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Reliability of a Commercial Kit To Test Groundwater for Arsenic in Bangladesh

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A comparison of field and laboratory measurements of arsenic in groundwater of Araihazar, Bangladesh, indicates that the most widely used field kit correctly determined the status of 88% of 799 wells relative to the local standard of 50 μg/L As. Additional tests show that the inconsistencies, mainly underestimates in the 50−100 μg/L As range, can be avoided by increasing the reaction time from 20 to 40 min. Despite this limitation, the field data already compiled for millions of wells by the Bangladesh Arsenic Mitigation and Water Supply Project, in combination with information on well location and depth, should prove to be extremely useful to prioritize interventions in thousands of affected villages.

Introduction

A compilation of recent estimates suggests that over 100 million villagers of Bangladesh, West Bengal (India), Vietnam, China, and several other South Asian countries drink and cook with groundwater drawn from shallow wells containing over 10 μg/L As, the World Health Organization guideline value for arsenic in drinking water (*1*−*4*). In addition, one-third of the wells in Bangladesh producing water with less than 10 μg/L As do not meet the WHO guideline for Mn in drinking water of 500 μg/L (*3*). Technically plausible approaches to mitigate the situation have not been tested on anything beyond the pilot scale (*5*). A viable strategy to provide safe water throughout rural Bangladesh and other affected countries has yet to be articulated, let alone implemented. Even the value of past testing campaigns to identify safe and unsafe wells with field kits, the logical first phase of any mitigation effort, has been questioned by an influential group because of purported discrepancies between field kit results and laboratory measurements (*6*).

This report strikes a more optimistic note on the basis of the experiences of an interdisciplinary team of health, social, and earth scientists working since early 2000 in a 25 km^2 study area that encompasses ∼6600 tube wells and a population of 70 000 in Araihazar Upazila, Bangladesh (*7*−*8*). We focus here on the performance of a field kit for As that has been used to test millions of wells in Bangladesh since its introduction by the Hach Company (Loveland, CO) in 2001. NGO workers contracted by the Bangladesh Arsenic Mitigation and Water Supply Project (BAMWSP) used the Hach kit to test all tube wells in our 25 km^2 study area in 2003. Groundwater from many of the same wells had been sampled in 2000−2001 and analyzed in our laboratories by graphite-furnace atomic absorption (GFAA; *8*). During our sampling of 993 wells in Araihazar in 2003, 349 of which had already been sampled in 2000−2001, the outcome of the earlier BAMWSP tests was compiled by recording the color of the paint on the spout of each well, green or red, corresponding to estimates of As concentration <50 or ≥50 μg/L As, respectively. This resampling effort was motivated by reports of discrepancies between the field tests and laboratory results in our study area, as well as concerns about potential changes in groundwater As concentrations over time.

Methods

Sample Collection for Laboratory Analysis. Groundwater was collected and analyzed in the laboratory from 4999 wells in March−June 2000, an additional 972 wells in November−December 2001, and 993 wells in April 2003, of which 349 had already been sampled in 2000 or 2001. To re-identify individual wells, geographic coordinates were determined with handheld global positioning system (GPS) receivers and numbered stainless steel plates were attached to the base of each well pump on the first sampling occasion.

All well-water samples were collected without filtration in acid-cleaned bottles after pumping for ∼5 min and acidified in the field to 1% HCl (Seastar, Fisher Scientific). The addition reduced the pH to the point where Fe oxyhydroxides do not precipitate because the amount of acid in the sample (0.12 N) exceeds by a factor of 6 the highest alkalinities reported for Bangladesh groundwater (*3*). Steps taken to determine the reliability of the sampling procedure and analyses by GFAAS for the 2000−2001 samples have been described elsewhere (*8*). A similar quality control procedure was followed in 2003 with a subset of 71 wells where a replicate sample was collected and a third sample bottle was spiked in the field for recovery tests with a known amount of As. Well water was analyzed for As and 30 other constituents by high-resolution inductively coupled plasma mass spectrometry (HR ICP-MS) following 1:10 dilution (*9*). The analytical detection limit of this method for As is 0.1 μg/L. The minimum concentration of dissolved As that is reliably determined by the entire procedure is estimated to be 1 μg/L, taking into account small quantities of As released upon acidification by fine aquifer particles that are occasionally collected with a sample. In addition to all 993 samples collected in 2003, groundwater collected in 2000−2001 from the subset of 349 wells sampled twice was analyzed by HR ICP-MS.

Field Kit Measurements. BAMWSP-trained NGO workers used the two-step Hach EZ arsenic kit (product 2822800) to analyze groundwater from all wells in the upazila in 2002−2003. The method is one of several existing variants of the 1879 Gutzeit method (*10*) and involves the addition of prepackaged sulfamic acid and zinc powder to ∼50 mL of groundwater. The generated arsine gas (AsH_3) is entrained with H_2 bubbles emanating from the acidified sample and trapped by a strip of paper impregnated with mercuric bromide. The option to trap sulfide with a lead acetate-impregnated cotton ball was taken out of the kit because sulfide levels are generally too low in Bangladesh groundwater

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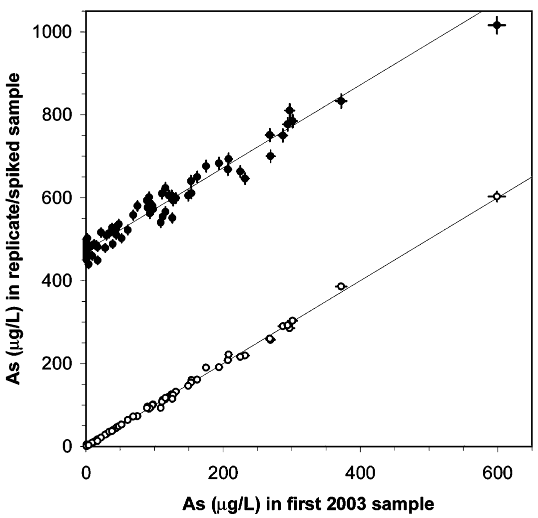

