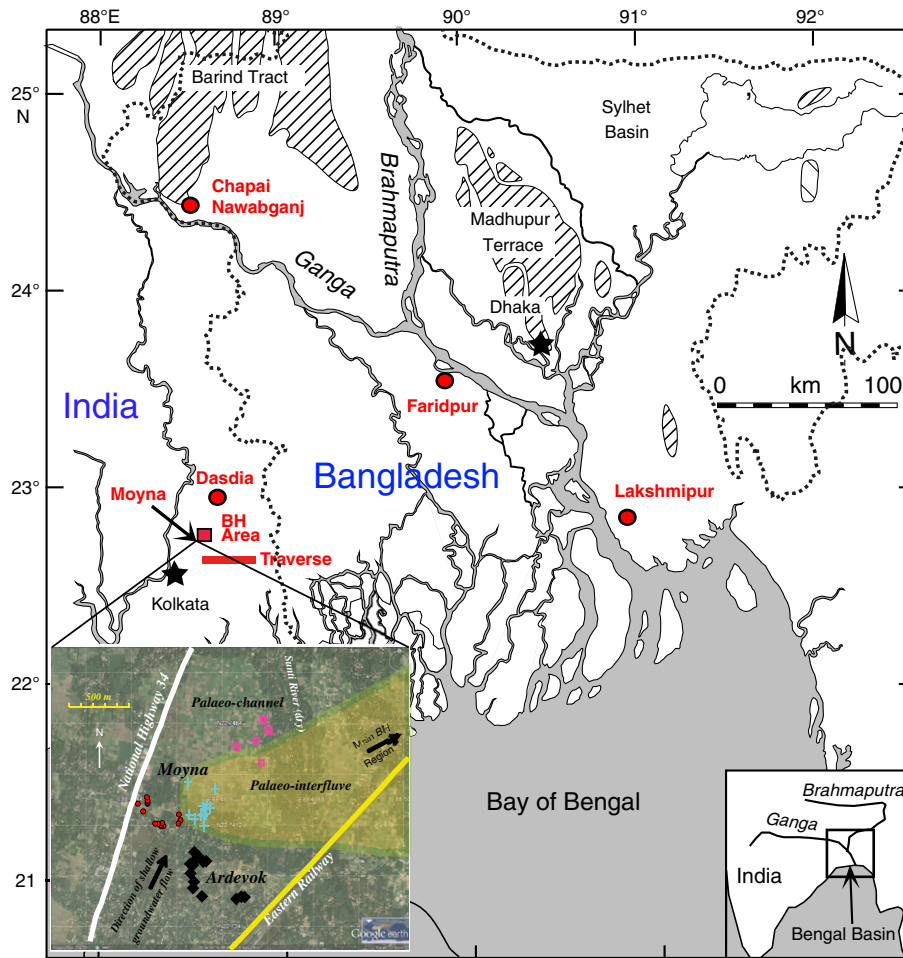
The impact on groundwater quality of sewage and waste-water is well documented and a major concern globally (Banks et al., 2002; Howard, 2007). The problem is summarized by Foster et al. (2011), who state that “*In-situ sanitation of urban areas presents a significant groundwater quality hazard*” and “*The hazard is further accentuated because self-supply from groundwater is generally more intensive where access is easiest—namely in the presence of shallow unconfined aquifers, which are the more vulnerable to pollution from the land surface.*”

In Bangladesh and West Bengal (the Bengal Basin; Fig. 1), “self supply” and “vulnerability” are closely coupled. More than 80% of the region's inhabitants (90 million in West Bengal; 160 million in Bangladesh) use shallow groundwater for domestic supply, overwhelmingly from depths <100 m. In many areas, the aquifers are semi-confined or unconfined (Fig. 3 of Ravenscroft, 2003). In urban areas, private tube-wells screened at <50 m bgl abound. Much waste-water in urban areas discharges to ground (Ravenscroft, 2003, p76). In rural areas, most domestic supply, and much irrigation water, is derived from shallow (<50 m) private wells, many of which are close to either septic tanks or pit latrines. Alternative disposal is direct to the land surface.

In the Bengal Basin, the effect on groundwater of waste water has been neglected in favour of investigation of the pollution by arsenic (As; DPHE, 1999, 2001; Jakariya et al., 2007; Nickson et al., 2007;

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**Fig. 1.** The Bengal Basin. Shown in red are the three areas sampled in West Bengal (Dasdia, Traverse and BH), and the three areas in Bangladesh (Lakshmipur, Faridpur, Nawabganj) for which groundwater composition was taken from a report of the Department of Public Health Engineering, Gov. Bangladesh (DPHE, 1999). Moyna is situated at the south-western corner of the BH area (left map inset; symbols for wells as for Fig. 3c). Base map modified from Goodbred and Kuehl (2000).

PHED, 1991; van Geen et al., 2003). Here, we use Cl/Br mass ratios, and concentrations in groundwater of Cl, NO<sub>3</sub>, SO<sub>4</sub>, and NH<sub>4</sub>, to show the extent to which groundwater in the Bengal Basin is contaminated by such waste-water. Our use of Cl/Br follows the development of this proxy to trace waste-water contamination of aquifers in Israel (Nissenbaum and Magaritz, 1991; Vengosh and Pankratov, 1998), North America (Davis et al., 2004, 1998; Katz et al., 2011; Panno et al., 2006), and Spain (Alcalá and Custodio, 2008). We then examine the impact of waste-water on the widespread pollution of groundwater by As in West Bengal and Bangladesh. Finally, we use the data of Winkel et al. (2011) to identify possible pollution by waste-water of aquifers in the Red River Basin of Vietnam.

## 2. Aquifer context, Bengal Basin

The shallow aquifers of the Bengal Basin (set here as those <150 m depth, following DPHE, 1999; Ravenscroft, 2003) occur in three main sedimentological settings: shallow palaeo-channels (SPC), deep palaeo-channels (DPC), and palaeo-interfluvial (PI). The deep palaeo-channels formed between 125 ka and 18 ka, when sea level fell approaching the last glacial maximum (LGM) and rivers incised deeply to maintain their base levels (Allison et al., 2003; Goodbred and Kuehl, 2000; Umitsu, 1993). The areas between these deep palaeo-channels comprised palaeo-interfluvial of brown, unconsolidated, sands that were capped by a red-clay palaeosol as a result of intense weathering during that period. Both PI and DPC sediments

are now buried beneath post-LGM sediments that were deposited as sea-level rose between 18 and 6 ka. These sediments comprise a range of lithologies including younger, shallower, palaeo-channel sands (the SPC setting) and floodplain silts, peats and clays, all deposited by post-LGM rivers.

Both deep and shallow palaeo-channels are in-filled with grey, unconsolidated, sands that form regional aquifers yielding As-polluted groundwater. The palaeo-interfluvial brown sands form regional aquifers that yield As-free groundwater. Downward recharge to PI aquifers is prevented by their impermeable palaeosol capping, so they are recharged at depth (typically 20–40 mbgl) by lateral flow from surrounding PC aquifers (McArthur et al., 2011a).

## 3. Sources of samples and data

Our groundwaters derive from tube wells installed in PI, DPC, and SPC settings, although in this paper we rarely distinguish further between SPC and DPC settings. The wells were located in the 3 areas of West Bengal listed below (Fig. 1). We look in most detail at Moyna, a peri-urban conurbation at the extreme south-western end of the BH area (inset, Fig. 1). We sampled mostly domestic wells screened <50 mbgl (Table S1) that served houses in villages, and a few irrigation wells in surrounding fields. Wells were assigned to either a PI aquifer or a PC aquifer through the use of owner information, drilling results, groundwater composition (Mn, As, Fe, V, Mo, and U; see McArthur et al., 2012), and by assessing the colour of

stain left by groundwater on well completions and domestic utensils (McArthur et al., 2011a).

To extend our investigation beyond West Bengal, we use compositions of groundwater in Bangladesh and Vietnam. To show how waste-water affects As-pollution, we use our Cl/Br,  $\text{SO}_4$ , and As data (Table S1). We refer also to  $\text{NH}_4$  concentrations in groundwaters given in McArthur et al. (2004) and for Bangladesh groundwaters by Hoque et al. (1998), who also provide data on faecal-coliform count and As concentrations in groundwater from 1859 wells across Bangladesh. Data for Cl, Br and As for the Bangladesh Districts of Lakshmipur, Faridpur, and Chapai-Nawabganj (Fig. 1) derive from a report of the Bangladesh Government's Department of Public Health Engineering (DPHE, 1999; Special Study Areas). The data for our study of the Red River Basin of northern Vietnam is taken from Winkel et al., 2011.

### 3.1. Dasdia samples

Dasdia groundwaters are from 150 wells located in, and within 2 km of, the village of Dasdia (86.60° E, 22.96° N), 60 km north of Kolkata, in Nadia District, West Bengal. The sedimentology of the area comprises mostly shallow palaeo-channel fill of grey sands that overly a full PI sequence of brown sands and capping palaeosol. An uppermost 4.5 m of organic-poor fine sand and sandy silt caps the sequence. Of sampled wells, 70% tap the shallow PC aquifer and 30% tap the deeper PI aquifer.

