Effectiveness and Reliability of Arsenic Field Testing Kits: Are the Million Dollar Screening Projects Effective or Not?

MOHAMMAD MAHMUDUR RAHMAN,† DEBAPRIYO MUKHERJEE,† MRINAL KUMAR SENGUPTA,† UTTAM KUMAR CHOWDHURY,† DILIP LODH,† CHITTA RANJAN CHANDA,† SHIBTOSH ROY,† M.D. SELIM,† QUAZI QUAMRUZZAMAN,† ABDUL HASNAT MILTON,# M.D. TOFIZUR RAHMAN,# AND DIPANKAR CHAKRABORTI*,#

School of Environmental Studies, Jadavpur University, Calcutta, India, Central Pollution Control Board, Calcutta, India, Dhaka Community Hospital, Baro Moghbazar, Dhaka, Bangladesh, and NGO Forum for Drinking Water Supply & Sanitation, Lalmatia, Dhaka, Bangladesh

The exposure of millions to arsenic contaminated water from hand tube wells is a major concern in many Asiatic countries. Field kits are currently used to classify tube wells as delivering arsenic below 50 μg/L (the recommended limit in developing countries) as safe, painted green or above 50 μg/L, unsafe and red. More than 1.3 million tube wells in Bangladesh alone have been tested by field kits. A few million U.S. dollars have already been spent and millions are waiting for the ongoing projects. However, the reliability of the data generated through field kits is now being questioned. Samples from 290 wells were tested by field kits and by a reliable laboratory technique to ascertain the reliability of field kits. False negatives were as high as 68% and false positives up to 35%. A statistical analysis of data from 240 and 394 other wells yielded similar rates. We then analyzed 2866 samples from previously labeled wells and found 44.9% mislabeling in the lower range (<50 μg/L) although mislabeling was considerably reduced in the higher range. Variation of analytical results due to analysts and replicates were pointed out adopting analysis of variance (ANOVA) technique. Millions of dollars are being spent without scientific validation of the field kit method. Facts and figures demand improved, environmentally friendly laboratory techniques to produce reliable data.

Introduction

Among the 21 countries in different parts of the world affected by groundwater arsenic contamination, the largest population at risk is in Bangladesh (1–4) followed by West Bengal in India (5–10). In recent years evidence of arsenic ground-water contamination has emerged from other Asiatic countries including Lao PDR, Cambodia, Mayanmar (11), and Nepal (12). In Vietnam (13), several million people consuming untreated groundwater may run a considerable risk of chronic arsenic poisoning.

From our analysis of more than 100 000 hand tube wells from West Bengal in India and 34 000 from Bangladesh, we found 9 out of the total 18 districts in West Bengal, India and 50 out of the total 64 districts of Bangladesh that carry arsenic levels in groundwater above 50 μg/L, the recommended value of arsenic in drinking water for India and Bangladesh although the World Health Organization (WHO) recommended value of arsenic in drinking water is 10 μg/L. The area and population of the 50 districts of Bangladesh are 118 849 km² and 104.9 million, respectively, and of the 9 districts of West Bengal are 38 865 km² and 50.0 million, respectively, but the actual number at risk is still under evaluation.

The British Geological Survey (BGS), on the basis of 3 534 hand tube water samples from throughout Bangladesh excluding the Chittagong Hill Tracts, estimated that 35 million inhabitants of Bangladesh drink arsenic contaminated water (above 50 μg/L) (14). The magnitude of arsenic contamination in Bangladesh surfaced only after the international conference (15) on arsenic in Dhaka, Bangladesh in February 1998. In a post-conference report (16) the World Bank’s local chief estimated that tens of millions of people are at risk for health effects and that 43 000 villages of 68 000 were presently at risk or could be at risk in future. In the same report (16), the World Health Organization (WHO) predicted that, within a few years, death across much of southern Bangladesh (1 in 10 adults) could be from cancers triggered by arsenic.