FIGURE 1. Comparison of As concentrations measured by HR ICP-MS for 71 sets of quality control samples. Open circles compare replicate samples relative to a line with a slope of 1 passing through the origin. Black circles compare the composition of unspiked and spiked water to a line with a slope of one and an intercept of 472 µg/L. Also shown are error bars corresponding to one standard deviation of the measurement uncertainty.

to cause significant interference. BAMWSP evidently judged, in our opinion correctly, that the very hypothetical sulfide interference was not worth the added complication and the risk of jeopardizing the results by wetting the test strip. After the 20-min reaction time stipulated by the manufacturer, the color of the orange-brown circle on the strip is compared visually to a reference scale showing readings corresponding to As concentrations of 0, 10, 25, 50, 100, 250, and 500 µg/L. For 799 out of 993 wells sampled in April 2003, the color of the paint applied on the spout of each well could be determined directly or by asking well owners for their card with the test result. Few if any traces of the paint adhered to the rusty spouts by October 2003 however.

Our own testing with the Hach kit had suggested that the field measurement might be sensitive to how long the sample is allowed to react. For this reason, a subset of wells was retested with the kit by following the recommended procedure and by doubling the reaction time to 40 min. A first set of 43 wells was selected randomly in April and June 2003; another 65 wells were retested in the field September 2003 specifically because of observed discrepancies between the laboratory and BAMWSP results. The total of 108 wells that were retested by our team may therefore be biased toward the type of groundwater that is difficult to analyze with the Hach kit.

Results

Quality Control of Laboratory Measurements. For groundwater analyzed by HR ICP-MS containing <1−600 µg/L As, differences in concentration for 71 sets of replicates averaged 0 ± 5 µg/L As (Figure 1). The difference in As concentration between the average of the two replicates and the corresponding spiked sample averaged 472 ± 22 µg/L, which corresponds to a recovery of 96 ± 4% relative to the expected value of 492 µg/L. Following the model derived in the Appendix of ref 8, the standard error of individual measurements by HR ICP-MS is estimated from the expression: $\sigma_{\mathrm{sing}} = \sqrt{(\theta^2\sigma_{\mathrm{cal}}{}^2 + \sigma_{\mathrm{meas}}{}^2)}$, where the As concentration is θ, the single measurement error $\sigma_{\mathrm{meas}} = (5\ \mu\mathrm{g/L})/\sqrt{2} = 4\ \mu\mathrm{g/L}$ is based on the reproducibility of replicates, and σ_{cal} is the relative calibration error of 0.02 derived from the reproducibility of the recovery tests corrected for variability in the dilution of the spike. The standard error for all HR ICP-MS measurements presented in this study was calculated according to this expression. An absolute uncertainty of 4 µg/L obtained from replicate analyses dominates below a concentration of 150 µg/L As. Above this concentration, a relative error of ∼2% because of calibration errors or minor matrix effects becomes the larger source of uncertainty.

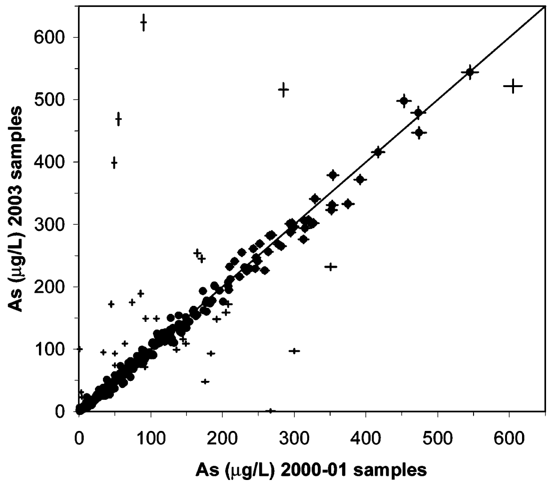

FIGURE 2. Comparison of laboratory results for samples collected from 349 wells in 2000−2001 and 2003. Pairs of samples showing consistent results, as defined in the text, are indicated by solid circles accompanied by error bars corresponding to one standard deviation of the measurement uncertainty. Thirty-one pairs of outliers are indicated by error bars only.

Comparison of As Concentrations in 2000−2001 and 2003. Relative to the Bangladesh standard of 50 µg/L for As in drinking water, the status of 331 (95%) out of 349 wells was unaffected by the outcome of the second sampling and analysis. Arsenic concentrations measured by HR ICP-MS were consistent for 318 (91%) of the 349 pairs of samples (Figure 2). Overlap of error bars corresponding to 3 times the standard error for individual HR ICP-MS measurements is the criterion that was used to determine consistency. The probability that As concentrations measured in the other 31 pairs of samples that do not meet this criterion are actually indistinguishable is therefore extremely low. The differences cannot be attributed to changes in As concentrations over time in the 2000−2001 sample bottles since previous determinations by GFAA are consistent with re-analysis by HR ICP-MS for all 31 pairs of samples, taking into account the larger uncertainty of the original GFAA measurements (*8*).