### 3.2. Barasat–Habra samples

Barasat–Habra (hereinafter BH) groundwaters are from 238 of the wells used in studies of As- and Mn-pollution by McArthur et al. (2011a, 2012), who give maps of sample distribution and details of sedimentology and groundwater composition. The groundwaters derive from 100 km<sup>2</sup> of (mostly) rural West Bengal between the towns of Barasat, in the southwest of the area, to Habra in its northeast. Across the BH area, PI aquifers are confined beneath about 20 m of peaty clays and silts and PC aquifers are semi-confined beneath 5–15 m of clayey silts.

Groundwaters from Moyna (Fig. 1) are considered separately for the purpose of demonstrating the relation between urbanization, Cl concentration, and Cl/Br. The area lies on the northern fringe of the town of Barasat at the extreme south-western corner of the BH area. Our 46 groundwaters from Moyna are grouped as follows: town, urban, peri-urban, and agricultural (Fig. 3; Table S1), in order to reflect the setting of their source wells within a gradient in population density from a full urbanized (town) in the south to a rural (agricultural) for irrigation wells in fields to the north. For Moyna samples, we do not distinguish between PI and PC settings because the limited width (through pinch-out) of the PI sediments beneath the fields to the north of Moyna (inset, Fig. 1) has allowed the northerly flow of PC groundwater to flush the PI aquifer with PC water. As a consequence, PI groundwater retains some characteristics of the PI setting ( $\text{As} < 2 \mu\text{g/L}$ ) but shows also characteristics of the PC setting ( $\text{Cl} > 10 \text{ mg/L}$ ). Further details of the hydrogeology and sedimentology of Moyna is given in McArthur et al. (2004, 2008) and Sengupta et al. (2008).

### 3.3. Traverse samples

These samples are from 263 wells along a 32 km traverse across south-central West Bengal, in the central part of North 24-Parganas district that extends eastward from a point 3 km east of Kolkata airport (Fig. 1; for details, see Hoque et al., 2012). The traverse crossed a major PI sequence flanked at the traverse ends by deep palaeo-channels. Shallow (post-LGM) palaeo-channel sands now form an upper cover across much of the area, but subordinate areas are buried beneath finer flood-plain deposits. The western third of

the traverse crossed fish-farms that occupy pits remnant from excavation of brick-clay and cover a contiguous area of around 40 km<sup>2</sup>. At any time, 90% of the area is permanently flooded by brackish water, with a salinity up to 3.5 psu, that is pumped from local tidal creeks.

## 4. Methods

### 4.1. Sampling and analysis

Samples were collected in 15 mL polythene tubes, one acidified in the field with 0.15 mL of 50% Analar® nitric acid, one unacidified. We collected also 11 samples of overflows from septic tanks in Moyna, West Bengal and one sample of urine from Moyna; all were filtered in the field through 0.22 micron membrane filters. Groundwater samples were unfiltered unless visibly turbid. Laboratory analysis for groundwaters and waste waters was done by ICP-MS for total As and total Br, with a detection limit around 0.1 and 1  $\mu\text{g/L}$  respectively. Bundles of three samples were bracketed by a blank and a standard in order to correct for instrumental drift. Memory effects for Br were minimised by placing a washout of 60 s with 1% nitric acid between each aspiration. Analysis for Cl,  $\text{NO}_3$  and  $\text{SO}_4$  was by ion chromatography. Detection limits for  $\text{NO}_3$  and  $\text{SO}_4$  were around 0.05 mg/L.

### 4.2. Systematics of Cl versus Cl/Br in groundwater

#### 4.2.1. Reservoirs

The systematics of using Cl concentrations and Cl/Br to identify groundwater contamination is summarized in Fig. 2 after Alcalá and

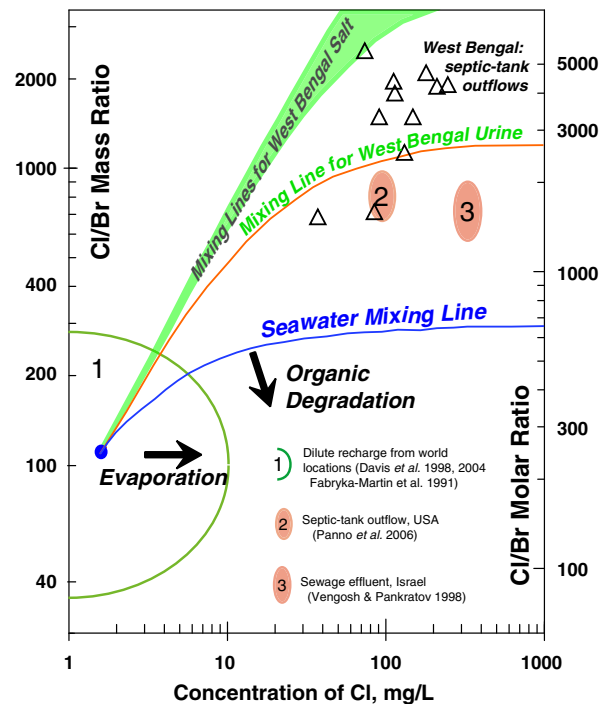


Fig. 2. Systematics of Cl/Br against Cl concentrations as used for evaluating sources of Cl to groundwater. In this paper, Cl/Br is always the mass ratio. Fields are: 1, upper-range of Cl and Cl/Br in dilute groundwaters and precipitation (Davis et al., 2004, 1998; Fabryka-Martin et al., 1991); 2, septic-tank leachate from the USA (Panno et al., 2006); sewage effluent from Israel (Vengosh and Pankratov, 1998). Mixing lines are between a dilute groundwater end-member (1.4 mg/L Cl, with Cl/Br of 110) and a) table-salt end-members representing the maximum (135 mg/kg) and minimum (53 mg/kg) concentrations of Br in 6 samples from retail outlets in West Bengal, b) urine from West Bengal, and c) seawater.

Custodio (2008), Davis et al. (1998, 2004), Katz et al. (2011), Panno et al. (2006) and Vengosh and Pankratov (1998). In this work, Cl/Br always represents the mass ratio. Field 1 delimits of Cl/Br and of Cl concentration in unmineralized, and so dilute, groundwaters from several locations (Davis et al., 2004, 1998; Fabryka-Martin et al., 1991). Evaporation of infiltrating water increases the Cl concentration in recharge but leaves Cl/Br unaffected. Field 2 is the composition of septic tank leachate from the USA (Panno et al., 2006). Field 3 delineates the composition of treated sewage effluent in Israel used for aquifer recharge (Vengosh and Pankratov, 1998). These end-member fields are illustrative only because the Cl concentration and Cl/Br of sewage effluent and waste-water are affected by numerous variables considered by the authors listed above. To constrain these ranges, we include in Fig. 2 the data for 11 septic-tank waste-waters from Moyna, West Bengal.

Organic matter concentrates Br over Cl. Nevertheless, leachate from human sewage has high Cl/Br because of addition of common salt (see above). Where that addition is absent, organic leachates typically have Cl/Br < 200. Leachate from animal dung has Cl/Br between 35 and 167 (Hudak, 2003). Values of Cl/Br as low as 4 occur in groundwater from the Hula Valley of Israel as a result of the degradation of lignite and peat (Nissenbaum and Magaritz, 1991). Values of Cl/Br between 6 and 10 were found for degrading organic matter in soils of Western Australia (Gerritse and George, 1988) and in peats from Chile (Biester et al., 2006) and Germany (Biester et al., 2012). It follows that mineralisation of natural organic matter in aquifers decreases Cl/Br in groundwater by increasing concentrations of bromide with respect to chloride.

#### 4.2.2. Mixing lines and end-members

Mixing lines are shown in Fig. 2 between our most dilute groundwater and three high-Cl end-members: seawater, table/cooking salt, and urine from West Bengal (Table S1). The dilute groundwater end-member has a Cl of 1.4 mg/L and Cl/Br of 110, derived from our most dilute samples (Table S1). The low values for both Cl concentration and Cl/Br derive from the need to reflect actual groundwater composition and also realistically constrain most data to lie between the mixing lines for salt and seawater. We use this single dilute end-member composition for all our study areas, including those in Bangladesh and Vietnam. We recognise that this is unlikely to be representative of all newly infiltrated, uncontaminated, groundwater, the Cl and Cl/Br of which will be influenced by a range of factors that differ between regions, including distance from the coast (Davis et al., 2004) and degree of evaporation and evapotranspiration. Nevertheless, we do so in order to make the treatment tractable, and because the end result of using this assumption seems reasonable. As the Cl concentration of the dilute end-member increases, an increasing number of groundwaters plot above the salt mixing-line; at 10 mg/L Cl many, possibly most, samples do so. The end-member Cl/Br of 110 is less than the value of 288 for seawater, but within the range of 50 to 200 reported for young groundwaters from elsewhere (Davis et al., 2004, 1998; Fabryka-Martin et al., 1991; Nissenbaum and Magaritz, 1991).

