**Impacts of physical and chemical aquifer heterogeneity on basin-scale solute transport:
vulnerability of deep groundwater to arsenic contamination in Bangladesh**

Holly A. Michael^{a,b,*} and Mahfuzur R. Khan^a

^aDepartment of Geological Sciences, University of Delaware, Newark, DE, USA, 19716

^bDepartment of Civil and Environmental Engineering, University of Delaware, Newark, DE, USA, 19716

*Corresponding author, hmichael@udel.edu

Abstract

Aquifer heterogeneity presents a primary challenge in predicting the movement of solutes in groundwater systems. The problem is particularly difficult on very large scales, across which permeability, chemical properties, and pumping rates may vary by many orders of magnitude and data is often sparse. An example is the fluvio-deltaic aquifer system of Bangladesh, where naturally-occurring arsenic (As) exists over tens of thousands of square kilometers in shallow groundwater. Millions of people in As-affected regions on deep (≥ 150 m) groundwater as a safe source of drinking water. The sustainability of this resource has been evaluated with models using effective properties appropriate for a basin-scale contamination problem, but the extent to which preferential flow affects the timescale of downward migration of As-contaminated shallow groundwater is unknown. Here we imbed detailed, heterogeneous representations of hydraulic conductivity (K), pumping rates, and sorptive properties (K_d) within a basin-scale numerical groundwater flow and solute transport model to evaluate their effects on vulnerability and deviations from simulations with homogeneous representations. Advective particle tracking shows that heterogeneity in K does not affect average travel times from shallow zones to 150 m depth, but the travel times of the fastest 10% of particles decreases by a factor of ~ 2 . Pumping distributions do not strongly affect travel times if irrigation remains shallow, but increases in the deep pumping rate substantially reduce travel times. Simulation of advective-dispersive transport with sorption shows that deep groundwater is protected from contamination over a sustainable timeframe (>1000 y) if the spatial distribution of K_d is uniform. However, if only low-K sediments sorb As, 30% of the aquifer is not protected. Results indicate that sustainable management strategies in the Bengal Basin should consider impacts of both physical and chemical heterogeneity, as well as their correlation. These insights from Bangladesh show that preferential flow exerts a strong control on breakthrough of both conservative and reactive solutes even at large spatial scales, with implications for predicting water supply vulnerability in contaminated heterogeneous aquifers worldwide.

Keywords: Aquifer Heterogeneity; Preferential Flow; Solute Transport; Bengal Basin; Arsenic; Groundwater Modeling

1. Introduction

It is well known that heterogeneity in physical aquifer properties exerts a strong control on subsurface contaminant transport [e.g., 1–4]. Though critical for remediation of groundwater contamination and protection of water supply, prediction of solute transport in natural systems continues to confound hydrogeologists because of the difficulty in characterizing ubiquitous, multi-scale geologic heterogeneity and representing its effects in models. Groundwater flow models that are well calibrated to hydraulic head data may poorly simulate solute transport due to preferential flow through high-permeability conduits [e.g., 5–7]. Dense data collected at well-studied sites has provided insights into field-scale transport behavior. In relatively homogeneous aquifers such as those at the Cape Cod [e.g., 8,9] and Borden [10] experimental sites, transport may be well predicted by upscaled Fickian dispersion. However, heterogeneity plays an increasingly important role where permeability contrasts are greater. At the Macrodispersion Experiment (MADE) site, simulations through well constrained heterogeneous fields on a 4 m-scale show that preferential flow dominates early solute arrival: 40% of flow occurred along the fastest 5% of flowpaths [11]. On a 150 m scale, mass transfer into immobile domains such as small low-permeability zones modeled both implicitly [12] and explicitly [13] can explain solute distributions at both early and late times observed at that site. Smaller-scale sandbox experiments also show that the connectivity of high- and low-permeability zones exerts a strong influence on solute breakthrough curves [14,15], even when permeability contrasts are low [16].

Studies of geochemical heterogeneity also demonstrate effects on solute transport that can be highly complex [17,18]. Geochemical heterogeneity, defined here as the spatial variation in K_d , can occur due to variation in sediment organic matter [19], clay content [20], mineralogy [21–23], and surface area [24]. Studies have shown both positive [25,26] and negative [27,28] correlation between grain size and K_d . Modeling studies that incorporate correlations between physical and chemical heterogeneity show that both variances in the properties and the nature of their correlation affect the distribution of solute arrival times, dispersion, and effective transport properties [29–37]. These studies highlight the importance of integration of multiple types of physical and geochemical data for improving prediction of transport in reactive aquifers [e.g., 38].

The vast majority of work on both conservative and non-conservative solute transport has been conducted on a plume (10-100 m) scale with a relatively low variance in K , and results can be difficult to extrapolate to larger scales and highly heterogeneous media [39]. Few studies have considered the large scale

necessary for widespread contamination problems or highly heterogeneous fields that result in preferential flow. Further, in many cases the focus is on the long end of the distribution of solute arrival times [40], more relevant for remediation, rather than the short end that is more relevant for water supply vulnerability.

We explore the effects of physical and chemical aquifer heterogeneity on basin-scale solute transport where the focus is the vulnerability of pumping wells to contamination from shallower strata using the example of arsenic contamination in the Bengal Basin of Bangladesh and India. There, high concentrations of geogenic arsenic in shallow groundwater [41–43] threaten the health of tens of millions of people [44]. Deep (≥ 150 m) groundwater is nearly uniformly low in arsenic, and deep wells are the preferred mitigation option of people in the affected region [45,46]. This resource is now being successfully exploited: tens of thousands of deep community wells have been installed and are providing low-arsenic drinking water across Bangladesh [47]. Basin-scale modeling has shown that pumping deep groundwater for drinking supply is not likely to induce downward migration of arsenic over much of the arsenic-affected area if irrigation remains shallow [48,49]. However, incorporation of local hydrogeological details in such large-scale models is challenging, so the extent to which physical and geochemical heterogeneity affect this predicted sustainability is unknown. Simulations explicitly incorporating heterogeneity around the mega-city, Dhaka, show that preferential flow can greatly increase vulnerability of deep groundwater to arsenic migration in the presence of intensive pumping [7], but this effect has not been explored in more rural areas where pumping is more evenly distributed.

Models used to evaluate the large-scale vulnerability of deep, arsenic-safe aquifers have represented the complex heterogeneity of the fluvio-deltaic Bengal Aquifer System [50] as either upscaled vertical anisotropy in hydraulic conductivity [48,49,51,52] or layered stratigraphy [53]. These studies capture average flow behavior and have identified areas likely to be vulnerable to downward flow. However, in areas where downward flow is simulated, these approaches do not capture the full distribution of advective velocities expected in a heterogeneous system, the short end of which indicates the true local-scale vulnerability [7,54]. Further, in areas that are not predicted to be vulnerable - where flowpaths are horizontal and originate outside of high-arsenic areas on average - the potential for downward flow along a few vertical preferential flowpaths is unknown. Models have also represented pumping as evenly distributed spatially. While this may be acceptable for domestic handpump wells with low yield, flowpaths may differ to higher-yield wells, such as those that supply water for irrigation or piped water systems. Indeed, smaller-scale simulations in West Bengal, India with generalized heterogeneous stratigraphy and higher deep pumping rates that include irrigation indicate that shallow arsenic could

migrate to depth within a few decades of the onset of pumping [55]. These flowpaths could explain observations of high concentrations of arsenic in deep groundwater [47,55–57], though there may be alternate reasons such as poor well construction [58] and deep, in-situ release of arsenic.