The agreement of laboratory measurements for the vast majority of the 349 wells sampled in 2000−2001 and 2003 is noteworthy for several reasons. The results demonstrate that the procedure followed to label the wells, relocate them, and sample and analyze the water was not flawed in any major way. The identification of specific wells would have been ambiguous if they had not been tagged, especially in those cases where relatives from the same cluster own more than one well. We have no explanation for the limited number of discrepancies that were observed and are in the process of retesting the wells and informing the owners of the results. No systematic temporal trend can be inferred from the data. The number of outlier pairs indicating higher concentrations in 2003 ($n = 18$) is only slightly higher than the number of pairs with higher concentrations in 2001 ($n = 13$). When the 31 outliers are excluded, the differences in As concentrations determined by HR ICP-MS averages 2 ± 9 µg/L ($n = 318$) for samples collected in 2000−2001 and 2003. The limited amount of well-documented monitoring data available for Bangladesh aquifers suggest limited, if any, seasonal varia-

TABLE 1. Comparison of Laboratory and Field Kit Results for 799 Wells Tested by BAMWSP and a Partially Overlapping Set of 108 Wells that Were Retested by Our Team[a]

As concn (HR ICP-MS)	<10 μg/L	10−50 μg/L	50−100 μg/L	>100 μg/L	entire range
no. of sampled wells with BAMWSP paint	236	187	139	237	799
no. of wells with incorrect result (%)					
BAMWSP paint	3 (1)	15 (8)	61 (44)	20 (8)	99 (12)
no. of wells retested in the field	28	18	43	19	108
no. of wells with incorrect result (%)					
BAMWSP paint	4 (14)	10 (56)	43 (100)	14 (74)	71 (66)
Hach 20 min	0 (0)	0 (0)	34 (79)	3 (16)	37 (34)
Hach 40 min	2 (7)	4 (22)	1 (2)	0 (0)	7 (6)

[a] The laboratory data are taken as the reference to evaluate the field data.

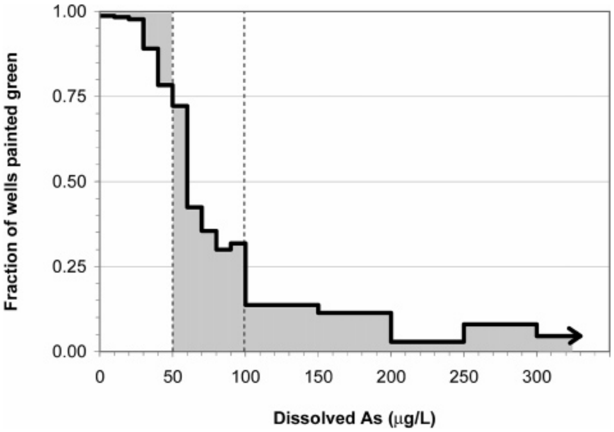

FIGURE 3. Comparison of BAMWSP field tests with laboratory measurements for 799 randomly selected wells sampled in 2003. Each As concentration interval of 10 μg/L below 100 μg/L and of 50 μg/L from 100 to 300 μg/L is represented by at least 20 wells. The 300−1000 μg/L As concentration interval contains 44 wells. The shading emphasizes the area where the proportion of green wells does not agree with the laboratory data.

tions in groundwater As concentrations (*3*). One significant implication of the outcome of the resampling effort is that As measurements made in the field with a kit should in the vast majority of cases agree with the laboratory results, even if a particular well was tested in a different year or a different season.

Comparison of Laboratory and Field Data. In this analysis, we use HR ICP-MS data as the reference for evaluating the reliability of field tests with the Hach kit on the basis of which wells were painted red or green by BAMWSP workers (Table 1). Comparison of the results by the two methods shows that the spouts of 99 (12%) out of a total of 799 randomly selected wells were painted with the incorrect color. The largest proportion of errors (44%) is observed in the 50−100 μg/L range of As concentrations ($n = 139$). A different compilation of the results provides a better way of evaluating the actual threshold, if any, corresponding to the change in paint color applied by the BAWMSP workers (Figure 3). When the set of 799 BAMWSP results is subdivided into concentration intervals of 10 μg/L, the proportion of wells painted green gradually declines from ∼95% at 30 μg/L As to ∼15% at 100 μg/L As, rather than the sharp drop at 50 μg/L that was expected (Figure 3). These results should be robust since each of the concentration intervals is represented by at least 20 wells. Whereas the largest drop in the proportion of wells painted green is in the 50−60 μg/L range, the proportion of incorrectly classified wells is up to 15% even for As concentrations >100 μg/L (Figure 3).

The proportion of wells incorrectly classified by BAMWSP was particularly high (66%) for the subset of 108 wells selected by our team for retesting in the field (Table 1). To some extent, this reflects the selection of over half the wells on the basis of discrepancies relative to laboratory results. This is probably not the only explanation, however, since field tests by our team using a 20-min reaction time reduced the proportion of incorrect results for the same set of wells to 34%. More significantly, the proportion of incorrect results was reduced to 6% for the same set of wells by increasing the reaction time from 20 to 40 min (Table 1). The effect of increasing the reaction time was particularly dramatic in the 50−100 μg/L range of As concentrations, where the proportion of incorrect results was reduced from 79% to 2% ($n = 43$). The longer reaction time, however, also increased from 0 to 12% ($n = 49$) the proportion of wells containing <50 μg/L As that were incorrectly classified as unsafe relative to the Bangladesh standard. Analysis of an additional 30 inorganic constituents that included Na, Mg, Al, Si, P, S, K, Ca, Mn, Fe, Zn, and Sr (listing only those present at concentrations >10 μg/L) did not reveal any systematic relationship between groundwater composition and whether laboratory and field data agreed or not (Supporting Information).

Discussion and Recommendations

Reliability of the Field Kit. The Hach kit, as deployed by BAMWSP workers in Araihazar in 2003, correctly classified 88% of wells relative to the Bangladesh standard for As in drinking water of 50 μg/L. Retesting of a subset of wells in the field by our team indicated that increasing the reaction time to 40 min is a modification of the procedure that could greatly increase measurement accuracy, which could be of particular benefit for the wells with concentrations between 50 and 100 μg/L As. Many of these wells had been incorrectly labeled as containing less than 50 μg/L As. The longer reaction time is desirable even if it is likely to discourage drinking or cooking with water containing 10−50 μg/L As since those wells do not meet the stricter WHO guideline for As in drinking water. Clearly, the Hach kit should continue to be used to test wells throughout Bangladesh and other countries affected by elevated As in groundwater.