For our high-Cl end-members, we use seawater because infiltration of brackish water from fish-farms affects some of our groundwaters. Seawater contains 67 mg/L Br, and has a Cl/Br of 288. We use table/cooking salt because it forms a major component of waste-waters. Mixing models have a low sensitivity to variation in the concentration of Br in salt. To illustrate this, we use two end-member compositions for salt, which are the minimum and maximum concentrations of Br (53, 135 mg/kg; Table S1) in 6 samples of table/cooking salt obtained from retail outlets in West Bengal. We also mix with urine because it contributes to diffuse as well as point-source contamination. Our end-member for urine is a sample from Moyna, West Bengal, with 1910 mg/L of Cl, and 1880 mg/L of SO<sub>4</sub>, concentrations typical of urine (Putnam, 1971; Kirchmann and

Pettersson, 1995; Yoshinaga et al., 2000). The sample's Br concentration was 1540 µg/L (Table S1), giving a Cl/Br of 1240.

To assess the amount of contamination of well water by wastewater, we model the proportion based on end-member mixing between our dilute groundwater end-member and two contaminant end-members. One is a waste-water end-member (126 mg/L Cl, Cl/Br 1561) representing the mean of 11 septic-tank effluents from Moyna. The other is a sewage end-member (Cl 400 mg/L, Cl/Br 700), based on data for sewage from Vengosh and Pankratov (1998). We do not model mixing proportions for Traverse groundwaters, or BH groundwaters other than those in Moyna, because of the complicating effects of salinization and organic degradation on such waters, which introduces to the mixing two additional end-members that cannot be quantified, thereby precluding useful calculation.

## 5. Results

Results are given in Supplementary Table S1 and in Figs. 3 to 5, which are introduced in turn below by area, and then by species, whether analyzed or obtained from the literature. Table S1 also gives screen depths of wells in metres below ground level (mbgl) and their GPS co-ordinates to WGS84 datum. Concentrations are in mg/L (Cl, Br, NO<sub>3</sub>, SO<sub>4</sub>, NH<sub>4</sub>) or µg/L (As) and Cl/Br is the mass ratio.

### 5.1. Dasdia, West Bengal

Palaeo-interfluvial groundwaters have lower Cl concentrations, and Cl/Br, than do palaeo-channel groundwaters (Fig. 3). Concentrations of Cl in PI groundwaters are up to 6.2 mg/L, with Cl/Br between 119 and 297. Only 1 out of our 41 PI groundwaters contains more than 2% of waste-water (Fig. 4). In contrast, PC groundwaters mostly plot along a broad band towards high Cl/Br that indicates mixing with Cl-rich sources of waste-water. Around 28% of PC groundwaters contain > 10% of waste-water (Fig. 4). Groundwater from Well 42 (Fig. 3, Table S1), which is 60 feet deep and next to a pit latrine (Fig. S1), contains 65 mg/L of Cl and a Cl/Br of 1767. It also contains 30 mg/L of NO<sub>3</sub>, 31 mg/L of SO<sub>4</sub>, and < 1 µg/L of As.

### 5.2. BH (Barasat–Habra), West Bengal

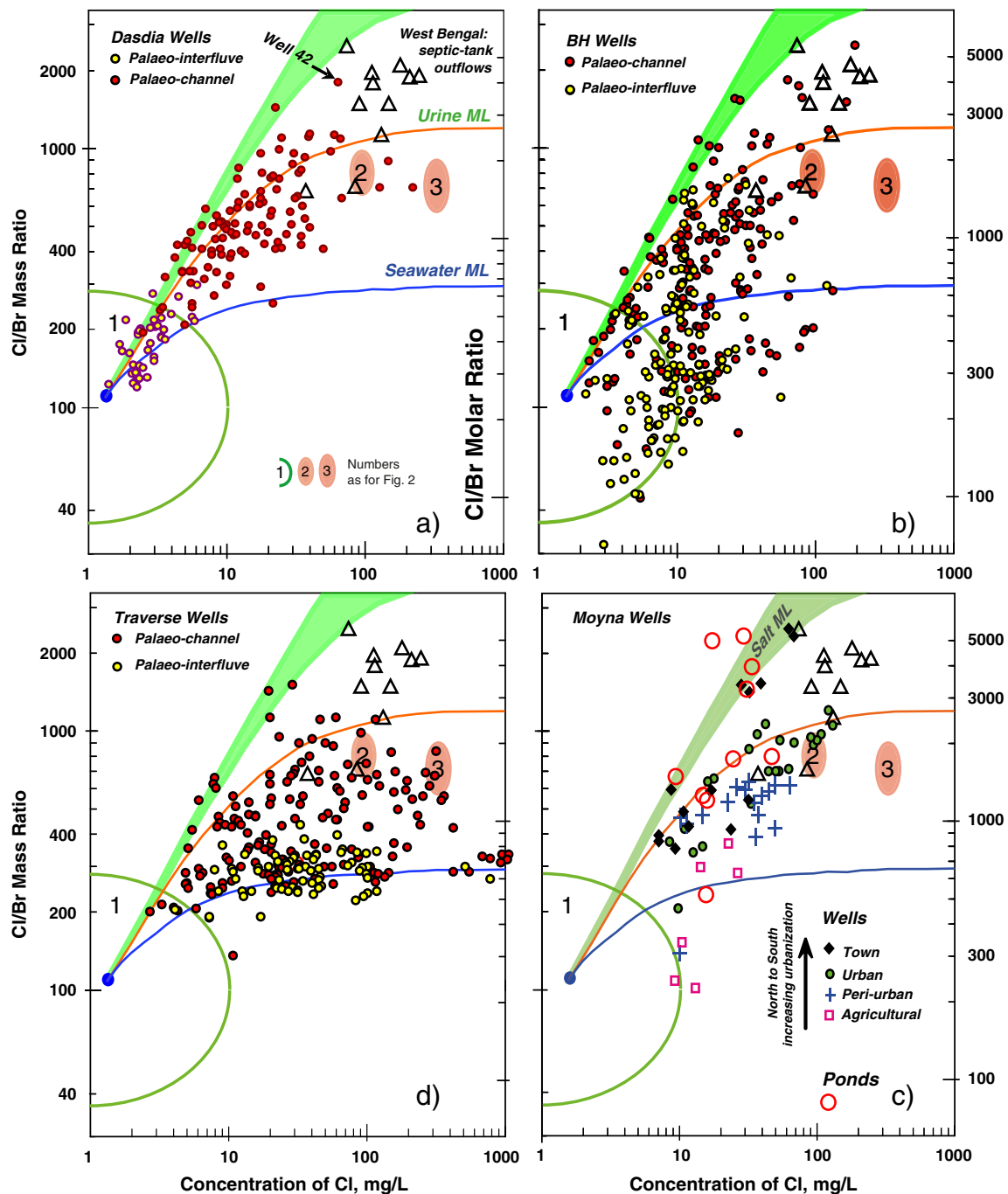
Of groundwaters from PI settings, some 70% plot below or on the seawater mixing-line, and at lower Cl concentrations than most palaeo-channel groundwaters, with Cl/Br ranging down to around 40. Some 30% plot along mixing lines towards septic-tank waste-water; these PI wells occur mostly around the margins of the palaeo-interfluvium (McArthur et al., 2011a), where recharge occurs of water from palaeo-channels that is contaminated by waste-water. Most groundwaters from PC settings plot on trends of mixing towards septic-tank waste-water, with around 10% being similar in Cl content and Cl/Br to waste-water (Fig. 3). Some 15% plot below the seawater mixing-line, ranging down to Cl/Br around 40.

Concentrations of Cl in groundwater in and around Moyna are mostly above 10 mg/L (Fig. 3). At any particular Cl concentration, Cl/Br tends to increase with increasing urbanization, with Cl/Br scattering between the mixing lines for salt and seawater and ranging up to 2500. A majority of groundwaters from the town and urban settings (inset, Fig. 1) plot close to, or amongst, the samples of septic-tank waste-water. Those in agricultural settings (irrigation wells) have Cl/Br down to 100. Of the 46 groundwaters from Moyna, 51% contain > 10% waste-water (Fig. 4).

### 5.3. Traverse, West Bengal

There is a clear separation of PI and PC groundwaters (Fig. 3). Of groundwaters from PI wells, only 4% plot below the seawater mixing-line, whilst most plot close to it and have Cl concentrations





**Fig. 3.** Relation of Cl/Br to Cl concentration for the groundwaters from a) Dardia, b) BH (Barasat–Habra) c) Moyna; d) Traverse. See Fig. 1 for locations. Palaeo-interfluvial and palaeo-channel waters are differentiated on the basis of owner information, drilling, well-colour survey (McArthur et al., 2011a), and groundwater chemistry (see text). They are not differentiated in Moyna, for reasons given in the text, but instead grouped according to population density: Cl/Br increases with increasing population density, although there is some scatter to the trend.