Reaction with aquifer sediments has the potential to delay migration of arsenic from shallow to deep aquifer zones relative to advection only. On a 10 m scale, one-dimensional reactive transport simulation based on laboratory observations of sorption behavior showed that oxidized sediments may delay arsenic breakthrough tens to hundreds of years [59]. On the basin scale, three-dimensional modeling using equilibrium adsorption coefficients modeled from deep in-situ push-pull experiments indicated that breakthrough of arsenic to depths >150 m may be delayed by hundreds to thousands of years in some areas [49]. While it is clear that sorption is important to As transport, the sorptive properties of sediments vary greatly [59–62]. Most of these values are obtained from batch experiment or small column studies with relatively homogenous sediments. Some are from in-situ push-pull tests [49], which give a more realistic representation of the impacts of sorption on transport in the aquifer. However, these are confined to a relatively small aquifer zone due to the short time frame of the tests relative to large-scale migration. Field measurements on a 1000 m scale in a similar Pleistocene Aquifer in Vietnam indicated a retardation factor of 16-20 [63]. This value is lower than most derived on smaller scales, perhaps indicating effects of inhomogeneity, potentially correlated to flow properties. The spatial distribution of sorption properties on the 10-1000 m scale relevant for shallow-deep migration and the relationship to aquifer hydraulic properties is not known, despite efforts to delineate patterns in sediment color and age [64–66].

Here we explore the extent to which explicitly incorporating either physical or chemical heterogeneity in aquifer properties and pumping distribution alters predictions based on large-scale models with homogeneous, upscaled parameters. We investigate this effect using the extensive and highly heterogeneous Bengal Aquifer System as an example. We imbed detailed heterogeneous representations of physical and chemical aquifer properties and pumping rates within a basin-scale numerical groundwater flow model. Two locations are chosen for comparison: a more vulnerable area where large-scale simulations indicate that vertical gradients are driving downward flow, and a less vulnerable area where simulated flowpaths originate in As-safe areas. For each case the impacts of heterogeneity on vulnerability of deep, low-As groundwater to contamination from shallower strata are evaluated. In the vulnerable area, flowpaths predicted by a homogeneous model are downward, so the analysis evaluates the impact of heterogeneity on fast travel times. In the less vulnerable area, predicted flowpaths are lateral, originating outside of the high-arsenic zone, so the analysis evaluates the potential for development of devious vertical flowpaths.

2. Methods

The MODFLOW [67] model of Michael and Voss [48] was used as the large-scale framework for the simulations. Grid size was 5000 x 5000 m, with cell thickness varying from 5 m to 650 m, except the 1 m thick top layer used for assigning a prescribed head at the elevation of the land surface. Flow conditions were steady-state. Although the climate is monsoonal, seasonal hydraulic head variations have minimal effect on the basin-scale flowpaths which may span thousands of years [68], and the water table rises to near land surface or above in most of the aquifer system during each wet season. The split pumping scenario of Michael and Voss [48] was used as a base case, where irrigation pumping was assigned at approximate present-day depths of 15-50 m and domestic pumping was assigned to low-As depths of 150-175 m. This represents an arsenic-mitigation scenario; currently most domestic pumping occurs in the As-contaminated shallow aquifer zone. Pumping rates were assigned by district in both Bangladesh and India at a rate of 50 L/d/capita. District-wise population statistics were updated from the prior version of the model to data from 2011 [69,70]. Irrigation pumping rates were estimated from the 2008 irrigated area for Bangladesh [71] and FAO global irrigation data for India [72].

Two areas within the basin-scale model (Figure 1) were targeted for refinement based on flowpaths simulated with MODPATH [73]. On the bases of the homogeneous model results, a *More Vulnerable* area was chosen, where simulated flowpaths were relatively vertical, originated within the high-As zone, and had a median travel time of less than 1000 y (range: 600 to 3,500 y). A *Less Vulnerable* area was chosen, where most of the simulated flowpaths originated outside of the high-As zone and simulated travel times ranged from 600 y to 6,000 y with a median of 2000 y. The grid was refined using the MODFLOW-LGR v.2 package [74] over 50 x 50 km areas. Grid size in the refined model areas was 1000 x 1000 x 5 m (with the exception of the 1 m thick top layer).

The large-scale model was calibrated as part of its development to available data throughout the basin: hydraulic heads, ^{14}C groundwater age dates, and effective properties derived from driller logs. The details of the calibration and results are given in [51]. The hydraulic conductivity (K) value in homogeneous simulations was anisotropic, with the calibrated horizontal value (K_h) of 5×10^{-4} m/s and vertical value (K_v) of 5×10^{-8} m/s. The heterogeneous hydraulic conductivity fields were generated based on 54,429 driller log data points from 793 boreholes (Figure 1) obtained from Department of Public Health Engineering, Bangladesh [75]. Lithologic descriptions were grouped into three categories: *medium* &

coarse sand, fine sand, and silt & clay (see Supplementary Section 1). Variogram models fitted to the data were used in sequential indicator simulation [76] (see Supplementary Section 2) to produce 20 realizations of heterogeneous lithology. These were not conditioned to local data so that the same realizations could be used in both model areas. A comparison between the input variograms obtained from data and the variograms of the simulated lithofacies is given in Supplementary Figure S3. In order to maintain consistency and enable direct comparison to the homogeneous simulations, the Kh and Kv values of each lithologic category were varied for each individual realization to obtain equivalent Kh and Kv values over the refined grid identical to that of the coarse, homogeneous grid (within a tolerance of 2%). The equivalent Kh and Kv values were determined by simulating horizontal and vertical flow through each field separately, by specifying a hydraulic head gradient and using the simulated volumetric flow rate to calculate K. A summary of the statistics of the K values assigned to lithologic categories in the heterogeneous realizations is given in Table 1 and Supplementary Figure S4. Values for each realization are given in Supplementary Table S3.

Both domestic and irrigation pumping were assigned uniformly within each district for the base model, representative of pumping by closely-spaced (scale smaller than the area of a model cell, i.e. 1 km²), low-capacity handpumps or irrigation pumps. Several pumping configurations were tested for practical management alternatives (Table 2). Three factors were tested (i) the depth of irrigation pumping, (ii) the spatial distribution of domestic pumping, and (iii) the rate of both irrigation and domestic pumping. Irrigation pumping was always distributed, meaning that pumping was assigned to all model cells, only the depth and quantity was varied. Domestic pumping was either distributed evenly or concentrated in regularly spaced cells (one well over a 1 km² cell was assigned the pumping for a 25 km² area). The concentrated pumping can be regarded as piped water supply systems where a few centralized wells supply all the domestic water in a union (approximately 25 km² area). Domestic pumping rates were 8x10⁶ and 5x10⁶ m³/year and irrigation pumping rates were 100x10⁶ and 51x10⁶ m³/year for the Less Vulnerable and More Vulnerable areas, respectively. For heterogeneous K simulations, the pumping zones were assigned homogeneous effective K values in order to avoid large drawdowns caused by unrealistic pumping from low-K cells. Pumping rates were also varied from the base case to evaluate potential future pumping scenarios. The impact of grid discretization was tested by refining the grid by a factor of 25 (200 x 200m cells) for concentrated pumping case (Scenario #2) in the More Vulnerable area, as this is the case where impacts are likely to be greatest. The 20 heterogeneous and 1 homogeneous simulations were run. Results are given in Supplementary Section 4, Table S4, and Figure S5.