Beginning in 1997 the World Bank, UNICEF, WHO and other international aid agencies came forward to combat the situation. A unanimous decision was taken to test all the hand tube wells to gauge the magnitude of the calamity. Both in Bangladesh and West Bengal, India, it was decided to use field test kits to determine the arsenic concentration in hand tube wells and to color tube wells having arsenic less than 50 μg/L green and those above 50 μg/L red. Based on the available published reports (17–22), at least 1.3 million water samples from hand tube wells were analyzed by field kits and an estimated 1 million hand tube wells were colored red (>50 μg/L) or green (<50 μg/L) based on the Merck kit which has 100 μg/L of arsenic as the minimum detection limit. Using the same kit, the Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP) analyzed 617 366 hand tube wells (17), and DPHE-UNICEF (18) analyzed 403 651 tube wells. The Dhaka Community Hospital (DCH) analyzed 137 971 samples by Merck kit and 19 436 samples by National Institute of Preventive and Social Medicine (NIPSOM) kit (19). Other organizations from Bangladesh such as the NGO Forum (20), Grameen Bank (21), CARE (21), BRAC (22) also used the Merck kit and NIPSOM kit for testing. Only a few thousand samples were analyzed by the General Pharmaceuticals Limited (GPL) kit. By 2001, the Merck doubling kit (minimum detection limit 10 μg/L) and the Hach kit (minimum detection limit 10 μg/L) were considered for use in the ongoing projects by many organizations. Wide scale use of the Arsenator field kit has not been reported. The government of West Bengal and UNICEF launched a 1.1 million dollar project (23) in 1999 to test the hand tube wells with the All India Institute of Hygiene and Public Health (AIH&PH) field kit.

* Corresponding author phone: +91-33-41464233; fax: +91-33-4146266; e-mail: dcsoesju@vsni.com.
† Jadavpur University.
‡ Central Pollution Control Board.
§ Dhaka Community Hospital.
# NGO Forum for Drinking Water Supply & Sanitation.

10.1021/es020591o CCC: $22.00 © xxx American Chemical Society
Published on Web 00/00/0000 PAGE EST: 9.5

VOL. xx, NO. xx, xxxx / ENVIRON. SCI. & TECHNOL. • A
All field kits used to date are based on the principle of mercuric bromide stain method (24). The accuracy of the bromide stain method was evaluated in a round robin exercise, and it was reported that the arsenic concentrations for a solution of arsenate at 50 μg/L in distilled water had a relative standard deviation (RSD) of 75% (24). It was further reported (24) that the mercuric bromide stain method was incapable of producing quantitative meaningful results with RSD > 10% below a concentration 150 μg/L of arsenic. A recent publication (25) notes that the Merck field kit “is not only inadequate to screen water samples containing less than 100 ppb of arsenic, but also provides toxic arsine gas that may be a health hazard”.

We have been working in the villages of Bangladesh for the last 7 years to know the magnitude of the contamination and the number of people affected. While working in the field during last 4 years, we found many tube wells were colored either ‘red’ or ‘green’ by field workers after testing by field kits. During our survey we collected samples from time to time from tube wells colored red/green and found after analyzing these samples by flow injection hydride generation atomic absorption spectrometry (FI–HG–AAS) technique that a good percentage of the tube wells were not correctly colored. This discrepancy initiated us to study the efficiency of the field kits.

Mode of Evaluation

This paper will evaluate the efficiency of field kits and show how far the field kits are justified to be used in villages to color hand tube wells red (> 50 μg/L) or green (< 50 μg/L) to indicate unsafe or safe and whether the adopted millions of dollar in projects using field kits are justified or not.

Our field kit evaluation had 3 phases.

First Phase. When we started field kit evaluation in Bangladesh in 1998, 3 kits, NIPSOM, GPL and Merck (see Table 1), were widely used, but the Merck (doubling method) kit was not available at that time. In the first phase, we analyzed 229 samples by NIPSOM, GPL and Merck kits and compared the results with flow injection hydride generation atomic absorption spectrometry (FI–HG–AAS) to test the accuracy of these kits. Several organizations used the Merck kit for coloring hand tube wells red (< 50 μg/L) or green (< 50 μg/L). Since the Merck kit has a minimum detection limit for arsenic of 100 μg/L, we excluded Merck kit results below 100 μg/L from our first phase evaluation study. After evaluation of the field kit, we collected 2866 field samples from hand tube wells colored red/green on the basis of field kit testing and analyzed these samples by FI–HG–AAS.

Second Phase. From 2000 onward the Merck (doubling method) kit was used in the field for minimum detection of 10 μg/L level of arsenic. In August 2000, BRAC–Bangladesh reported (22) analytical results of 240 water samples from Panisara Union, Jikargachha police station of Jessore district. The samples were analyzed by the Asia Arsenic Network (AAN) field kit and by the Merck (doubling method) kit and cross-checked by continuous flow hydride generation AAS by Intronics Technology Center (ITC), Bangladesh. We made a statistical evaluation of the results of all 240 samples that were reported by BRAC in their report (22) to compare the accuracy of the AAN kit and the Merck (doubling method) kit.