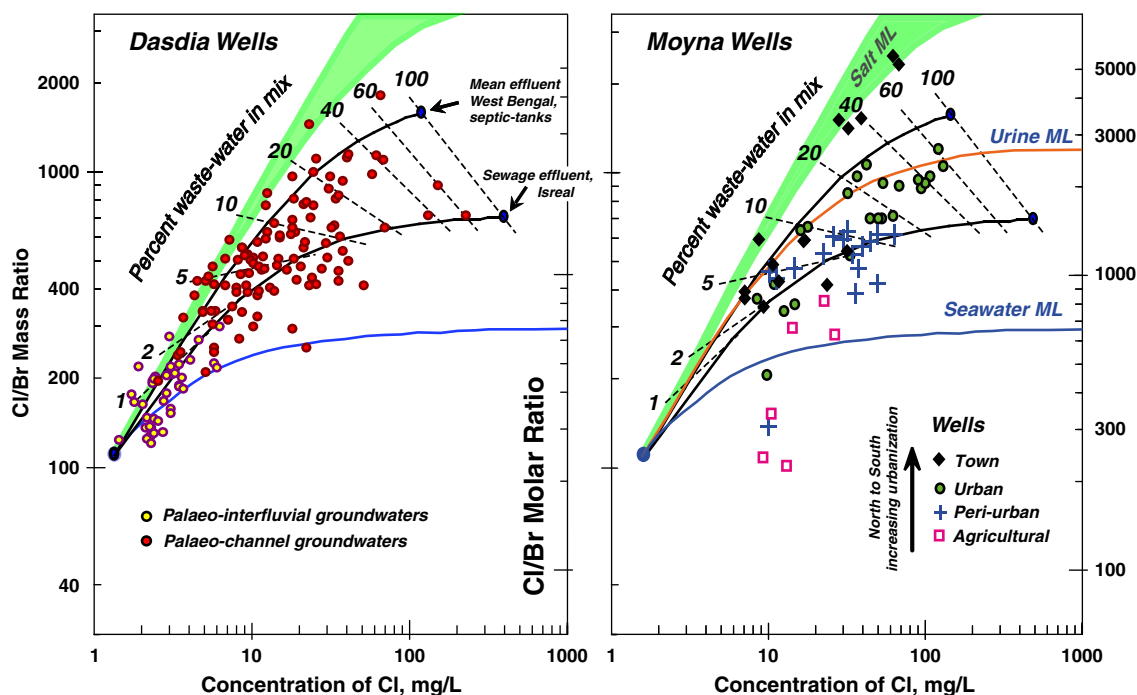
up to 780 mg/L. Of groundwaters from PC settings, Cl/Br in around 70% is >300 and concentrations of Cl are >10 mg/L Cl. Around half of all PC groundwaters have Cl/Br >400.

#### 5.4. Bangladesh

In going from coastal Lakshmipur, in south-eastern Bangladesh, through Faridpur, to Nawabganj, in inland western Bangladesh, the proportion of groundwater plotting on or below the seawater line decreases, and the proportion plotting above it increases (Fig. 5).

For coastal Lakshmipur, around 75% of groundwaters plot on the seawater mixing line. Only 8% (5 waters) appear to be much influenced by waste-water, having Cl/Br >400 and measurable amounts of  $\text{NO}_3$  (up to 29 mg/L). Measurable concentrations of  $\text{SO}_4$  occur only in 6% of well waters and these well waters have Cl/Br >288.

For Faridpur, 70% of samples plot below the seawater mixing line, whilst only about 15% show the influence of waste-water. In contrast, 70% of samples in Nawabganj have Cl/Br that plot towards the waste-water end-member, whilst only 30% have Cl/Br below the seawater mixing line.



**Fig. 4.** Quantification of mixing between the dilute groundwater and both sewage and septic-tank effluent for well-waters from Dasdia and Moyna, West Bengal. Sewage end-member is 400 mg/L Cl with Cl/Br 700, based on Vengosh and Pankratov (1998). Septic tank end-member is mean of 11 septic tank effluents from Moyna, West Bengal, and contains 126 mg/L Cl with Cl/Br of 1561. Dilute groundwater end-member has a Cl concentration of 1.4 mg/L and Cl/Br of 110. For 109 palaeo-channel groundwaters from Dasdia, 28% contain >10% waste-water. Of the 46 groundwaters from Moyna, 51% contain >10% waste-water.

### 5.5. Other contaminant indicators: $\text{NH}_4$ , $\text{NO}_3$ , $\text{SO}_4$ , faecal coliforms

Groundwaters in Bangladesh typically contain around 3 mg/L of  $\text{NH}_4$  but concentrations range up to 20 mg/L (Hoque et al., 1998; DPHE, 1999, 2001). The concentrations of  $\text{NH}_4$  correlate with faecal coliform count (Fig. 9 of Ravenscroft et al., 2001), whilst concentrations of As are inversely related to both faecal-coliform count and Cl/Br (Fig. 6). Groundwaters in Moyna contain up to 3.5 mg/L of  $\text{NH}_4$  (McArthur et al., 2004).

Only 3% of our wells from West Bengal contain >1 mg/L of  $\text{NO}_3$ . The highest  $\text{NO}_3$  concentration (30 mg/L) occurs in water from Well 42 at Dasdia, which plots amongst septic-tank waste-waters in Fig. 3 and contains around 70% waste-water (Fig. 4). In the Bangladesh database (DPHE, 1999) around 12% of wells contain more than 5 mg/L of  $\text{NO}_3 + \text{NO}_2$ , with one well (BTS306) contains 306 mg/L as  $\text{NO}_3$  but undetectable concentrations of As.

Close to 17% of our groundwaters from West Bengal contain excess- $\text{SO}_4$  (Fig. 7; Table S1), defined here as  $\text{SO}_4$  concentrations in groundwater after correction for  $\text{SO}_4$  in marine salt. All but four such groundwaters from the BH region plot above the seawater mixing-line and most have Cl/Br  $\gg$  288. Water from Well 42 at Dasdia contains 31 mg/L  $\text{SO}_4$ , is 60 feet deep and is sited next to a pit latrine (Fig. S1). In Bangladesh (DPHE, 1999 database) around 40% of groundwaters have >1 mg/L of excess- $\text{SO}_4$  (Fig. 7), in half of which Cl/Br exceeds 288. Bangladesh well BTS306 (DPHE, 2001), which contains 306 mg/L of  $\text{NO}_3$ , also contains 63 mg/L of excess- $\text{SO}_4$ .

## 6. Discussion

### 6.1. The composition of recharge, Bengal Basin

#### 6.1.1. Chloride

Between 1.5 and 4 m of rain falls each year across the Bengal Basin, the amount increasing from southwest to northeast. Rainwater typically contains <2 mg/L of Cl (Sengupta et al., 2008), so recharge to aquifers

might be expected to reflect that fact. In Dasdia, the study area in which groundwater is affected least by human influence, its concentrations of Cl is typically <3 mg/L and it ranges down to 1.4 mg/L (Table S1). Following Davis et al. (2004) for the USA and McArthur et al. (2012) for the Bengal Basin, we therefore set an upper concentration limit 10 mg/L Cl for fully-infiltrated, uncontaminated, groundwater. This limit allows evaporative concentration of recharge by a factor of at least 5 to acknowledge the fact that stable isotopic compositions of groundwaters record a signal of evaporation (Aggarwal et al., 2000; Mukherjee et al., 2007; Sengupta et al., 2008; Stute et al., 2007).

The limit of 10 mg/L, and the evaporative factor, may be too high for several reasons and a limit of 5 mg/L may be more appropriate. Firstly, concentrations <10 mg/L are common in shallow groundwater of the Bengal Basin. Of our 850 (mostly) published Cl analyses of groundwater from West Bengal, 29% were <10 mg/L (Table S1 for 606 analyses. See others in McArthur et al., 2004, 2008, 2011a, 2012). For a further 562 groundwaters from the Bengal Basin reported in other literature (see Table S1 for a listing), 25% were <10 mg/L Cl. Of 523 samples (excluding duplicates) of drinking water from Bangladesh (BBS/UNICEF, 2011), 55% of Cl concentrations were <10 mg/L, with 14% being  $\leq$  1 mg/L. Secondly, Cl concentrations down to 5 mg/L occur in groundwaters from the core of a PI aquifer that, owing to its width (kms), absence of vertical recharge, and slow movement of groundwater, is unlikely to have been affected in its core by historical contamination by Cl (Fig. 2 of McArthur et al., 2012). Thirdly, the distribution of data on Cl vs Cl/Br plots (Figs. 3–5) tightly constrains the range of dilute end-member Cl and Cl/Br because of the requirement that most data fall between mixing lines.