Advective transport of arsenic was simulated using MODPATH in the locally-refined models. Particles were tracked backward from a depth of 150 m to end points at 50 m depth, the approximate lower boundary of the consistently high-As zone. Particles were categorized as originating outside of the high-As zone if the endpoint location was outside the area of the red contour shown in Figure 1, following Michael and Voss [48]. Advective-dispersive transport was simulated with MT3DMS [77] only on the refined grid in the More Vulnerable model area. For these simulations, in order to more easily show effects of hydraulic and chemical heterogeneity, topography was made uniform (elevation 1 m), and pumping was distributed evenly across the area (equivalent total pumping, but no changes across district boundaries). Sorption was simulated with a linear isotherm as a sorption coefficient (K_d). A K_d value of 1.0 L/kg was assumed after the in-situ and batch experiments of Radloff et al. [49], corresponding to a retardation factor of 9.25 (assuming a bulk density of 1650 kg/m³ and a porosity of 20%). The conceptual model is shown in Supplementary Figure S6. For simulations with chemical heterogeneity, two scenarios were considered. Both assumed, for the sake of demonstration, a perfect correlation between hydraulic and chemical properties. In both cases, it was assumed that a sediment sample with lithofacies proportions consistent with the driller log dataset (66% sand and 34% silt and clay) was used in a batch experiment to obtain the bulk K_d value. If, hypothetically, we assume that only sands sorb, the sand K_d value would be 1.5 L/kg to obtain the bulk K_d of 1.0 L/kg with silt and clay K_d values of 0.0 L/kg. Conversely, silt and clay K_d values of 3.0 L/kg would be necessary with a sand K_d of 0 L/kg. For heterogeneous fields, these values were calculated in proportion to the simulated facies (Supplementary Table S5). Longitudinal dispersivity was 10 m and transverse dispersivity values were 0.01 and 0.001 m. Simulations were run for 1000 y to evaluate both management timeframes (decades) and long-term sustainability.

3. Results

3.1. Patterns of Groundwater flow

3.1.1. Physical heterogeneity – K distributions

Homogeneous simulations showed that the recharge location of water reaching the top of the deep pumping zone (150 m depth) was much different in the two areas for the base case pumping scenario. More-vertical hydraulic gradients in the More Vulnerable area produced local flowpaths: 88% of particles originated within the refined model area and 100% originated in the high-arsenic zone (Figure 2a). In contrast, more-horizontal gradients in the Less Vulnerable area resulted in longer flowpaths (Figure 2b): only 0.2% of particles originated within the refined model area and 9% originated in the high-As zone.

Travel times were also different. Median travel time in the Less Vulnerable area was about twice that of the More Vulnerable area (1407 y and 748 y, respectively). However, the maximum (4596 y and 4389 y, respectively) and minimum travel times (319 y and 478 y, respectively) were similar (Table 3).

Vulnerability differed between heterogeneous and equivalent homogeneous simulations for the base case scenario. In the Less Vulnerable area, incorporation of heterogeneity generally resulted in shorter flowpaths and travel times. The recharge locations of some particles were shifted from low-As areas to the high-As zone (Figures 2b and d, 3b, and Supplementary Figure S7). On average, 20% of particles originated in the high-As zone with a maximum of 34%, compared to 9% in the homogeneous case (Figure 3b, Table 3). Travel times were shorter: the median travel time (of particles within each model) averaged over the 20 heterogeneous realizations was 989 y compared to 1407 y for the homogeneous simulation (Table 3). In the More Vulnerable area, differences were not as great and in some cases heterogeneous realizations were less vulnerable than the homogeneous equivalent. Flowpaths were shifted to As-safe areas in 6 of the 20 simulations, though the maximum proportion originating outside the high-As area was only 7% (Figure 3a, Table 3). The average median travel time was 833 y in the heterogeneous case, compared to 748 y in the homogeneous simulation (Table 3). While the smaller difference between heterogeneous and equivalent homogeneous simulations for the More Vulnerable area is likely due to the shorter nature of the flowpaths overall, it could also be due in part to the difference in pumping rates – pumping in the Less Vulnerable area is nearly double that of the More Vulnerable area because of differences in land use and population. An important aspect of the simulation results is that in both areas the travel times were distributed across a much wider range in the heterogeneous cases, which means that the tails of the distributions were much longer (Figure 3b). Although there are only small differences on average in the quartile values (Figure 3c), the minimum travel times are much less, on average, in heterogeneous cases compared to the equivalent homogeneous case: 171 y compared to 319 y in the Less Vulnerable area, and 98 y compared to 478 y in the More Vulnerable area (Table 3). This has important implications for management and monitoring, as the shortest flowpaths determine initial breakthrough.

3.1.2. Physical heterogeneity - Pumping Distributions

The spatial distribution of domestic pumping – whether it is distributed or concentrated - does not strongly affect overall vulnerability in both focus areas, as shown by comparison of pumping scenario #1 with #2 (shallow irrigation and deep domestic) and #4 with #5 (half shallow irrigation and deep domestic

+ half irrigation), where the second in each pair has concentrated domestic pumping. The origin of flowpaths for both homogeneous and heterogeneous K distributions is similar for the two scenarios in each pair (Figure 4a). Travel time distributions are also very similar (Table 3; Figure 4b). In the More Vulnerable area, the average median travel times for the heterogeneous simulations were 856 y and 754 y for the distributed (#1) and concentrated (#2) scenarios, respectively, and minimum travel times were 158 y and 139 y, respectively, considering only particles tracked from cells with pumping in Scenario #2. In the Less Vulnerable area, average heterogeneous median travel times were 970 y and 893 y and minimum travel times were 263 y and 217 y for scenarios #1 and #2, respectively. In Scenarios #4 and #5, in which half of irrigation pumping is drawn from deeper in the aquifer, the particle tracking results are nearly identical. This is because the irrigation pumping, distributed among all cells in the deep pumping zone, masks the effect of concentrated domestic pumping, which is more than ten times less than irrigation. The only differences are in the less vulnerable area, where median travel times for the heterogeneous cases in Scenarios #4 and #5 are 167 y and 159 y, respectively. We note that these results are somewhat dependent on grid discretization, since the pumping intensity is determined by cell size when pumping is concentrated in a single cell. We tested the effect on Scenario #2 in the More Vulnerable area and found that minimum and maximum travel times are reduced when discretization increases, up to 17% on average for a 25x increase in discretization. However, mean and quartile values were similar within 5% (Supplementary Section 4).

Higher pumping rates result in greater vulnerability. The domestic pumping rate was doubled in scenario #3 relative to #2. This nearly doubled the area of the deep pumping zone from which water was drawn through the high-As zone in both the homogeneous and heterogeneous simulations in the Less Vulnerable area (Figure 4a; Table 3). Increased pumping reduced both the shortest travel times (Figure 4b) and the median (Table 3). The median travel time averaged over the 20 heterogeneous simulations was 556 y for scenario #3 compared to 754 y for scenario #2 in the More Vulnerable area, and 414 y compared to 549 y in the Less Vulnerable area, considering only particles tracked from deep pumping cells. The irrigation pumping was reduced to zero for scenario #7 relative to the base case (#1), as if irrigation water were taken from surface sources to minimize As application to crops. Eliminating irrigation pumping did not substantially change the area vulnerable to contamination (Figure 4a). Travel times increased, but to a lesser extent than doubling domestic pumping. Median travel times averaged over heterogeneous simulations were 1085y and 1062 y without irrigation pumping, compared to 833 y and 989 y with irrigation pumping in the More Vulnerable and Less Vulnerable areas, respectively (Table 3).

Pumping depth affects vulnerability most strongly for the cases tested, as shown by comparison of scenarios #1, #4, and #6. These scenarios have distributed pumping with current estimated irrigation and domestic pumping rates, but in scenario #1 all irrigation pumping is shallow, in #4, half of irrigation pumping is deep, and in #6, all irrigation pumping is deep. In the More Vulnerable area, the origin of deep groundwater is nearly all in the high-As zone, so the scenarios are similar. However, in the Less Vulnerable area, substantially more particles originated in the high-As zone and flowpaths are more vertical for scenarios #4 and #6 compared to #1 (Figure 4a, Supplementary Figure S7). The median travel times for scenarios #1, #4, and #6 averaged over the 20 heterogeneous simulations were 833 y, 184 y, and 102 y, respectively, in the More Vulnerable area, and 989 y, 167 y, and 82 y, respectively, in the Less Vulnerable area. The shortest travel times were also significantly affected (Figure 4b). The average minimum travel times were as low as 19 y and 10 y in scenarios #4 and #6, respectively, compared to 98 y in scenario #1 in the More Vulnerable area. Minimum travel times were even shorter in the Less Vulnerable area in scenarios #5 and #6: 16 y and 8 y, respectively, compared to 171 y in scenario #1 (see Table 3). This indicates that moving even a portion of irrigation pumping deeper in the aquifer has a very large impact on vulnerability, resulting in advective travel times well within a typical management timeframe.