Comparison of the BAMWSP results with our team's Hach kit data also suggests that BAMWSP workers may not always have allowed the reaction to proceed for the prescribed 20 min in our study area (Table 1). This was confirmed by anecdotal reports of field workers feeling pressed for time because of the need to complete a certain number of tests within the day. Incentives may therefore be needed to reward good quality measurements in the field.

The outcome of this comparison of laboratory and field measurements is considerably more optimistic than that of similar studies conducted in Bangladesh (*5*) and West Bengal, India (*6*). One possible reason is that the three kits in ref 6 used a smaller sample volume (5−15 mL) than the Hach kit (50 mL). Our results clearly indicate that sending every tube well sample to a central laboratory for testing should not be a high priority, as was also pointed out in ref 11. The probably unintended consequence of such a recommendation issued in West Bengal has been that, because of the complex logistics involved in shipping samples and returning the results to the well owners, current government policy is to test only community wells while the vast majority of existing wells, which are private, remain untested.

Implications for Arsenic Mitigation. Considerable variations in the proportion of unsafe wells between neighboring villages have been pointed out by previous studies (*3*, *8*). The prioritization of interventions should therefore be based on information disaggregated at the village level and not at the level of the upazila which typically covers several hundred villages (*12*). The comparison of BAMWSP data with our laboratory results indicates that field tests compiled for millions of wells provide a sound basis for ranking the severity of the situation faced by individual villages throughout the country (http://www.bamwsp.org/search.htm).

Effective mitigation of the groundwater As crisis is urgently needed in Bangladesh and several other affected countries. Aside from its known association with various cancers and cardiovascular disease (*13*−*15*), new evidence shows that exposure to even low levels of As impairs the cognitive development of children (*16*). As a short-term measure, the sharing of existing wells could be promoted in villages where BAMWSP data indicate a significant proportion of existing safe wells (*7*, *17*). The installation of safe community wells appears to be the most viable option for many villages in the medium term (*18*). In Araihazar, we have sponsored the installation of nearly 50 community wells that tap deeper aquifers that are low in As. The community wells in Araihazar have become very popular and are each used, on average, by ∼100 households living within a distance of 150 m (*18*). Nearly all these wells draw their water from sandy deposits with a characteristic orange-brown color. Periodic monitoring shows that most of the community wells consistently meet the WHO guideline of 10 μg/L for As as well as the 500 μg/L guideline for Mn in drinking water (unpublished data, A.v.G.). The minimum drilling depth that was required to reach these aquifers varied from 50 to 200 m within the study area, however. This is a reflection of the variability of the local geology and supports the notion that the village is the appropriate scale to consider for mitigation (*8*, *18*).

The sustained impact of both forms of interventions in our study area, the promotion of sharing of safe wells and the installation of community wells, has been confirmed by a dramatic drop of urinary As levels, a reliable indicator of exposure (unpublished data, J.H.G.). To our knowledge, the impact of a mitigation effort of this scale has not been documented for other approaches based on surface water treatment, As removal from groundwater, or rainwater collection. There are concerns about the long-term viability of deep wells, but these may have been exaggerated (*3*, *8*, *19*). In our study area, the groundwater withdrawal for personal use with hand-pumps is comparable to the recharge rate of the deeper aquifers tapped by the community wells (*20*). The much larger withdrawals by mechanized pumps for irrigation should be banned from using the deeper aquifers, however.

This study has shown that existing BAMWSP data based on field kits could in short order be used to prioritize and target the installation of community wells in thousands of affected villages. In parallel, it appears that a network of reliable testing services would have a major impact at the village level. In contrast to a national blanket testing campaign where many wells need to be tested in a day, the consequences of increasing the reaction time from 20 to 40 min to improve accuracy of routine testing at the local scale should be minimal. The installation of a community well to a safe depth is likely to result in the installation of private wells to the same depth. Because of the considerable geographic and depth variability of groundwater As concentrations, these wells will also need to be tested. If such a network can be created with help from the international community, then the parallel deployment of field kits for Mn should also be considered.

Acknowledgments

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Supporting Information Available

Additional well data (Excel). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Dhar, R. K.; Biswas, B. K.; Samanta, G.; Mandal, B. K.; Chakraborti, D.; Roy, S.; Jafar, A.; Islam, A.; Ara, G.; Kabir, S.; Khan, A. W.; Ahmed, S. A.; Hadi, S. A. Groundwater arsenic calamity in Bangladesh. *Curr. Sci.* **1997**, *73*, 48−59.

(2) Mandal, B. K.; Chowdhury, T. R.; Samanta, G.; Mukherjee, D. P.; Chanda, C. R.; Saha, K. C.; Chakraborti, D. Impact of safe water for drinking and cooking on five arsenic-affected families for 2 years in West Bengal, India. *Sci. Total Environ.* **1998**, *218*, 185−201.

(3) BGS; DPHE. *Arsenic Contamination of Groundwater in Bangladesh*; Kinniburgh, D. G., Smedley, P. L., Eds.; Final Report, BGS Technical Report WC/00/19; British Geological Survey: Keyworth, UK, 2001.

(4) Berg, M.; Tran, H. C.; Nguyen, T. C.; Pham, H. V.; Schertenleib, R.; Giger, W. Arsenic contamination of groundwater and drinking water in Vietnam: A human health threat. *Environ. Sci. Technol.* **2001**, *35*, 2621−2626.

(5) BRAC. *Combating a Deadly Menace: Early Experiences with a Community-Based Arsenic Mitigation Project in Bangladesh*; Research Monograph Series No. 16; Dhaka, Bangladesh, 2000.