#### 6.1.2. Nitrate and sulphate

Natural concentrations of  $\text{NO}_3$  and  $\text{SO}_4$  in rainfall are vanishingly small. During recharge, little  $\text{NO}_3$  escapes the soil-zone in the absence of over-application of  $\text{NO}_3$ -containing fertilizers and such loadings are probably rare amongst the subsistence farmers who dominate agriculture in southern West Bengal. The groundwaters in our study

areas, and those in Bangladesh (DPHE, 1999), are anoxic below depths of around 10 m bgl, so the small natural concentrations of  $\text{NO}_3$  and  $\text{SO}_4$  in recharge in those areas, and anthropogenic additions, are rapidly removed by reduction. Unpolluted anoxic groundwaters therefore contain undetectable  $\text{NO}_3$ , and typically  $<0.1$  mg/L of  $\text{SO}_4$ .

In summary, unless contaminated by saline water, the unpolluted anoxic groundwaters of the Bengal Basin contain neither  $\text{NO}_3$  nor  $\text{SO}_4$ , have  $<10$  mg/L Cl, and Cl/Br around 110. Given these guidelines, we explore below the degree to which anthropogenic influences across the Bengal Basin have affected these groundwater compositions.

## 6.2. Sources of Cl to groundwater, Bengal Basin

Concentrations of Cl in groundwater of  $<10$  mg/L can derive from rainwater. Groundwaters that plot above the seawater mixing-line in Figs. 3 and 5, and contain  $>10$  mg/L of Cl, contain contaminant Cl. This contaminant Cl is not the result of evaporation because groundwaters do not plot along lines of evaporation on Cl/Br diagrams (Figs. 3, 5). The possible sources of this contaminant Cl are de-icers, evaporites, landfill leachate, agricultural chemicals, industrial chemicals, recharge from village ponds, mixing with saline connate water or brackish water from fish-farms, and domestic waste-water.

De-icers are not used in tropical West Bengal/Bangladesh. There are no evaporite deposits in the shallow aquifers of the Bengal Basin, which are annually and fully recharged during the summer monsoon (Shamsudduha et al., 2011). Our sample locations are remote from sites of landfill. The use of agricultural chemicals is widespread but light across our study areas, which support only subsistence farming of smallholdings. Chemical industries appear absent from our study areas. Village ponds are typically small ( $\approx 10^2$  m<sup>2</sup>), collect rain water, undergo evaporation, and receive salt. The yearly mean concentrations of Cl in ponds in Moyna were up to 46 mg/L Cl, but were typically around 25 mg/L (Sengupta et al., 2008), concentrations similar to those found in 2012 for the same ponds (Table S1).

Unlike pit latines that are designed and made to leak waste-water, ponds are designed and made to hold water. Nevertheless, ponds in Moyna do leak water to underlying aquifers. They have high Cl/Br (Fig. 3c) but can generate little of the groundwater contamination in

Moyna because pond waters are chemically and isotopically distinct from groundwaters (Sengupta et al., 2008). Of 82 groundwaters from Moyna reported in McArthur et al. (2004; up to 144 mg/L), most exceeded the yearly mean Cl concentration of nearby ponds (see also Fig. 3). As the exemplar, we cite a piezometer installed in Moyna at Site AP of McArthur et al. (2004). This site lies between two ponds, neither of which is more distant than 30 m from the piezometer (for locations, see Fig. 1 of Sengupta et al., 2008). The yearly mean Cl concentrations of these ponds in 2004 were 7 and 17 mg/L (Sengupta et al., 2008) and in February 2012 were 9 and 16 mg/L, with respective Cl/Br of 662 and 536 (Table S1). Were any site to be affected noticeably by pond water, it would be Site AP. In the upper aquifer at AP in February 2012, Cl concentrations exceeded 100 mg/L and Cl/Br exceeded 900 (Fig. 8). Taken together, these data show that the contribution to groundwater made by ponds in Moyna is not responsible for most of the Cl/Br signals we see in Moyna's groundwater. Our finding echoes those of others who found no noticeable signature of pond water in groundwater at Moyna (Sengupta et al., 2008) or further north in West Bengal (Datta et al., 2011). Away from these study areas, Cl and  $\text{SO}_4$  contamination of aquifers by ponds may be greater (Harvey et al., 2002; McArthur et al., 2011b; Knappett et al., 2012).

In West Bengal, our westerly Traverse samples have been salinized by leakage of brackish water from fish-farms created in redundant clay-pits (Fig. 3; Table S1). Salinization occurred within a few years of the start of flooding with local brackish water (salinity up to 3.5 psu), according to the report of local inhabitants. Infiltration was likely promoted by the removal of around 3 m of clay from the upper aquitard over the entire area excepting along roads and trackways, and around a scattering of remaining houses, and by the density contrast between brackish water and groundwater. Elsewhere in our study areas, the influence of saline water is weak. In contrast, in Lakshmipur, in coastal Bangladesh (Fig. 1), the effect of saline water is pronounced (Fig. 5).

There are no other sources known to us in the recharge areas of our wells that could introduce contaminant Cl (i.e.  $\text{Cl} > 10$  mg/L) to groundwater. By elimination, contaminant Cl derives from waste-water (urine, sewage, sullage), and from marine salt (mostly modern saline intrusion). Using Cl vs Cl/Br, these end-members can be distinguished.

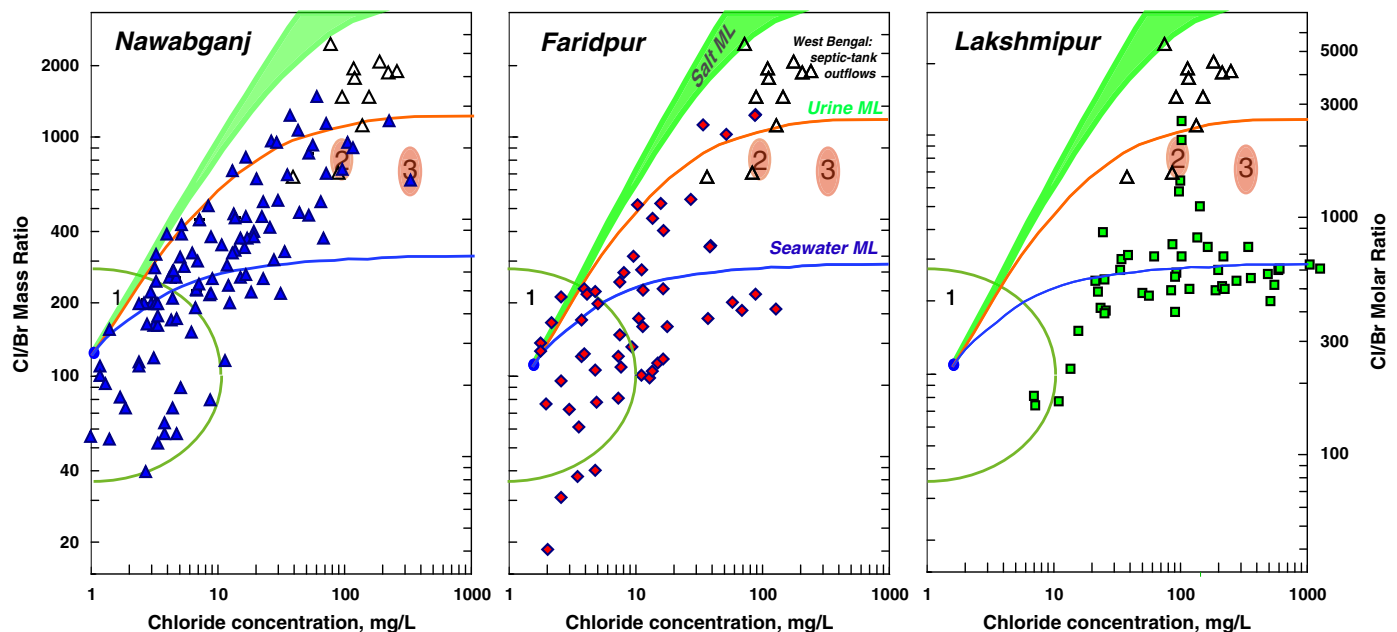
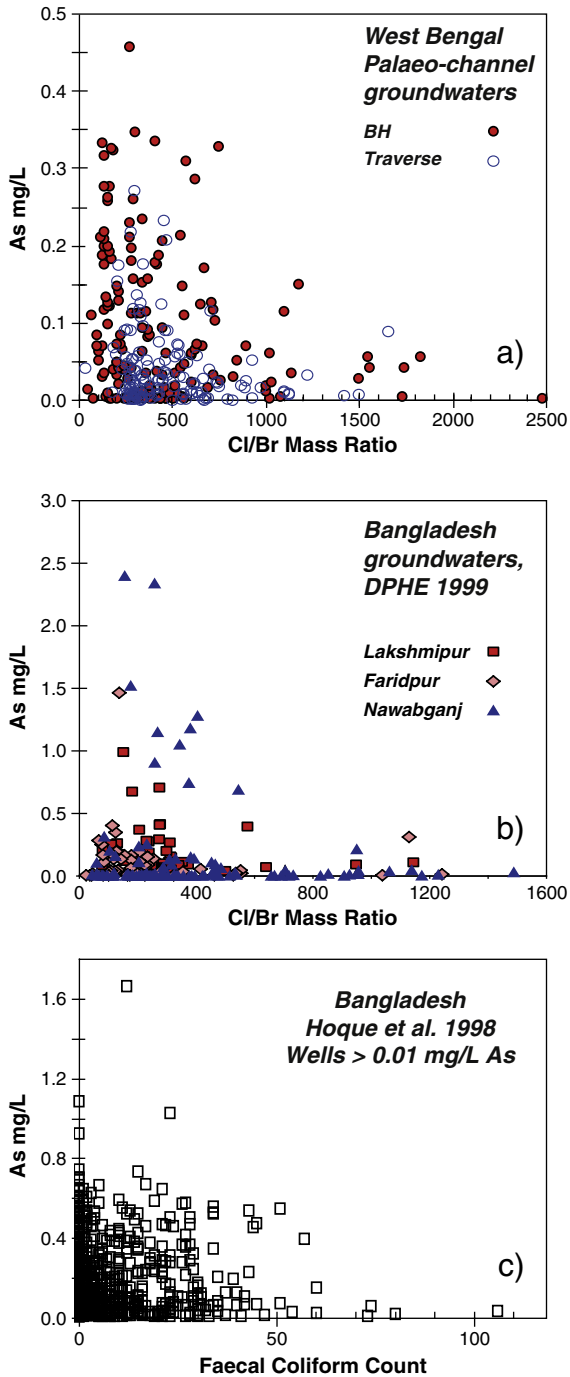