3.2. Arsenic Migration: Effects of Sorption and Chemical Heterogeneity

Arsenic sorption strongly influences vulnerability for both homogeneous and heterogeneous distributions of K_d . For the homogeneous case with no sorption, 100% of the model area at a depth of 150 m and 51% of the initially uncontaminated aquifer volume had a concentration greater than 10% of the initial value after 1000 y, compared to 0% of the area and 14% of the volume with a uniform K_d of 1.0 L/kg (Figures 5a,b; 6a, Table 4). Heterogeneity in permeability results in strong gradients in concentration, with much higher concentrations than the equivalent homogeneous case (Figure 5c,a), but less of the area (80%) is contaminated ($C/C_0 > 0.1$). With uniform sorption, that value is reduced to <1% (Figure 6a, Table 4). Without sorption, C/C_0 is nearly uniformly greater than 0.1 throughout the 100 m interval between the bottom of the high-As zone and the top of the deep pumping zone (Figure 7). With uniform sorption, the proportion contaminated decreases rapidly with depth, reaching <10% by 100 m depth for most realizations (Figure 7). Association of sorption with particular lithofacies – an assumption of perfect correlation between lithofacies, hydrofacies, and chemofacies – strongly affects the role of sorption in reducing vulnerability to arsenic migration (Figure 5d-f, Table 4). When a K_d equivalent to that which would result in a bulk K_d of 1.0 L/kg is assigned to sand only (1.6 ± 0.3 ; see Supplementary Table S5), the proportion of the area at a depth of 100 m with $C/C_0 > 0.1$ decreases slightly on average, from 7.3% to

6.6%, though the range increases (Table 4). The average decreases because nearly all of the water flows through the sand, and the K_d is greater for sand than the case with uniform sorption. In contrast, when a K_d equivalent to that which would result in a bulk K_d of 1.0 L/kg was assigned only to silt and clay lithofacies (3.1 ± 1 ; see Supplementary Table S5), the proportion of the aquifer contaminated was much greater: 45% on average, compared to 7% with uniform sorption (Figure 6, Table 4). The depth distribution of contaminated area also shows that the case of sand-only sorption is very similar to the uniform sorption case, whereas the case of silt and clay-only sorption is intermediate between the uniformly sorbing and non-sorbing cases (Figure 7).

4. Discussion

Simulations using upscaled, homogeneous representations of hydraulic conductivity reasonably predict average flow behavior and indicate the relative vulnerability of areas within the Bengal Basin to vertical migration of As. Recharge locations and average travel times between shallow and deep aquifer zones were similar in homogeneous and heterogeneous cases for both focus areas considered (Figure 3). However, consideration of heterogeneity in hydraulic properties increases predicted vulnerability as determined by the most vertical and fastest flowpaths compared to simulations using upscaled homogeneous models with equivalent hydraulic conductivity. In vulnerable areas where gradients drive primarily vertical flow, the recharge areas did not shift much (Figure 2; Figure 3a) but the short end of the travel time distribution had a longer tail (shorter travel times) in heterogeneous simulations (Figure 3b) because some water flowed through preferential, near-vertical sandy flowpaths. This results in minimum travel times (Figure 3c) and the average of the fastest 10% of flowpaths (Figure 4) that are much less than in the homogeneous case. This is true for all pumping scenarios simulated. In less vulnerable areas where homogeneous simulations predict more-horizontal flowpaths that originate outside of high-As areas, heterogeneity can create devious vertical flow, shifting some flowpaths to recharge locally (Figure 2; Figure 4). The low end of the travel time distribution for heterogeneous models had longer tails than that of the homogeneous case (Figure 3b), but the deviation is less than in the higher vulnerability area for both the fastest particle (Figure 3c) and the average of the fastest 10% of particles (Figure 4).

Concentrating pumping for domestic use had a small effect on recharge locations and travel times, even in heterogeneous simulations. This indicates that installation of wells with mechanized pumps to supply drinking water through piped systems will not likely to substantially increase vulnerability of those wells to arsenic contamination. However, increasing pumping rates increases vulnerability to a greater

extent. Doubling deep domestic pumping, as might occur if behavior changes as a result of piped supply installation, reduced short travel times in both focus areas and shifted recharge areas in the more vulnerable area. Adding even half of the irrigation pumping to the deep zone reduced travel times to less than 20 y in some cases.

While sorption protects deep groundwater from As contamination [49,63,78], the spatial distribution of sorptive properties and their relationship to hydraulic properties are critical to determining the extent of that protection. Simulations showed that chemical heterogeneity increases vulnerability if high K_d values are correlated with low K values. In this case, upscaled models with homogeneous K_d values based on the bulk combination of all sediments predict lower As concentrations in deep groundwater and significantly more As-safe groundwater at depth where flowpaths are vertically downward. This suggests that modeling transport using bulk K_d values from batch experiments is less desirable than using those developed from in-situ tests. However, by necessity in-situ experiments are performed on a much smaller scale than the regional migration considered here, which means that they likely encounter a much narrower range of the distribution of hydrofacies and chemofacies; thus even in-situ tests may not fully capture preferential flow behavior. This demonstration assumed a 1:1 hydraulic-chemical correlation, which is not realistic. While fine-grained sediments have been shown to have greater sorptive capacity than coarse-grained sediments [23,24,27], there are many other factors that may affect the distribution, and evidence suggests that correlations between K and K_d can be positive or negative, though data is sparse [25,27,36,79]. Further, in the Bengal Basin, sediment age or oxidation extent may be much more important than lithology in controlling K_d .

The results of this study show that preferential flow through heterogeneous aquifers has a significant impact on large-scale contaminant transport in the presence of pumping. In the vulnerable area where flowpaths were vertical, advective breakthrough occurred ~5x faster on average than predicted by an equivalent homogeneous model, resulting in contamination within a 100-year management timeframe. This justifies the use of long timescales (i.e., the 1000-year threshold used in this and other studies) for evaluating the sustainability of pumping strategies with respect to aquifer contamination when using homogeneous models, and even heterogeneous models where substantial heterogeneity may exist on the sub-grid scale. The simulation results reinforce prior findings using homogeneous models [48,49] that deep irrigation pumping presents a substantial threat to the quality of deep groundwater. While concentrated domestic pumping on the village scale did not substantially enhance preferential flow, certainly deep pumping for domestic use in urban centers in the Bengal Basin, such as those in Kolkata [e.g., 80] and Dhaka [7,81,82], present a threat to deep, low-As groundwater. Lastly, we show that the

combination of physical and chemical heterogeneity can reduce the protective effects of sorption. Where sorptive properties of aquifer components with different hydraulic properties are different, as has been observed [25–27], incorporating this correlation in models rather than using bulk or upscaled representations of both physical and chemical properties can be critical for predicting contaminant migration rates.

5. Conclusions

We considered effects of heterogeneity in aquifer hydraulic properties, pumping rates, and sediment sorption characteristics on basin-scale contaminant transport. We used the Bengal Basin as an example case where widespread arsenic contamination in shallow aquifers threatens deeper parts of the aquifer that are low in arsenic. The analysis shows that vulnerability is greater when heterogeneity is considered explicitly: the short end of the travel time distributions is extended in heterogeneous simulations compared to equivalent homogeneous models. The effect is greater in areas where flowpaths are primarily lateral (less vulnerable) than in areas where they are primarily downward (more vulnerable), as preferential conduits may result in devious vertical flowpaths. While concentrating pumping into small areas increases vulnerability somewhat, the deep pumping rate is the most important factor affecting vulnerability of deep, low-As groundwater. Spatial heterogeneity in sorptive properties also have a strong influence in large-scale contaminant migration. Simulations with negative correlation between sorption coefficient and hydraulic conductivity result in much greater contamination of deep groundwater than simulations with uniform sorptive properties or a positive correlation.