(6) Rhaman, M. M.; Mukherjee, D.; Sengupta, M. K.; Chowdhury, U. K.; Lodh, D.; Chanda, C. R.; Roy, S.; Selim, Md.; Quamruzzam, Q.; Milton, A. H.; Shadidullah, S. M.; Rahman, Md. T.; Chakraborti, D. Effectiveness and reliability of arsenic field testing kits: Are the million dollar screening projects effective or not? *Environ. Sci. Technol.* **2002**, *36*, 5385−5394.

(7) van Geen, A.; Ahsan, H.; Horneman, A. H.; Dhar, R. K.; Zheng, Y.; Hussain, I.; Ahmed, K. M.; Gelman, A.; Stute, M.; Simpson, H. J.; Wallace, S.; Small, C.; Parvez, F.; Slavkovich, V.; LoIacono, N. J.; Becker, M.; Cheng, Z.; Momotaj, H.; Shahnewaz, M.; Seddique, A. A.; Graziano, J. H. Promotion of well-switching to mitigate the current arsenic crisis in Bangladesh. *Bull. WHO* **2002**, *80*, 732−737.

(8) van Geen, A.; Zheng, Y.; Versteeg, R.; Stute, M.; Horneman, A.; Dhar, R.; Steckler, M.; Gelman, A.; Small, C.; Ahsan, H.; Graziano, J.; Hussein, I.; Ahmed, K. M. Spatial variability of arsenic in 6000 tube wells in a 25 km2 area of Bangladesh. *Water Resour. Res.* **2003**, *39* (5), 1140; doi: 10.1029/2002WR001617.

(9) Cheng, Z.; Zheng, Y.; Mortlock, R.; van Geen, A. Rapid multi-element analysis of groundwater by high-resolution inductively coupled plasma mass spectrometry. *Anal. Bioanal. Chem.* **2004**, *379*, 513−518.

(10) Gutzeit, H. *Pharm. Zeitung* **1879**, *24*, 263.

(11) Kinniburgh, D. G.; Kosmus, W. Arsenic contamination in groundwater: some analytical considerations. *Talanta* **2002**, *58*, 165−180.

(12) Gelman, A.; Trevisani, M.; Lu, H.; van Geen, A. Direct data manipulation for local decision analysis, as applied to the problem of arsenic in drinking water from tube wells in Bangladesh. *Risk Anal.* **2004**, *24*, 1597−1612.

(13) Chen, C. J.; Chuang, Y. C.; Lin, T. M.; Wu H. Y. Malignant neoplasms among residents of a blackfoot disease-endemic area in Taiwan: high-arsenic artesian well waters and cancer. *Cancer Res.* **1985**, *45*, 5895−5899.

(14) Engel, R. R.; Hopenhayn-Rich, C.; Receveur, O.; Smith, A. H. Vascular effects of chronic arsenic exposure: A review. *Epidemiol. Rev.* **1994**, *16*, 184−209.

(15) Smith, A. H.; Goycolea, M.; Haque, R.; Biggs, M. L. Marked increase in bladder and lung cancer mortality in a region of Northern Chile due to arsenic in drinking water. *Am. J. Epidemiol.* **1998**, *147*, 660−669.

(16) Wasserman, G. A.; Liu, X.; Parvez, F.; Ahsan, H.; Factor-Litvak, P.; van Geen, A.; Cheng, Z.; Slavkovich, V.; Hussain, I.; Momotaj, H.; Graziano, J. H. Water arsenic exposure and children's intellectual function in Araihazar, Bangladesh. *Environ. Health Perspect.* **2004**, *112*, 1329−1333.

(17) Caldwell, B. K.; Caldwell, J. C.; Mitra, S. N.; Smith, W. Searching for an optimum solution to the Bangladesh arsenic crisis. *Social Sci. Med.* **2003**, *56*, 2089−2096.

(18) van Geen, A.; Ahmed, K. M.; Seddique, A. A.; Shamsudduha, M. Community wells to mitigate the current arsenic crisis in Bangladesh. *Bull. WHO* **2003**, *81*, 632−638.

(19) Burgess, W. G.; Burren, M.; Perrin, J.; Ahmed, K. M. Constraints on sustainable development of arsenic-bearing aquifers in southern Bangladesh. Part 1: A conceptual model of arsenic in the aquifer. In *Sustainable Groundwater Development;* Hiscock, K. M., Rivett, M. O., Davidson, Eds.; Geological Society: London, 2000; Special Publications pp 193, 145−163.

(20) Zheng, Y.; van Geen, A.; Stute, M.; Dhar, R.; Mo, Z.; Cheng, Z.; Horneman, A.; Gavrieli, I.; Simpson, H. J.; Versteeg, R.; Steckler, M.; Grazioli-Venier, A.; Goodbred, S.; Shanewaz, M.; Shamsudduha, M.; Ahmed, K. M. Geochemical and hydrogeological contrasts between shallow and deep aquifers in two villages of Araihazar, Bangladesh: Implications for arsenic mobility. Submitted to *Geochim. Cosmochim. Acta*.

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Comment on "Reliability of a Commercial Kit to Test Groundwater for Arsenic in Bangladesh"

In a recent publication, "Reliability of a commercial kit to test groundwater for arsenic in Bangladesh" (*1*) regarding the effectiveness of the Hach EZ arsenic kit (product 2822800), Van Geen et al. remarked "Clearly the Hach kit should continue to be used to test wells throughout Bangladesh and other countries affected by elevated arsenic in groundwater". They studied only 799 wells in a 25-sq-km study area, when in Bangladesh there are 8−10 million wells (*2*) and more than two-thirds of the geographical area (140 000 sq km) is arsenic-affected. It has been reported (*3*) that the reliability of a kit depends on concentration distribution in the survey area and there is a short-range variability (over 1 km or so) of arsenic concentration in Bangladesh. Notably, out of the total 4.95 million tubewells tested in Bangladesh, 2.36 million were tested by the Hach kit in 147 upazillas in a study employing more than 54 000 field team members in 2002−2003 (*4*). The rest were tested by other kits; among them BAMWSP alone tested 0.67 million tubewells by using a Merck kit. The authors should have employed several groups across Bangladesh and analyzed (by Hach kit) a couple of hundred samples at least from each of the geomorphological regions of Bangladesh. They should have checked the efficiency of other kits widely in use in other countries before giving a global clearance to the Hach kit.