Fig. 5. Relation of Cl/Br to Cl concentrations for Bangladesh groundwaters at Lakshmipur, Faridpur, and Chapai-Nawabganj. For locations see Fig. 1. Fields as for Fig. 2. Palaeo-interfluvial and palaeo-channel aquifers cannot be distinguished. In Lakshmipur, to avoid saline water, wells are screened either  $<15$  m bgl or  $>150$  m bgl. Data from DPHE (1999).



**Fig. 6.** General inverse relation between As concentration and both Cl/Br and faecal coliform count in a) BH and Traverse samples of groundwater (Fig. 1 for locations); b) groundwaters from Bangladesh (data from DPHE, 1999, 2001). c) Relation of As concentrations and faecal coliform count for 1860 well water across Bangladesh. All three plots are consistent with waste-water suppressing FeOOH-reduction and, possibly, sequestering As in neoformed pyrite, so reducing As-pollution. c) Data of Hoque et al. (1998).

6.3. Groundwater Cl/Br

Figs. 3–5, and 8, show that most groundwaters of the Bengal Basin are mixed with waste-water from septic-tanks, pit latrines, and surface disposal of waste. Of our sites, we expected contamination to be least in Dasdia because of the low (for West Bengal) density of the rural population and the wide spacing between houses. Yet more than 28% of PC groundwaters in Dasdia contain >10%

waste-water. In Dasdia (Fig. 3) the effect of waste-water is exemplified by Well 42, which plots amongst the septic-tank effluents. Its Cl/Br is 1767, which suggests that it is 70% waste-water (Fig. 4). The severity and pervasiveness of waste-water contamination in Dasdia probably results from the high permeability of the area's upper 5 m of fine sands and silty sands, which allow rapid infiltration and dispersion of recharge and waste-water, coupled to the close proximity of wells to pit latrines.

We expected most contamination in Moyna because of the high density of housing, wells, and pit-latrines. Indeed, around 51% of groundwaters tapped by wells in Moyna contain >10% waste-water. A minority of groundwaters approach the end-member for septic-tank waste-water from Moyna, which shows that they are heavily contaminated. The Cl/Br reflects to some degree the intensity of urbanization around the sampled wells: the highest Cl/Br are found where urbanization is densest (town samples, inset of Figs. 1, 3), and the lowest is found in an agricultural setting (agricultural wells, inset of Figs. 1, 3). The prevalence of high concentrations of NH<sub>4</sub> in groundwaters across the Bengal Basin (Hoque et al., 1998; DPHE, 1999, 2001) suggests that similar percentages to those found in Dasdia and Moyna could apply wherever wells are found, which is overwhelmingly in and around conurbations, whether rural or urban.

Groundwaters from PI settings in West Bengal are less affected by waste-water contamination than those from PC settings. This is expected because of the impermeable palaeosol capping that protects PI aquifers from downward leakage of pollution or contamination. Many groundwaters in PI settings plot close to, or below, the mixing line for seawater. Those that plot below (and an unknown number of PC groundwaters that fall above) must be affected by the input of Br from degrading natural organic matter, in which Cl/Br may range as low as 6 (Nissenbaum and Magaritz, 1991; Gerritse and George, 1988; Biester et al., 2006, 2012). The high incidence of organic-rich sediments in the BH area, compared to the Traverse and Dasdia areas, explains the high incidence of Br-enriched groundwater in the BH area. Peat is abundant in the sediments of the Bengal Basin (DPHE, 1999; Ravenscroft et al., 2001; Sarkar et al., 2009). Peat and organic-rich sediment, overlie most of the PI sequence in the BH area (McArthur et al., 2011a, 2012). The peat likely supplies organics to groundwater that moves laterally above the impermeable palaeosol to the edge of the nearest palaeo-channel, where it rolls over the margin of the palaeosol to contribute to PI recharge occurring by lateral flow from the palaeo-channel. In contrast, organic-rich sediments have not been observed in Dasdia (U. Ghosal pers. comm. 2012) and are uncommon in the Traverse area (Hoque et al., 2012).

In PI groundwaters within a few tens of metres of PI margins, the chemical distinction between the PI groundwater and PC groundwater is often lost because natural flow and irrigation pumping of groundwater from the PI aquifers draws water into them from surrounding palaeo-channels. The flow contaminates PI margins with PC water, an effect seen most notably in high concentrations of Cl. This is exemplified at Moyna (Fig. 3), where the PI region is downflow of Barasat town and of small lateral extent (inset, Fig. 1). In consequence, it is especially susceptible to the impact of waste-water from the denser urbanization to the south and the groundwater of the PI sequence contains Cl at concentrations ranging from 10 to 62 mg/L (Table S1, McArthur et al., 2008).

Around 15% of Traverse groundwaters (Fig. 3) have Cl concentrations > 126 mg/L, the mean for septic-tank waste-water. These samples come from wells sited close to brackish water fish-farms, which is the likely source of this high-Cl water. Some of the salinized Traverse groundwaters in turn appear to mix towards the waste-water end-member, thereby lowering their Cl concentrations whilst increasing Cl/Br.

In Bangladesh, the proportion of shallow groundwater bearing the imprint of waste-water differs widely between Lakshmipur, Faridpur,



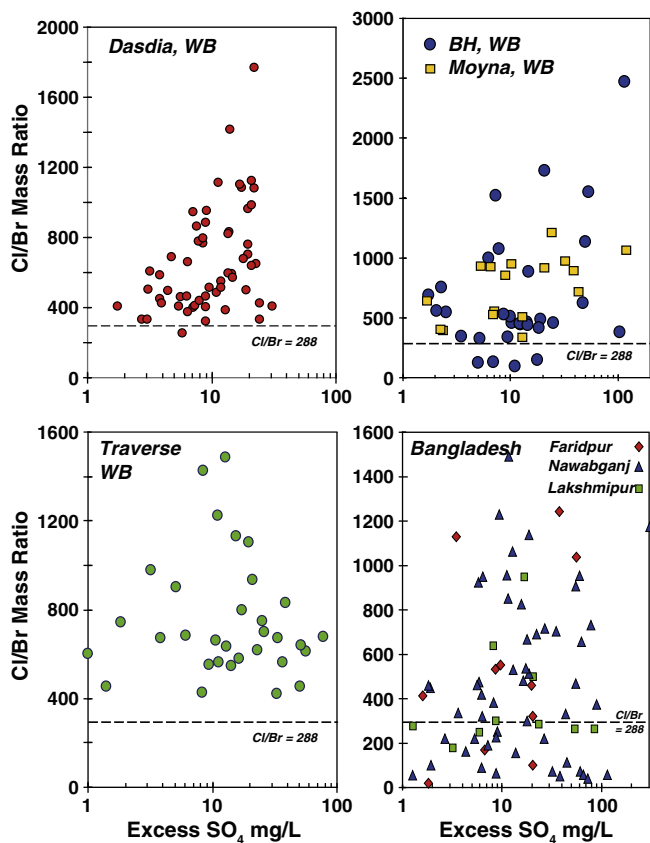


Fig. 7. Relation of excess- $\text{SO}_4$  in mg/L in groundwaters to Cl/Br. Excess- $\text{SO}_4$ , calculated as (measured  $\text{SO}_4 - 2700 \times \text{Cl} / 19,400$ ), is  $\text{SO}_4$  in excess of that derived from sea-salt. Excess- $\text{SO}_4$  is present mostly in well water having Cl/Br above 288, the marine value, which shows that the well waters have mixed with domestic waste-water.

and Chapai-Nawabganj, as does the imprint of degrading natural organics which is identifiable by Cl/Br values that plot below the seawater mixing-line. Lack of sedimentological information prevents us in determining whether the samples in Bangladesh derive from PI or PC settings, so we cannot tell how such settings affect these differences. Nevertheless, if these observations typify Bangladesh, then groundwater in many areas of that country is likely to be seriously contaminated by waste-water.