This work shows that although spatial heterogeneity may be very difficult to determine on a large scale, it can have an important influence on basin-scale transport. Although heterogeneous and equivalent homogeneous simulations produce similar management insights, the spatial distributions of properties and their correlation can increase rates and alter directions of solute transport relative to equivalent homogeneous systems. Thus, in highly heterogeneous aquifer systems, contamination in localized areas may be anticipated in the presence of pumping, even in areas where low vulnerability is expected based on bulk estimates of hydraulic gradients and hydrogeological and geochemical properties. These insights illustrate the need for extensive monitoring networks for protection of human health in the Bengal Basin and other heterogeneous aquifers threatened by contamination.

Acknowledgements

The authors thank Mohammad Koneshloo for assistance with geostatistical calculations and Richard Winston for technical assistance with modeling. This work was funded in part by the National Science Foundation (EAR-1151733) and by a Delaware Environmental Institute Fellowship to MRK.

References

- [1] Gelhar LW, Axness CL. Three-dimensional stochastic analysis of macrodispersion in aquifers. *Water Resour Res* 1983;19:161–80. doi:10.1029/WR019i001p00161.
- [2] Dagan G. Solute transport in heterogeneous porous formations. *J Fluid Mech* 1984;145:151–77. doi:10.1017/S0022112084002858.
- [3] Bellin A, Salandin P, Rinaldo A. Simulation of dispersion in heterogeneous porous formations: Statistics, first-order theories, convergence of computations. *Water Resour Res* 1992;28:2211–27. doi:10.1029/92WR00578.
- [4] Fiori A, Jankovic I. On Preferential Flow, Channeling and Connectivity in Heterogeneous Porous Formations. *Math Geosci* 2012;44:133–45. doi:10.1007/s11004-011-9365-2.
- [5] Fogg G. Groundwater Flow and Sand Body Interconnectedness in a Thick, Multiple- Aquifer System. *Water Resour Res* 1986;22:679–94.
- [6] Scheibe T, Yabusaki S. Scaling of flow and transport behavior in heterogeneous groundwater systems. *Adv Water Resour* 1998;22:223–38. doi:10.1016/S0309-1708(98)00014-1.
- [7] Khan MR, Koneshloo M, Knappett PSK, Ahmed KM, Bostick BC, Mailloux BJ, et al. Mega-city pumping and preferential flow threaten groundwater quality: insights from Dhaka, Bangladesh. *Nat Commun* 2016;in press.
- [8] Garabedian SP, LeBlanc DR, Gelhar LW, Celia MA. Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts: 2. Analysis of spatial moments for a nonreactive tracer. *Water Resour Res* 1991;27:911–24. doi:10.1029/91WR00242.
- [9] Rajaram H, Gelhar LW. Plume-scale dependent dispersion in aquifers with a wide range of scales of heterogeneity. *Water Resour Res* 1995;31:2469–82. doi:10.1029/95WR01723.
- [10] Sudicky EA. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer: Spatial Variability of Hydraulic Conductivity and Its Role in the Dispersion Process. *Water Resour Res* 1986;22:2069–82.
- [11] Bianchi M, Zheng C, Tick GR, Gorelick SM. Investigation of small-scale preferential flow with a forced-gradient tracer test. *Ground Water* 2011;49:503–14. doi:10.1111/j.1745-6584.2010.00746.x.
- [12] Harvey C, Gorelick S. Rate- limited mass transfer or macrodispersion: Which dominates plume evolution at the macrodispersion experiment (MADE) site? *Water Resour Res* 2000;36:637–50.
- [13] Ronayne MJ, Gorelick SM, Zheng C. Geological modeling of submeter scale heterogeneity and its influence on tracer transport in a fluvial aquifer. *Water Resour Res* 2010;46:1–9. doi:10.1029/2010WR009348.
- [14] Berkowitz B, Scher H, Silliman SE. Anomalous transport in laboratory-scale, heterogeneous porous media. *Water Resour Res* 2000;36:149–58.
- [15] Zinn B, Meigs LC, Harvey CF, Haggerty R, Peplinski WJ, Von Schwerin CF. Experimental

- visualization of solute transport and mass transfer processes in two-dimensional conductivity fields with connected regions of high conductivity. *Environ Sci Technol* 2004;38:3916–26. doi:10.1021/es034958g.
- [16] Heidari P, Li L. Solute transport in low-heterogeneity sandboxes: The role of correlation length and permeability variance. *Water Resour Res* 2014;50:8240–64. doi:10.1002/2013WR014654.
 - [17] Attinger S, Dimitrova J, Kinzelbach W. Homogenization of the transport behavior of nonlinearly adsorbing pollutants in physically and chemically heterogeneous aquifers. *Adv Water Resour* 2009;32:767–77. doi:10.1016/j.advwatres.2009.01.011.
 - [18] Abulaban A, Nieber JL. Modeling the effects of nonlinear equilibrium sorption on the transport of solute plumes in saturated heterogeneous porous media. *Adv Water Resour* 2000;23:893–905. doi:10.1016/S0309-1708(00)00010-5.
 - [19] Huang W, Peng P, Yu Z, Fu J. Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. *Appl Geochemistry* 2003;18:955–72. doi:10.1016/S0883-2927(02)00205-6.
 - [20] Vereecken H, Döring U, Hardelauf H, Jaekel U, Hashagen U, Neuendorf O, et al. Analysis of solute transport in a heterogeneous aquifer: The Krauthausen field experiment. *J Contam Hydrol* 2000;45:329–58. doi:10.1016/S0169-7722(00)00107-8.
 - [21] Fuller CC, Davis JA, Coston JA, Dixon E. Characterization of metal adsorption variability in a sand and gravel aquifer, Cape Cod, Massachusetts, U.S.A. *J Contam Hydrol* 1996;22:165–87. doi:10.1016/0169-7722(95)00090-9.
 - [22] Coston JA, Fuller CC, Davis JA. Pb²⁺ and Zn²⁺ adsorption by a natural aluminum- and iron-bearing surface coating on an aquifer sand. *Geochim Cosmochim Acta* 1995;59:3535–47.
 - [23] Sakata M. Relationship between Adsorption of Aresenic (III) and Boron by Soil and Soil Properties. *Environ Sci Technol* 1987;21:1126–30.
 - [24] Singh AK, Hasnain SI, Banerjee DK. Grain size and geochemical partitioning of heavy metals in sediments of the Damodar River - a tributary of the lower Ganga, India. *Environ Geol* 1999;39:90–8. doi:10.1007/s002540050439.
 - [25] Allen-King RM, Halket RM, Gaylord DR, Robin MJL. Characterizing the heterogeneity and correlation of perchloroethene sorption and hydraulic conductivity using a facies-based approach. *Water Resour Res* 1998;34:385–96. doi:10.1029/97WR03496.
 - [26] Allen-King RM, Divine DP, Robin MJL, Alldredge JR, Gaylord DR. Spatial distributions of perchloroethylene reactive transport parameters in the Borden Aquifer. *Water Resour Res* 2006;42:1–13. doi:10.1029/2005WR003977.
 - [27] Robin MJL, Sudicky EA, Gillham RW, Kachanoski RG. Spatial Variability of Strontium Distribution Coefficients and Their Correlation with Hydraulic Conductivity in the Canadian Forces Base Borden Aquifer. *Water Resour Res* 1991;27:2619–32. doi:10.1029/91WR01107.
 - [28] Barber LB, Thurman EM, Runnells DD. Geochemical heterogeneity in a sand and gravel aquifer: Effect of sediment mineralogy and particle size on the sorption of chlorobenzenes. *J Contam Hydrol* 1992;9:35–54. doi:10.1016/0169-7722(92)90049-K.
 - [29] Dentz M, Le Borgne T, Englert A, Bijeljic B. Mixing, spreading and reaction in heterogeneous media: A brief review. *J Contam Hydrol* 2011;120-121:1–17. doi:10.1016/j.jconhyd.2010.05.002.
 - [30] Valocchi AJ. Spatial moment analysis of the transport of kinetically adsorbing solutes through stratified aquifers. *Water Resour Res* 1989;25:273–9. doi:10.1029/WR025i002p00273.
 - [31] Burr DT, Sudicky EA, Naff RL. Nonreactive and reactive solute transport in three-dimensional