Third Phase. The AIIH&PH field kit results from hand tube wells of Murshidabad and Malda districts were also compared with FI–HG–AAS in our laboratory. UNICEF, Calcutta sent 394 field samples to our laboratory, which were simultaneously measured by the AIIH&PH field kit for comparison with the field kit results.

### TABLE 1. Details of Three Field Kits (NIPSOM, GPL and Merck)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NIPSOM (National Institute of Preventive and Social Medicine) Kit</th>
<th>GPL (General Pharmaceuticals Ltd.) Kit</th>
<th>Merck Kit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design</td>
<td>Box oversize and heavy; contents scatter during transit</td>
<td>Box oversize and heavy; contents scatter during transit</td>
<td>Compact and light; contents intact during transit</td>
</tr>
<tr>
<td>Minimum detection limit (μg/L)</td>
<td>10</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Arsenic detection range (μg/L)</td>
<td>10, 20, 50, 100, 200, 300, 400, 500 &amp; 700</td>
<td>10, 50, 100, 200, 400, 600, 800, 1000 &amp; 1500</td>
<td>0, 100, 500, 1000, 1700 &amp; 3000</td>
</tr>
<tr>
<td>Chemicals used</td>
<td>HCl (1:1), KI (reagent 1), Zn powder (reagent 2), SnCl2 (reagent 3), bromide paper (test strip)</td>
<td>HCl (1:1), KI (reagent 1), SnCl2 (reagent 2), Zn powder (reagent 3), bromide paper (test strip), lead acetate cotton wool</td>
<td>Mixture of KI, SnCl2 and Zn as reagent 1 and HCl as reagent 2</td>
</tr>
<tr>
<td>Procedure</td>
<td>Place the disk paper between flattened surface of two glass flanges and secure the flanges with the clip. Take 15 mL of test solution in a test tube and add 0.1 g of reagent 1, 0.5 g of reagent 2 and 0.1 g of reagent 3. Now add 4 mL of 1:1 HCl and insert the end of the flange in the test tube and shake gently. Allow to stand for 5 min. Remove the clipped flanges from the test tube and compare the color change obtained on disk paper with the color scale.</td>
<td>Place 15 mL of water in the reaction test tube and add 4 mL of HCl, one level spoonful of reagent 1 and same amount of reagent 2. Shake gently and wait for 10 min. While waiting 10 min, use forceps to place bromide paper between the two sections of flange unit and secure with clamp. After 10 min, add one level spoonful of reagent 3 to the reaction mixture in the test tube. Immediately fit the flange unit into the mouth of the test tube. Gently shake the test tube and wait for 10 min. Using forceps, remove bromide paper and compare to color chart.</td>
<td>Insert a test strip into the slot in the cap of reaction vessel. Place 5 mL of test solution in the reaction vessel and add 1 measuring spoonful of reagent 1 and shake. Add 10 drops of reagent 2 and close the reaction vessel immediately with cap. Allow to stand for 2–3 times. Immerses briefly in water and compare with color scale.</td>
</tr>
<tr>
<td>Time required for test</td>
<td>5 min</td>
<td>20 min</td>
<td>30 min</td>
</tr>
<tr>
<td>Health hazard</td>
<td>(i) Accidental spillage of acid</td>
<td>(i) Accidental spillage of acid</td>
<td>(i) Accidental spillage of acid</td>
</tr>
<tr>
<td></td>
<td>(ii) Toxic arsenic gas may cause health hazard</td>
<td>(ii) Toxic arsenic gas may cause</td>
<td>(ii) Toxic arsenic gas may cause</td>
</tr>
<tr>
<td></td>
<td></td>
<td>health hazard</td>
<td>health hazard</td>
</tr>
<tr>
<td>Cost per test in U.S. ($)</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

(approximate)
Experimental Section

Study Area. For the first phase, 290 hand tube wells were selected from 6 police stations (Songargaon, Moulavibazar sadar, Rajnagar, Srimangal, Kamalganj and Baro Lekha) of 2 districts (Narayanganj and Moulavibazar) of Bangladesh to compare arsenic determination by the field kits (NIPSOM, GPL, Merck) with FI–HG–AAS analysis. In the first phase, the accuracy of the field kits was evaluated. We then analyzed 2,866 samples from hand tube wells by FI–HG–AAS already colored red or green (Figure 1) on the basis of field kit testing.
from 60 villages of 20 police stations in 10 districts of Bangladesh. Figure 2 shows the distribution of groundwater contamination by arsenic in Bangladesh and the districts from where we collected red/green hand tube well water samples for arsenic analysis.