#### 6.4. Other contaminant indicators

##### 6.4.1. $\text{NO}_3$ and $\text{SO}_4$

Contamination of groundwater by waste-water is often revealed by the presence of  $\text{NO}_3$ , and/or of  $\text{SO}_4$  in amounts greater than expected from marine contributions (i.e.  $\text{NO}_3/\text{Cl}$  mass ratios  $> 0.0002$  and  $\text{SO}_4/\text{Cl}$  mass ratios  $> 0.14$ ). The converse is not true; the absence of  $\text{NO}_3$  or  $\text{SO}_4$  does not indicate that waste-water is absent because the reducing conditions of groundwaters in aquifers across most of the Bengal Basin rapidly remove both  $\text{SO}_4$  and  $\text{NO}_3$  from recharge (e.g. Zheng et al., 2004; Lowers et al., 2007; Buschmann and Berg, 2009), a fact which emphasises the value of Cl/Br vs Cl plots for identifying contamination.

Only 3% of our wells from West Bengal contain  $> 1$  mg/L of  $\text{NO}_3$  because any infiltrating is rapidly consumed by reduction. The  $\text{NO}_3$  concentration of 30 mg/L in Well 42 at Dasdia, must derive from a nearby pit-latrines (Fig. S1), as the well-water is  $> 60\%$  waste-water (Fig. 4). In the Bangladesh database of DPHE (1999, 2001) around 12% of wells contain more than 5 mg/L of  $\text{NO}_3 + \text{NO}_2$ , with the highest being 306 mg/L in BTS306, these figures placing a lower limit onto the scale of waste-water contamination.

Given the distribution of groundwaters towards the end-members for sewage and septic-tank waste-water (Figs. 3, 5) and concentrations of several thousand mg/L of  $\text{SO}_4$  in urine (Table S1; Putnam, 1971), the excess- $\text{SO}_4$  in samples from West Bengal and Bangladesh (Fig. 7; Table S1) must derive from degrading sewage, septic-tank waste-water and urine. We therefore reject the suggestion of McArthur et al. (2004) that this excess- $\text{SO}_4$  derives from building materials. Were the groundwaters not capable of reducing  $\text{SO}_4$ , a greater impact on them of waste-water might be revealed by  $\text{SO}_4$  data. The concealing effect of reduction is seen best in Lakshmipur, where salt-corrected concentrations of  $\text{SO}_4$  range down to  $-189$  mg/L, showing that as much as 189 mg/L of  $\text{SO}_4$  has been removed from groundwater by that process.

## 7. Implications for pollution of groundwater by arsenic

### 7.1. Does waste diminish As-pollution?

Pollution of groundwater in PC aquifers by naturally-occurring As is widespread in the Bengal Basin. The impact on the health of consumers has been, and remains, strong and adverse (Argos et al., 2010; Dhar et al., 1997; Smith et al., 2000). The pollution arises from microbial reduction of sedimentary iron oxyhydroxides (FeOOH) and release of their sorbed As to groundwater (Gulens et al., 1979; Nickson et al., 1998; et seq). What controls the severity and distribution of the pollution is only partly understood. Our results suggest that waste-water may influence both.

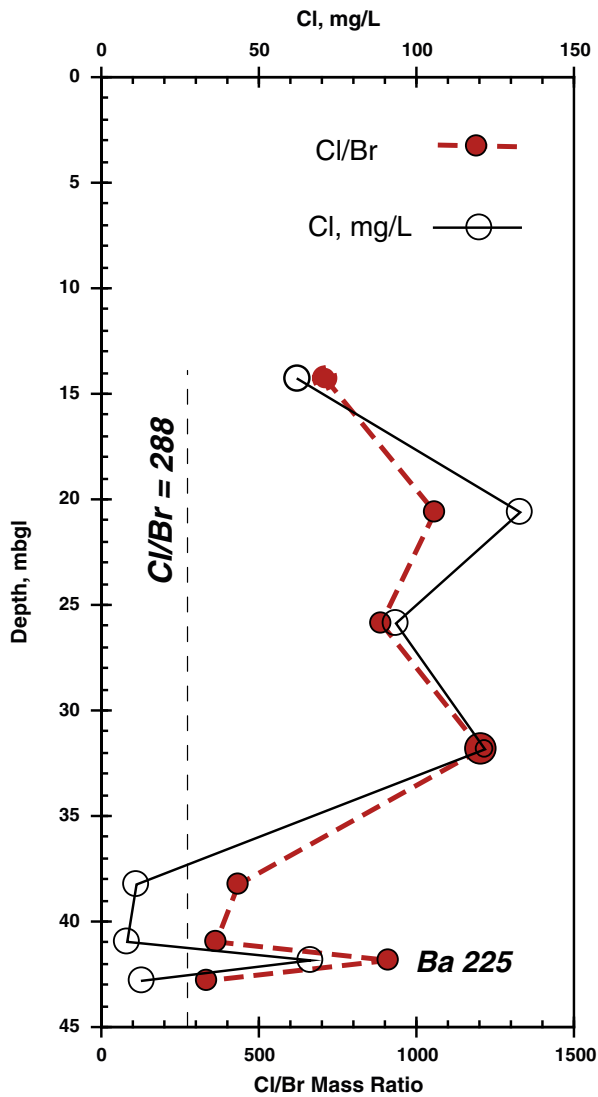
At the basin scale, both faecal coliform counts and Cl/Br, as proxies for waste-water, appear to be inversely related to the concentration of As (Hoque et al., 1998; Fig. 6), suggesting that waste-water decreases As-pollution. In Matlab and Araihaaz in Bangladesh, As-polluted groundwaters have lower counts of coliform bacteria than do groundwaters that are free of As (van Geen et al., 2011). In contrast, faecal coliform count was unconnected to As-pollution in Moyna (McArthur et al., 2004), possibly because the confining aquitard at Moyna is less permeable than the equivalent at Araihaaz.

When  $\text{NO}_3$  is present in a waste-water plume, it will be reduced before FeOOH is reduced, so the presence of  $\text{NO}_3$  should diminish As-pollution. Indeed, groundwaters in Bangladesh that contained  $\text{NO}_3$  were noted to be usually free of As (Nickson et al., 2000). As further examples, Well 42 at Dasdia (Table S1) and Well BTS306 in Bangladesh (DPHE, 1999) contain respectively 30 and 306 mg/L  $\text{NO}_3$  respectively but undetectable amounts of As, despite being surrounded by As-polluted wells.

Pollution by As may also be diminished by incorporation of As in neoformed pyrite in a contaminant plume. Diagenetic pyrite from the anoxic sediments of the Bengal Basin contains  $10^2$  to  $10^3$  mg/kg of As (DPHE, 1999; Ravenscroft et al., 2001; Buschmann and Berg, 2009; Lowers et al., 2007), so the ability of pyrite to sequester As is clear. One potential driver for pyrite formation is urine, which contains several thousand mg/L of  $\text{SO}_4$  (Table S1, Putnam, 1971). Sequestration of As into pyrite around waste-water sources raises the possibility that, when abandoned in the future, those sources will, if in the unsaturated zone, oxidise and possibly release that As to groundwater. In coastal aquifers globally, where concentrations of  $\text{SO}_4$  may be naturally high from intrusion of seawater or from sea-spray, As-pollution may be diminished by pyrite formation in the absence of pollutant- $\text{SO}_4$  (Lowers et al., 2007; Buschmann and Berg, 2009; Wang et al., 2012).

### 7.2. Can waste-water exacerbate As-pollution?

Reduction of FeOOH causes As-pollution and requires metabolizable organic carbon to drive it. Addition to groundwater of metabolizable organic carbon in waste-water will therefore promote reduction of FeOOH once more readily reduced oxidants, such as  $\text{NO}_3$ , have been utilised. Urine alone contains between 2000 and 5000 mg/L of C, mostly



**Fig. 8.** Concentrations of Cl, and Cl/Br, with depth in Piezometer AP at Moyna in February, 2012. For location and full analysis of water composition in 2004, see McArthur et al., 2004. High Cl and Cl/Br at depth in well Ba225 results from localised drawdown of water by intermittent motorised pumping of this piezometer alone since before 2004. This well is 20 m north east of, and so downflow of, other piezometers at AP.

as urea (Putnam, 1971). Given the clear impact of waste-water from pit latrines on groundwater in the Bengal Basin, and elsewhere in the world (e.g. Banks et al., 2002), a re-examination is required of the suggestion (McArthur et al., 2004; Ravenscroft et al., 2001) that domestic waste-water contributes in only a minor way to driving As-pollution in the Bengal Basin; those authors may have underestimated its impact. The need for further study is, perhaps, made more urgent by the knowledge that waste-water carries pathogenic bacteria and viruses (Taylor et al., 2004; Yates et al., 1985), the latter of which are particularly mobile in the subsurface (Deborde et al., 1999; Hunt et al., 2010).