The authors reported, despite having actua1 concentrations >50 μg/L, 12% ($n = 799$) of the tested wells were analyzed to be safe (<50 μg/L) by the Hach kit. Extrapolating, with 12% of 2.36 million tubewells tested by Hach kit reported as safe, about 0.283 million reportedly safe ones may be actually unsafe (>50 μg/L). On average, 24 people use one tubewell in Bangladesh (*5*). So 0.283 million × 24 (6.8) million people may drink contaminated water considering it safe. In the opinion of van Geen et al., the inconsistencies in the Hach kit mainly underestimate in the range 50−100 μg/L. Analyzing by FI-HG-AAS technique, we found 31% of 52 000 samples from different parts of Bangladesh (*5*) were contaminated (>50 μg/L). Among the contaminated samples, 27% contained arsenic between 50 and 100 μg/L (unpublished data, D.C.). So a good percentage of unsafe tubewells (>50 μg/L) could have been misclassified as safe by Hach kit.

Various factors act behind erroneous field kit measurement. van Geen et al. stated "...field workers feeling pressed for time because of the need to complete a certain number of tests within the day" is one of them. Elaborating, Erickson (*6*) noted "BAMWSP worked out an agreement with the World Bank, which financed a U.S. $50 million loan for the effort, to complete screening and mitigation of wells in 147 upazillas or subdistricts, in Bangladesh by June 2003. According to Rosenboom, the work had not even begun as of past October, and BAMWSP has asked the World Bank for a second extension". BAMWSP subcontracted the World Bank Project to different groups based on the number of households in an Upazilla. While working, field team members found that the actual number of households was more than they were asked to cover and they were denied any additional money.

In an evaluation survey (1998−2001) we dealt with three then widely used field kits (NIPSOM, GPL, and Merck) analyzing 2866 samples from hand tubewells already colored red or green from 60 villages of 20 police stations in 10 districts of Bangladesh (*7*). We observed from field experience in Bangladesh and West Bengal that, due to repeated subcontracting to inexperienced, ill-qualified persons/groups, the overall quality of work suffers a lot. NAMIC Bangladesh informed (*4*) "To conduct the survey efficiently, training was given at three levels. BAMWSP provided training to master trainers. Master trainers provided training to Regional Project management team, NGOs, Upazilla coordinators, and field mobilizers, and then they provided training to the Field Team members." So there remains ample scope for dilution of "expertise" in the mid-steps of this "top down" approach. Our experience in the BAMWSP−World Bank project [names of their field workers: Jharna, Harun Rasid, Sahina, Muffazul, Md. Khorsed Alam] in Bangladesh is narrated below.

Date, 25th June 2001; Village, Disaband; Union, Khiladi; P.S, Laksham, Comilla. Field workers told Jubeida Begum (F/40) that her tubewell was arsenic-contaminated and she had arsenical skin lesions. We tested her tubewell water and the results showed that it contained less than 10 μg/L of arsenic. Our dermatologist could not detect arsenical skin lesions on her.

This is one of many examples.

There are some technical constraints of Hach or any other field kit, as follows: (1) The authors stated that the sulfides trap in the Hach kit could jeopardize the result by "wetting test strips" and advocated its removal since Bangladesh water does not have sulfide problems. However, a recent report (*8*) shows areas in Pakistan (e.g., Sargodha) with reducing groundwater where anoxic compounds such as dissolved iron, hydrogen sulfide, or methane are found. (2) There have been EPA-funded efforts (*6*) at developing mercury- and/or lead-free arsenic test kits to overcome environmental hazards associated with disposal of used test strips. In most cases the used test strips are thrown near the test site. (3) Conceding that the Hach kit in its present form may be inadequate for accurate measurement, van Geen et al. advocated increase of reaction time from 20 to 40 min, when already 2.36 million hand tubewells have already been measured by the Hach kit. (4) Recent reports (*9*, *10*) suggest harmful effects of arsine gas generated during field kit testing.

The paper also suffers from some minor discrepancies as detailed below.

The press release from Hach (*11*) regarding method of using Hach EZ arsenic kit mentioned the 70 μg/L reference point on the scale, which the authors missed in the methods section.

Reference 6 (*7*) of van Geen's paper mostly featured our group's work in Bangladesh not on West Bengal.

The authors mentioned that in West Bengal "the current government policy is to test only community wells while the vast majority of existing wells remain untested." This is not supported by any reference.

The authors opined that a long-term solution lies in "community wells that tap deep aquifers that are low in As", suggesting a drilling depth between 50 and 200 m. In West Bengal many tubewells installed by PHED to depths around 100 m (*12*), although initially safe, became contaminated over time.

On the basis of two experiences in Cambodia with the Hach kit—one "good" and another "bad", Dave Polya (*13*) expressed his concerns about (i) lack of precision; (ii) criticality of training of and implementation by field operators, and (iii) the amount of information lost in using field kits rather than laboratory ICP or AA analysis. The South East Asia Regional Director of WHO commented, "We are now at a stage to support the development of standardized laboratory testing of arsenic" (*14*).