- heterogeneous porous media: Mean displacement, plume spreading, and uncertainty. *Water Resour Res* 1994;30:791–815. doi:10.1029/93WR02946.
- [32] Brusseau ML, Hu Q, Srivastava R. Using flow interruption to identify factors causing nonideal contaminant transport. *J Contam Hydrol* 1997;24:205–19. doi:10.1016/S0169-7722(96)00009-5.
 - [33] Cvetkovic V, Dagan G, Cheng H. Contaminant transport in aquifers with spatially variable hydraulic and sorption properties. *Proc R Soc A Math Phys Eng Sci* 1998;454:2173–207. doi:10.1098/rspa.1998.0254.
 - [34] Bosma WJP, Bellin A, Van der Zee SEATM, Rinaldo A. Linear equilibrium adsorbing solute transport in physically and chemically heterogeneous porous formations: 2. Numerical results. *Water Resour Res* 1993;29:4031–43.
 - [35] Sassen DS, Hubbard SS, Bea SA, Chen J, Spycher N, Denham ME. Reactive facies: An approach for parameterizing field-scale reactive transport models using geophysical methods. *Water Resour Res* 2012;48:1–20. doi:10.1029/2011WR011047.
 - [36] Tompson AFB, Schafer AL, Smith RW. Impacts of physical and chemical heterogeneity on cocontaminant transport in a sandy porous medium. *Water Resour Res* 1996;32:801–18. doi:10.1029/95WR03733.
 - [37] Yang C, Samper J. Numerical evaluation of multicomponent cation exchange reactive transport in physically and geochemically heterogeneous porous media. *Comput Geosci* 2009;13:391–404. doi:10.1007/s10596-009-9127-0.
 - [38] Scheibe TD, Fang Y, Murray CJ, Roden EE, Chen J, Chien YJ, et al. Transport and biogeochemical reaction of metals in a physically and chemically heterogeneous aquifer. *Geosphere* 2006;2:220–35. doi:10.1130/GES00029.1.
 - [39] Rajaram H. Time and scale dependent effective retardation factors in heterogeneous aquifers. *Adv Water Resour* 1997;20:217–30. doi:10.1016/S0309-1708(96)00021-8.
 - [40] Berglund S, Cvetkovic V. Contaminant Displacement in Aquifers: Coupled Effects of Flow Heterogeneity and Nonlinear Sorption. *Water Resour Res* 1996;32:23–32. doi:10.1029/95WR02767.
 - [41] Nickson RT, McArthur J, Burgess W, Ahmed KM, Ravenscroft P, Rahman M. Arsenic poisoning of Bangladesh groundwater. *Nature* 1998;395:338.
 - [42] BGS and DPHE. Arsenic contamination of groundwater in Bangladesh Vol 2 : Final report. Keyworth: British Geological Survey; 2001.
 - [43] McArthur JM, Ravenscroft P, Safiulla S, Thirlwall MF. Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resour Res* 2001;37:109–17. doi:10.1029/2000WR900270.
 - [44] Flanagan S V, Johnston RB, Zheng Y. Arsenic in tube well water in Bangladesh: health and economic impacts and implications for arsenic mitigation. *Bull World Health Organ* 2012;90:839–46. doi:10.2471/BLT.11.101253.
 - [45] Johnston R, Hug SJ, Inauen J, Khan NI, Mosler H-J, Yang H. Enhancing arsenic mitigation in Bangladesh: Findings from institutional, psychological, and technical investigations. *Sci Total Environ* 2014;488-489:477–83. doi:10.1016/j.scitotenv.2013.11.143.
 - [46] Howard G, Ahmed MF, Shamsuddin AJ, Mahmud SG, Deere D. Risk assessment of arsenic mitigation options in Bangladesh. *J Health Popul Nutr* 2006;24:346–55.
 - [47] Ravenscroft P, Kabir A, Hakim SA, Ibrahim AKM, Ghosh SK, Rahman S, et al. Effectiveness of public rural waterpoints in Bangladesh with special reference to arsenic mitigation. *J Water, Sanit*

- Hyg Dev 2014;4:545–62. doi:<http://dx.doi.org/10.2166/washdev.2014.038>.
- [48] Michael HA, Voss CI. Evaluation of the sustainability of deep groundwater as an arsenic-safe resource in the Bengal Basin. *Proc Natl Acad Sci U S A* 2008;105:8531–6. doi:10.1073/pnas.0710477105.
 - [49] Radloff KA, Zheng Y, Michael HA, Stute M, Bostick BC, Mihajlov I, et al. Arsenic migration to deep groundwater in Bangladesh influenced by adsorption and water demand. *Nat Geosci* 2011;4:793–8. doi:10.1038/ngeo1283.
 - [50] Goodbred SL, Kuehl SA, Steckler MS, Sarker MH. Controls on facies distribution and stratigraphic preservation in the Ganges–Brahmaputra delta sequence. *Sediment Geol* 2003;155:301–16. doi:10.1016/S0037-0738(02)00184-7.
 - [51] Michael HA, Voss CI. Estimation of regional-scale groundwater flow properties in the Bengal Basin of India and Bangladesh. *Hydrogeol J* 2009;17:1329–46. doi:10.1007/s10040-009-0443-1.
 - [52] Hoque MA, Burgess WG. 14C dating of deep groundwater in the Bengal Aquifer System, Bangladesh: Implications for aquifer anisotropy, recharge sources and sustainability. *J Hydrol* 2012;444–445:209–20. doi:10.1016/j.jhydrol.2012.04.022.
 - [53] Zahid A, Hassan MQ, Ahmed KM. Simulation of flowpaths and travel time of groundwater through arsenic-contaminated zone in the multi-layered aquifer system of Bengal Basin. *Environ Earth Sci* 2014. doi:10.1007/s12665-014-3447-7.
 - [54] Bianchi M, Zheng C, Wilson C, Tick GR, Liu G, Gorelick SM. Spatial connectivity in a highly heterogeneous aquifer: From cores to preferential flow paths. *Water Resour Res* 2011;47:1–18. doi:10.1029/2009WR008966.
 - [55] Mukherjee A, Fryar AE, Scanlon BR, Bhattacharya P, Bhattacharya A. Elevated arsenic in deeper groundwater of the western Bengal basin, India: Extent and controls from regional to local scale. *Appl Geochemistry* 2011;26:600–13. doi:10.1016/j.apgeochem.2011.01.017.
 - [56] van Geen A, Cheng Z, Jia Q, Seddique AA, Rahman MW, Rahman MM, et al. Monitoring 51 community wells in Araihaazar, Bangladesh, for up to 5 years: implications for arsenic mitigation. *J Environ Sci Health A Tox Hazard Subst Environ Eng* 2007;42:1729–40. doi:10.1080/10934520701564236.
 - [57] Chakraborti D, Das B, Rahman MM, Chowdhury UK, Biswas B, Goswami AB, et al. Status of groundwater arsenic contamination in the state of West Bengal, India: A 20-year study report. *Mol Nutr Food Res* 2009;53:542–51. doi:10.1002/mnfr.200700517.
 - [58] Cheng Z, Van Geen A, Seddique AA, Ahmed KM. Limited temporal variability of arsenic concentrations in 20 wells monitored for 3 years in Araihaazar, Bangladesh. *Environ Sci Technol* 2005;39:4759–66. doi:10.1021/es048065f.
 - [59] Stollenwerk KG, Breit GN, Welch AH, Yount JC, Whitney JW, Foster AL, et al. Arsenic attenuation by oxidized aquifer sediments in Bangladesh. *Sci Total Environ* 2007;379:133–50. doi:10.1016/j.scitotenv.2006.11.029.
 - [60] Harvey CF, Swartz CH, Badruzzaman ABM, Keon-Blute N, Yu W, Ali MA, et al. Arsenic mobility and groundwater extraction in Bangladesh. *Science* 2002;298:1602–6. doi:10.1126/science.1076978.
 - [61] Nath B, Chakraborty S, Burnol A, Stüben D, Chatterjee D, Charlet L. Mobility of arsenic in the sub-surface environment: An integrated hydrogeochemical study and sorption model of the sandy aquifer materials. *J Hydrol* 2009;364:236–48. doi:10.1016/j.jhydrol.2008.10.025.
 - [62] Jung HB, Bostick BC, Zheng Y. Field, experimental, and modeling study of arsenic partitioning across a redox transition in a Bangladesh aquifer. *Environ Sci Technol* 2012;46:1388–95.