### 7.3. Flushing and cycling

The widespread presence in palaeo-channel groundwaters of concentrations of Cl/Br greater than the natural background values attests to the widespread contamination of PC groundwater with waste-water. Up to 51% of PC groundwaters contained  $\geq 10\%$  waste-water (Fig. 4). We deduce that the PC aquifers in our study areas in West Bengal, and those in Bangladesh, have been widely

flushed with water originating, in part, from waste-water. Direct evidence of flushing has been shown for sites in both West Bengal (McArthur et al., 2010) and Bangladesh (Harvey et al., 2002; Klump et al., 2006; van Geen et al., 2008).

Given our findings, what appears surprising is that contamination is not more severe. In conurbations, water is pumped from a well, used, and then discarded largely back onto the site of abstraction, presumably setting up a circular cycling in which contamination can be removed only by lateral advective groundwater flow. As a conurbation is likely to create a cone of depression, that advective transport may simply contain the contamination. Further studies of Cl/Br and Cl in groundwater of alluvial aquifers should help quantify the degree and distribution of such cycling.

### 8. Sampling bias

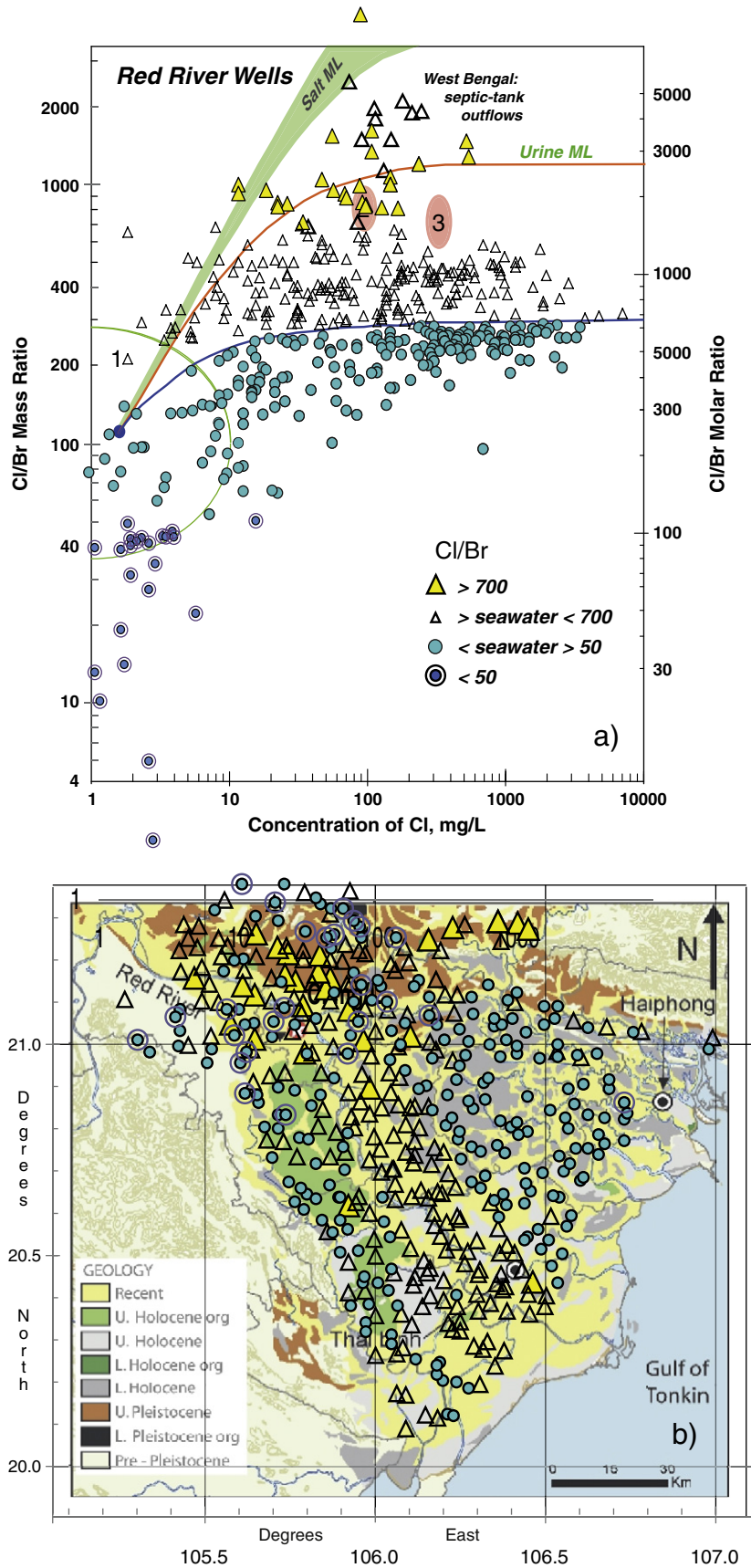
Most of the groundwaters we have examined are from private, domestic, tube wells in villages and small conurbations. They allow a proper examination of the threat to well-owners posed by waste-water contamination of the groundwater they use. They are unrepresentative of the aquifers of the Bengal Basin because they represent the aquifer underlying conurbations – we return to the theme of the opening quote by Foster et al. (2011). That fact, and the fact that domestic wells are frequently sited next to pit latrines for reasons of hygiene, suggests that the degree of contamination we report here is a biased measure of aquifer health generally across the Bengal Basin. In short, where there are people there are wells and pit latrine, so there is likely to be contamination. These conjunctions prevent an examination of groundwater quality under natural conditions.

### 9. Other localities: Vietnam

Using data from Winkel et al. (2011), we plot in Fig. 9 the Cl/Br versus Cl for groundwater from the aquifers of the Red River Basin of Vietnam. Values above 700 are confined to the (presumably) slightly older sediments around the north of the basin. Values between 300 and 700 occur mostly in groundwater from the recent deposits of the axial valley of the Red River (Fig. 9). Such high values may be indicative of local waste-water contributions. We emphasise *may*, because irrigation in the Red River basin is largely with river water. Two samples of Red River water from 10 km downstream of Hanoi had Cl/Br values of 380 and 500 (M. Berg and L. Winkel, pers. comm. 2012). Given that waste water from the city of Hanoi (pop. 2.6 million) discharges to the Red River, such high Cl/Br is not surprising. Until the Cl/Br in river water across the Red River Basin is known better, infiltrating irrigation water cannot be discounted as the reason why Cl/Br in the groundwater of the axial valley is high. The lowest Cl/Br, many  $< 288$ , are confined largely to northern areas around the regions showing the highest values. These low Cl/Br may be revealing Br additions from degrading organic matter, possibly peat, which may drive As-pollution in the Red River Basin (BGS, 1996, Fig. 16 of McArthur et al., 2004).

### 10. Conclusions

- Values of Cl/Br, coupled to Cl concentrations, permit quantification of the separate contributions to groundwater from seawater (Cl/Br = 288) and waste-water (Cl/Br  $\gg$  288).
- In our sampled wells, more than 10% waste-water is found mixed into 28% of palaeo-channel groundwaters from wells in a rural setting (Dasdia), and 51% of palaeo-channel groundwaters from wells in an urban setting (Moyna).
- Wells tapping palaeo-interfluvial aquifers generally contain negligible amounts of waste-water except for wells at the margins of the palaeo-interfluvial sequence where lateral invasion of the palaeo-interfluvial aquifer occurs from palaeo-channel groundwater.



**Fig. 9.** a) Cross plot of Cl/Br against Cl concentrations for groundwaters from the Red River Basin, Vietnam; b) distribution of Cl/Br in groundwater of the Red River Basin. Groundwaters above the seawater mixing line are found almost exclusively beneath the recent alluvial of the Red River. Base map and data from Winkel et al. (2011).



- Values of Cl/Br below the seawater mixing line reflect inputs to groundwater from degrading natural organic matter in localised regions of floodplain sediment containing peat.
- Concentrations of NH<sub>4</sub> at low mg/L in groundwater of the Bengal Basin, previously presumed to derive from natural organic degradation, most likely arise from domestic waste-water.
- Groundwater in the Bengal Basin contains SO<sub>4</sub> in excess of that derived from marine sources; Cl/Br data show that this SO<sub>4</sub> is sourced from domestic waste-water.
- Domestic waste-water appears to suppress As-pollution of groundwater in the proximal region of the source. It may exacerbate As-pollution distally from that source.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2012.07.068>.

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