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An endorsement such as that given by van Geen et al. may send the wrong signal as a nice advertisement for the manufacturer. In fact, a salesman (*15*) for Hach Company came to us and boasted that the superiority of their kit has been vindicated by a recent publication in an ACS journal. Though we understand the pertinence of evaluating test kits, considering the urgent need to screen millions of tubewells in Bangladesh, any kind of premeditated judgment on the basis of a small subset of a total database (799 wells make up only 0.008% of the total 10 million tubewells in Bangladesh) can have long-term implications on arsenic screening as well as mitigation programs

Literature Cited

(1) van Geen, A.; Cheng, Z.; Seddique, A. A.; Hoque, M. A.; Gelman, A.; Graziano, J. H.; Ahsan, H.; Parvez, F.; Ahmed, K. M. Reliability of a Commercial Kit to Test Groundwater for Arsenic in Bangladesh. *Environ. Sci. Technol.* **2005**, *39* (1), 299−303.

(2) van Geen, A.; Zheng, Y.; Versteeg, R.; Stute, M.; Horneman, A.; Dhar, R.; Steckler, M.; Gelman, A.; Small, C.; Ahsan, H.; Graziano, J.; Hussein, I.; Ahmed, K. M. Spatial variability of arsenic in 6000 tubewells in a 25 km^2 area of Bangladesh. *Water Resour. Res.* **2003**, *35* (5), 1140.

(3) Kinniburg, D. G.; Kosmus, W. Arsenic contamination in groundwater: some analytical considerations. *Talanta* **2002**, *58*, 165−180.

(4) Project Director, NAMIC, BAMWSP, Dhaka, Bangladesh. Personal communication, 2005.

(5) Chakraborti, D.; Sengupta, M. K.; Rahman, M. M.; Ahamed, S.; Chowdhury, U.K.; Chowdhury, U. K.; Hossain, M. A.; Mukherjee, S. C.; Pati, S.; Saha, K. C.; Dutta, R. N.; Zaman, Q. Q. Groundwater Arsenic Contamination and Its Health Effects in the Ganga-Meghna-Brahmaputra Plain. *J. Environ. Monit.* **2004**, *6*, 74−83.

(6) Erickson, B. E. Field kits fail to provide accurate measurement of arsenic in groundwater. *Environ. Sci. Technol.* **2003**, *37*, 35A−38A.

(7) Rahman, M. M.; Mukherjee, D. P.; Sengupta, M. K.; Chowdhury, U. K.; Lodh, D.; Chanda, C. R.; Roy, S.; Selim, M.; Zaman, Q. Q.; Milton, A. H.; Sahidulla, S. M.; Rahman, M. T.; Chakraborti, D. Effectiveness and Reliability of Arsenic Field Testing Kits: Are the Million Dollar Screening Projects Effective or Not? *Environ. Sci. Technol.* **2002**, *36* (24), 5385−5394.

(8) Proceedings of Inter-Regional Conference on Water Quality−Arsenic Mitigation, Taiyuan, Sganxi, China, November 23−26, 2004; Jointly organized by MOH−PRC, MWR−PRC, UNESCAP, UNICEF, UNN, and WHO.

(9) Hussam, A.; Alauddin, M.; Khan, A. H.; Rasul, S. B.; Munir, A. K. M. Evaluation of arsenic generation in arsenic field kit. *Environ. Sci. Technol.* **1999**, *33*, 3686−3688.

(10) Oklahoma Poison Control Center. Arsine fact sheet. http://www.oklahomapoison.org/prevention/arsine.asp. Accessed March 29, 2005.

(11) http://www.hach.com. http:/www.hach.com/fmmimghach?/CODE: L37785090|1; http:/www.hach.com/fmmimghach?/CODE: 2800088808|1; http:/hachww/hach_www/Press/pr99.htm (HACH Press Release on December 14, 2001, no longer available on web)

(12) Rahman, M. M.; Mandal, B. K.; Chowdhury, T. R.; Sengupta, M. K.; Chowdhury, U. K.; Lodh, D.; Chanda, C. R.; Basu, G. K.; Mukherjee, S. C.; Saha, K. C.; Chakraborti, D. Arsenic Groundwater Contamination and Sufferings of People in North 24-Parganas, One of the Nine Arsenic Affected Districts of West Bengal, India: The Seven Years Study Report. *Environ. Sci. Health* **2003**, *A38* (1), 27−59.

(13) Polya, D. Manchester University, UK. Personal Communication, 2005.

(14) World Health Organization Homepage. http://w3.whosea.org/rdhome/rdspeech/workshop_for_the_development_of_.htm/ (accessed March 29, 2005).

(15) Product Executive, Orbit Technologies Pvt. Ltd., Kolkata, India. Personal Communication, 2005.

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Response to Comment on "Reliability of a Commercial Kit to Test Groundwater for Arsenic in Bangladesh"

Muhkkerjee et al. raise three main objections to our recent recommendation that a commercial field kit continue to be used to test well water for arsenic throughout Bangladesh (*1*, *2*): (1) our study did not have broad enough coverage to constitute a representative evaluation of the kit; (2) many wells have been and will continue to be misclassified on the basis of field kits; (3) poor training and certain types of groundwater can lead to incorrect field-kit results.

Before responding to these concerns, we wish to applaud Dr. Chakraborti and his colleagues and students for the absolutely central role they have played in documenting the scale of the arsenic calamity in India and Bangladesh over the past 20 years. Soon after the first signs of disease in West Bengal were linked to elevated arsenic concentrations in groundwater in 1984, Dr. Chakraborti started to orchestrate heroic efforts to sample tens of thousands of wells and accurately measure the arsenic content of well water in his laboratory at Jadavpur University. Without Dr. Chakarborti's tenacity in bringing to the world's attention the plight of millions of people drinking groundwater with elevated levels of arsenic, the inertia of government and international organizations in responding to the crisis might still not have been overcome. In the following paragraphs, we try to explain why, despite our enormous respect for Dr. Chakraborti's achievements, we disagree with his current stance on testing with field kits.