doi:10.1021/es2032967.

- [63] van Geen A, Bostick BC, Pham TKT, Vi ML, Nguyen-Ngoc M, Phu DM, et al. Retardation of arsenic transport through a Pleistocene aquifer. *Nature* 2013;501:204–7. doi:10.1038/nature12444.
- [64] Hoque MA, Burgess WG, Shamsudduha M, Ahmed KM. Delineating low-arsenic groundwater environments in the Bengal Aquifer System, Bangladesh. *Appl Geochemistry* 2011;26:614–23. doi:10.1016/j.apgeochem.2011.01.018.
- [65] Hoque MA, McArthur JM, Sikdar PK. Sources of low-arsenic groundwater in the Bengal Basin: investigating the influence of the last glacial maximum palaeosol using a 115-km traverse across Bangladesh. *Hydrogeol J* 2014. doi:10.1007/s10040-014-1139-8.
- [66] Pate RD, Goodbred SL, Khan SR. Delta Double-Stack: Juxtaposed Holocene and Pleistocene Sequences from the Bengal Basin, Bangladesh. *Sediment Rec* 2009;7:4–9.
- [67] Harbaugh A. MODFLOW-2005, the US Geological Survey modular ground-water model-the ground-water flow process. Reston, Virginia: US Geological Survey; 2005.
- [68] Michael HA, Voss CI. Controls on groundwater flow in the Bengal Basin of India and Bangladesh: regional modeling analysis. *Hydrogeol J* 2009;17:1561–77. doi:10.1007/s10040-008-0429-4.
- [69] Bangladesh Bureau of Statistics. Bangladesh Population and Housing Census 2011 Socio-Economic and Demographic Report National Series, Volume - 4. Dhaka: Bangladesh Bureau of Statistics, Statistics Division, Ministry of Planning, Govt. of the People's Republic of Bangladesh; 2011.
- [70] Government of India. Population Enumeration Data (Final Population). Popul Census India 2011 n.d. http://www.censusindia.gov.in/2011census/population_enumeration.html (accessed April 15, 2015).
- [71] Bangladesh Bureau of Statistics. Bangladesh Census of Agriculture 2008, National Series, Volume-1. Dhaka: Bangladesh Bureau of Statistics, Statistics Division, Ministry of Planning, Govt. of the People's Republic of Bangladesh; 2010.
- [72] FAO. Global Map of Irrigation Areas (GMIA). AQUASTAT website. Food and Agriculture Organization of the United Nations (FAO) 2015. <http://www.fao.org/nr/water/aquastat/irrigationmap/IND/index.stm> (accessed April 21, 2015).
- [73] Pollock D. User guide for MODPATH version 6: a particle tracking model for MODFLOW: Reston, Virginia: U.S. Geological Survey; 2012.
- [74] Mehl SW, Hill MC. MODFLOW-LGR - Documentation of ghost node local grid refinement (LGR2) for multiple areas and the boundary flow and head (BFH2) package. Reston, Virginia: 2013.
- [75] DPHE and JICA. Borelog Data Book. Dhaka: Department of Public Health Engineering, Local Government Division, Ministry of LGRD and Co-operatives, Government of the Peoples Republic of Bangladesh; 2010.
- [76] Journel A. Nonparametric estimation of spatial distributions. *J Int Assoc Math Geol* 1983;15:445–68.
- [77] Zheng C, Wang PP. MT3DMS: A Modular Three-Dimensional Multispecies Transport Model for simulation of advection, dispersion and chemical reactions of contaminants in groundwater systems. *Univ Alabama* 1999:239.
- [78] McArthur JM, Ravenscroft P, Banerjee DM, Milsom J, Hudson-Edwards KA, Sengupta S, et al. How paleosols influence groundwater flow and arsenic pollution: A model from the Bengal Basin

- and its worldwide implication. *Water Resour Res* 2008;44:n/a – n/a. doi:10.1029/2007WR006552.
- [79] Destouni G, Cvetkovic V. Field scale mass arrival of sorptive solute into the groundwater. *Water Resour Res* 1991;27:1315–25. doi:10.1029/91WR00182.
 - [80] Sahu P, Michael HA, Voss CI, Sikdar PK. Impacts on groundwater recharge areas of megacity pumping: analysis of potential contamination of Kolkata, India, water supply. *Hydrol Sci J* 2013;58:1340–60. doi:10.1080/02626667.2013.813946.
 - [81] Hoque MA, Hoque MM, Ahmed KM. Declining groundwater level and aquifer dewatering in Dhaka metropolitan area, Bangladesh: causes and quantification. *Hydrogeol J* 2007;15:1523–34. doi:10.1007/s10040-007-0226-5.
 - [82] Knappett PSK, Mailloux BJ, Choudhury I, Khan MR, Michael HA, Mondal DR, et al. Vulnerability of Low-Arsenic Aquifers to Municipal Pumping In Bangladesh. *J Hydrol* 2016;In Press. doi:10.1016/j.jhydrol.2016.05.035.

Figure 1. Location of the refined models. The More Vulnerable model area (purple box) is characterized by nearly vertical flowpaths, whereas the flowpaths are nearly horizontal and originate at the basin boundary in the Less Vulnerable model area (cyan box). Red dots represent locations of all 793 boreholes used in geostatistical simulations. The area where shallow As concentrations are widely elevated is shown by the red contour. Elevation data source: Consortium for Spatial Information (CGIAR-CSI) [36].

Figure 2. Simulated flowpaths for homogeneous models (a,b) and heterogeneous realization #20 (c,d) for the More Vulnerable (a,c) and Less Vulnerable (b,d) model areas. For better visualization only the part of the pathlines within the refined model areas are shown.

Figure 3. Particle tracking results for base case scenario. Particles were tracked from the depth of domestic pumping (150 m) backward to the point of recharge. Results are shown for 20 heterogeneous realizations and 1 equivalent homogeneous realization ("H" in panel a). a) Percentage of particles recharged in As-unsafe areas. b) Cumulative distribution functions of travel time. c) Box plots show the median (red line), 1st and 3rd quartile (blue box), range (whiskers), and outliers (red +) for the minimum, maximum, mean, and quartiles of travel time for heterogeneous simulations. Black dot is corresponding value for homogeneous simulation. Results for More Vulnerable area in left panels, Less Vulnerable area in right panels.

Figure 4. Particle tracking results for all pumping scenarios. Particles were tracked for 1000 y from the depth of domestic pumping (150 m) backward to the point of recharge. Results are shown for 20 heterogeneous realizations and the homogeneous model. Box plots show the median (red line), 1st and 3rd quartile (blue box), range (whiskers), and outliers (red +) for a) percentage of particles that originated in the high-As zone, and b) mean travel time of fastest 10% of particles. Black dot is corresponding value for homogeneous simulation. Results for More Vulnerable area in left panels, Less Vulnerable area in right panels.

Figure 5. Solute transport simulation results. Concentration distribution at depth of domestic pumping (150m) after 1000y for homogeneous field with a.) no sorption, b.) uniform $K_d=1.01/\text{kg}$, and example heterogeneous realization with c.) no sorption, d.) uniform sorption e.) sand-only sorption, and f.) silt- and clay-only sorption. K_d values are given in Supplementary Table S6. Percentage of area with greater than 10% maximum concentration shown above each panel.

Figure 6. Results of solute transport simulations after 1000y for homogeneous model and 20 heterogeneous realizations and different sorption scenarios. Values are percent area contaminated at a) 100m depth and b) 150m depth. Box plots show the median (red line), 1st and 3rd quartile (blue box), range (whiskers), and outliers (red +). Black dot is corresponding value for homogeneous simulation.

Figure 7. Depth distribution of the percent of area contaminated after 1000y for the 20 heterogeneous realizations and 4 sorption scenarios. The homogeneous realizations with and without sorption are shown with dashed lines.

Table 1. Mean and range of K values assigned to the lithofacies categories in the heterogeneous simulations.

	Silt & clay		Fine Sand		Medium & Coarse sand	
	Kh [m/s]	Kv [m/s]	Kh [m/s]	Kv [m/s]	Kh [m/s]	Kv [m/s]
Average	9.06×10^{-8}	9.06×10^{-9}	3.17×10^{-5}	9.06×10^{-7}	3.17×10^{-3}	3.17×10^{-4}
Minimum	3.02×10^{-8}	3.02×10^{-9}	1.47×10^{-5}	3.02×10^{-7}	1.47×10^{-3}	1.47×10^{-4}
Maximum	0.17×10^{-8}	0.17×10^{-9}	7.09×10^{-5}	0.17×10^{-7}	7.09×10^{-3}	7.09×10^{-4}

Table 2. Pumping scenarios simulated. Base pumping rates and pumping distributions are as described in methods. The shallow pumping zone is 15-50 m depth and deep pumping is 150-175m depth.

Scenario #	Shallow Pumping Rate	Deep Pumping Rate	Distribution
1	Base irrigation	Base domestic	All distributed
2	Base irrigation	Base domestic	Shallow distributed, Deep concentrated
3	Base irrigation	Double domestic	Shallow distributed, Deep concentrated
4	Half irrigation	Base domestic + half irrigation	All distributed
5	Half irrigation	Base domestic + half irrigation	Irrigation distributed, Domestic concentrated
6	None	Base domestic + base irrigation	All distributed
7	None	Base domestic	All distributed

Table 3. Summary statistics of particle tracking results. Particles were tracked backward from all cells in the deep pumping zone to 50 m depth. Numbers in parentheses represent results for particles tracked only from cells where deep pumping occurs in Scenarios #2, #3, and #5 and the same cells in Scenario #1 for comparison.

		Scenario #1 Base case		Scenario #2		Scenario #3		Scenario #4		Scenario #5		Scenario #6		Scenario #7	
		Heterogeneous Average	Homogeneous	Heterogeneous Average	Homogeneous	Heterogeneous Average	Homogeneous	Heterogeneous Average	Homogeneous	Heterogeneous Average	Homogeneous	Heterogeneous Average	Homogeneous	Heterogeneous Average	Homogeneous
MORE VULNERABLE AREA															
Particle Travel Time [y]	Minimum	98 (158)	478 (481)	96 (139)	442 (442)	70 (92)	345 (345)	19	133	19 (32)	133 (134)	10	73	120	620
	Maximum	23730 (14886)	4389 (3591)	38664 (12380)	5533 (3532)	24110 (7308)	5672 (2807)	1041	366	1041 (732)	366 (357)	483	176	17416	12411
	Mean	1353 (1381)	928 (949)	1411 (1203)	927 (863)	1081 (827)	720 (664)	208	169	208 (209)	169 (170)	114	93	1460	1200
	1 st Q	514 (529)	589 (606)	517 (454)	594 (557)	403 (341)	468 (428)	117	151	117 (117)	151 (150)	65	83	684	743
	2 nd Q	833 (856)	748 (759)	838 (754)	752 (697)	648 (556)	592 (537)	184	164	184 (183)	164 (164)	102	91	1085	964
	3 rd Q	1338 (1382)	1085 (1104)	1342 (1191)	1087 (1001)	1047 (902)	832 (757)	271	177	271 (270)	177 (178)	150	98	1707	1303
Particle Origin [% of total]	High-As zone	99	100	99	100	99	100	100	100	100	100	100	100	98	99
	Refined model area	89	88	89	89	86	86	94	97	94	97	94	98	88	88
LESS VULNERABLE AREA															
Particle Travel Time [y]	Minimum	171 (263)	319 (338)	173 (217)	318 (324)	103 (136)	312 (315)	16	106	16 (24)	102 (102)	8	60	190	389
	Maximum	35499 (7423)	4596 (4596)	20792 (5468)	4996 (3663)	12333 (5206)	4331 (3371)	1655	432	1831 (1177)	417 (412)	735	279	26414	3391
	Mean	1320 (1310)	1509 (1498)	1357 (1215)	1550 (1446)	1030 (915)	1173 (1027)	188	160	180 (179)	154 (153)	93	79	1409	1350
	1 st Q	606 (590)	759 (712)	617 (549)	777 (664)	488 (414)	671 (553)	107	129	102 (100)	125 (121)	52	63	676	774
	2 nd Q	989 (970)	1407 (1314)	1029 (893)	1451 (1282)	785 (661)	1054 (874)	167	143	159 (157)	135 (133)	82	68	1062	1269
	3 rd Q	1679 (1660)	2173 (2076)	1761 (1551)	2224 (2019)	1279 (1114)	1510 (1369)	237	178	229 (220)	169 (168)	121	79	1703	1814
Particle Origin [% of total]	High-As zone	20	9	20	10	35	20	77	75	79	77	86	85	18	10
	Refined model area	17	0	16	0	30	12	71	72	72	73	79	82	16	8

Table 4. Summary of solute transport simulation results

		No sorption	Uniform sorption	Sand-only sorption	Clay & silt-only sorption
AREA CONTAMINATED ($C/C_o > 0.1$) AT 100 m DEPTH [%]					
Heterogeneous Average	Minimum	84.0	2.0	1.0	11.0
	Maximum	99.0	19.0	28.0	72.0
	Mean	91.6	7.3	6.6	45.2
	Median	92.0	6.5	5.5	43.5
	Homogeneous	100.0	0.0	-	-
AREA CONTAMINATED ($C/C_o > 0.1$) AT 150 m DEPTH [%]					
Heterogeneous Average	Minimum	64.0	0.0	0.0	5.0
	Maximum	94.0	2.0	1.0	54.0
	Mean	79.7	0.8	0.1	29.5
	Median	80.5	1.0	0.0	29.5
	Homogeneous	100.0	0.0	-	-
CONTAMINATED ($C/C_o > 0.1$) AQUIFER VOLUME [%]					
Heterogeneous Average	Minimum	44.0	9.0	8.0	13.0
	Maximum	48.0	11.0	15.0	32.0
	Mean	46.0	9.9	10.3	21.9
	Median	46.0	10.0	10.0	21.5
	Homogeneous	51.0	14.0	-	-