Was the Evaluation Representative? We believe that comparing laboratory measurements of arsenic concentrations for 799 wells that were independently tested by NGO workers is sufficient to establish the reliability of a field kit under realistic conditions. Although the geographic extend of the area where the study was conducted is limited, the highly variable geology of Araihazar upazila afforded us the opportunity to sample a spectrum of aquifers representative of much of the country.

Laboratory vs Field Tests. We evaluated the Hach kit because we felt its novel design had overcome some of the limitations of other kits and because it had been widely used by NGOs in Bangladesh. The fact that less reliable kits have also been used in the past has no direct bearing on our recommendation that the Hach kit continue to be used in the future. We realize that good laboratories will produce more accurate arsenic measurements for the foreseeable future. The main drawback of laboratory testing, however, is that it is not realistic to expect such an approach to allow testing on demand. This is very important because wells continue to be installed throughout the country, partly in response to the previous test results. Of the 6000 wells within a 25 km^2 area that we tested in 2000–2001, for instance, approximately 1000 had already been replaced privately by 2004 (*3*). The logistics of testing millions of wells by setting up a few thousand hubs of field testers who rely on a good field kit throughout the country (e.g., at the union level) are daunting but conceivable. In contrast, it would be nearly impossible to perform millions of laboratory analyses in a few centralized locations and to communicate these results back to individual households.

Training and Matrix Effects. Our results actually show that 21% of wells containing >50 ug/L As ($n = 376$) were misclassified by BAMWSP workers (the 12% figure quoted by Muhkkerjee refers to the entire set of 799 wells, including safe wells). The proportion of misclassified wells containing >50 ug/L As was drastically reduced to 2% for the 62 wells that we tested by increasing the reaction time to 40 min. On the basis of these observations, we believe the level of misclassification for high As wells could be reduced to a few percent if testers are properly trained and motivated. This is not ideal but, in our opinion, the lesser of two evils if laboratory testing of a smaller number of wells is the only alternative. Whenever the Hach kit or other kits are used in different environments, e.g., in Pakistan, an initial comparison with laboratory measurements is imperative (With respect to the specific interference brought up in the comment, we'd like to point out that people generally do not drink water elevated in sulfide.).

Changes in Well Arsenic over Time. Perhaps the most important unknown of the Asian arsenic crisis at this point, alluded to in the comment from Dr. Chakraborti's team, is the issue of changes in well As concentrations over time. In this context, it is worth reminding the reader that our study included a comparison of laboratory results for 344 wells sampled 2 years apart in Araihazar which showed that As concentrations did not change significantly in the vast majority of wells over this period. The finding is consistent with one year of observations for a number of wells over a range of depths in other parts of the country by BGS/DPHE (*4*) and more detailed time series data for a set of 20 wells in Araihazar containing ≤ 50 ug/L As that were monitored every 2–4 weeks over a period of 3 years (*5*). Two of the wells that were monitored in Araihazar, however, did show worrisome increases in As concentrations over this period, in one case most likely because disconnected pipe sections led to the entrainment of groundwater from a shallow aquifer elevated in As. Other groups working in Bangladesh, the state of West Bengal in India, and Vietnam have reported seasonally changing As concentrations or increasing As concentrations. Such observations, which in our opinion do not warrant a wholesale rejection of the exploitation of aquifers that are presently low in As, serve only to reinforce the need for making testing services available at the village level throughout the affected regions.

We conclude our response to Dr. Chakraborti's surely well-intentioned comment by pointing out that the time for strident alarms may have passed. Decisive intervention to mitigate the arsenic crisis appears to be still lacking, but the affected populations might be better served if the scientific community could constructively reach out to entities such as the World Bank and UNICEF that have the wherewithal to scale up mitigation. A concrete joint activity that would be extremely valuable would be to set up a network of wells for monitoring representative aquifers that are presently low in As in Bangladesh, India, and other affected South Asian countries over a period of at least 10 years.

Literature Cited

(1) van Geen, A.; Cheng, Z.; Seddique, A. A.; Hoque, M. A.; Gelman, A.; Graziano, J. H.; Ahsan, H.; Parvez, F.; Ahmed, K. M. Reliability of a commercial kit to test groundwater for arsenic in Bangladesh. *Environ. Sci. Technol.* **2005**, *39* (1), 299–303.

(2) Mukherjee, A.; Sengupta, M. K.; Ahamed, S.; Hossaihn, M. A.; Das, B.; Nayak, B.; Chakraborti, D. Comment on "Reliability of a Commercial Kit to Test Groundwater for Arsenic in Bangladesh". *Environ. Sci. Technol.* **2005**, *39*, xxxx.

(3) Opar, A.; Pfaff, A.; Seddique, A. A.; Ahmed, K. M.; Graziano, J. H.; van Geen, A. Responses of 6500 households to arsenic mitigation in Araihazar, Bangladesh. Submitted for publication.

(4) BGS; DPHE. Arsenic Contamination of Groundwater in Bangladesh; Kinniburgh, D. G., Smedley, P. L., Eds.; Final Report,

10.1021/es050939q CCC: $30.25 © xxxx American Chemical Society
Published on Web 00/00/0000
PAGE EST: 1.2

BGS Technical Report WC/00/19,; British Geological Survey: Keyworth, UK, 2001.

(5) Cheng, Z.; van Geen, A.; Seddique, A. A.; Ahmed, K. M. Limited temporal variability of arsenic concentration in 20 wells monitored for 3 years in Araihazar, Bangladesh. *Environ. Sci. Technol.* Published online May 24, 2005, http://dx.doi.org/10.1021/es048065f.

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