Selection of Tube Wells and Sampling. The 290 water samples from hand tube wells were collected at random after pumping for at least 10 min. About 1 L water from each tube well was collected in a pre-cleaned and acid washed plastic container with 1 mL of concentrated nitric acid, thoroughly mixed and equally distributed among 10 pre-cleaned plastic containers of 50 mL capacity. Six containers were tested by field kit at a central site in each village; four went to the School of Environmental Studies (SOES) for analysis by FiaHG—AAS.

Estimation of Arsenic using Field Kits, Spectrophotometric Method and FiaHG—AAS Method. The 290 samples were evaluated by NIPSOM, GPL and Mercikits (Table 1) utilizing the color charts provided by the manufacturers (Figure 3).

Spectrophotometric Method. A Shimadzu (Japan) double beam Spectrophotometer (Model 1601) was used. Total arsenic in water was determined with Ag-DDTC—chloroform-hexamethylene tetraamine as absorbing solution (26—27). The determination limit of arsenic by the spectrophotometric method with 95% confidence is 30 μg/L.

Flow Injection Hydride Generation Atomic Absorption Spectrometry Method (FiaHG—AAS). AFIHG—AAS system was assembled from commercially available instruments and accessories in our laboratory. A Perkin-Elmer Model 3100 atomic absorption spectrometer equipped with a Hewlett-Packard Vectra Computer with GEM software, Perkin-Elmer EDL system, arsenic lamp (lamp current 400 mA) and Varian AAS Model Spectra AA-20 with Hollow Cathode As lamp (lamp current 10 mA) were used. The flow injection assembly consists of an injector, Teflon T-piece, tigon tubings and other parts for the Fia system from Omnifit, UK. The peristaltic pump (VGA-76) from Varian and Minipuls 3 from Gilson were incorporated into the Fia system. In the FiaHG—AAS system the sample was injected into a carrier stream of 5 M HCl by means of a six-port sample-injection valve fitted with 50 μL sample loop. The injected sample, together with carrier solution, met subsequently with a continuous stream of sodium borohydride (1.5%) dissolved in sodium hydroxide (0.5%). Mixing with sodium borohydride generates arsenic hydride (arsine), which subsequently entered into the ice water bath and then into the gas—liquid separator apparatus, which was cooled with ice-cold water. Carrier gas nitrogen transported the arsine to the quartz tube mounted in the air-acetylene flame for AA measurement. The minimum detection limit with 95% confidence level was 3 μg/L of arsenic. Details of the instrumentation, analytical procedures and analytical performances were reported in our earlier publications (27—29).

Statistical Analyses. Standard statistical techniques such as mean, standard deviation (SD), minimum, maximum and ANOVA were applied to study the variation among the values. Correlation coefficients and linear regression were utilized for the relationship of values obtained by two methods.

Interlaboratory Comparison and Analysis of Standard Reference Material. Aliquots of the field samples were sent to NGO Forum, Bangladesh for analysis of arsenic spectrophotometrically. After the analysis, the residual samples were sent by courier to the SOES laboratory, Calcutta for FiaHG—AAS Analysis. Three such batches (total 62 samples) were analyzed within 3—7 days for interlaboratory comparison. A similar interlaboratory study was done with the Environment and Public Health Organization (ENPHO), Nepal (30) which also used FiaHG—AAS, Standard Reference Materials (SRM) and an EPA water standard for arsenic were used to check the accuracy of FiaHG—AAS method (28, 31).

Analysis of 2866 Hand Tube Wells by FiaHG—AAS, which Were Colored Red/Green after Analyzing with Field Kits by Organizations in Bangladesh. Water samples from 2 866 hand tube wells, previously analyzed by field kits and colored either red or green, were stored in 10 mL plastic bottles with 1 drop of nitric acid added to each bottle as preservative. Around 5% of the samples was collected from the same sources in duplicate to check the variation of arsenic concentration among the two samples. Samples were analyzed by FiaHG—AAS at the SOES laboratory within 3 to 7 days.

Statistical Analysis of the Results of 240 Samples Measured by the Merck (Doubling Method) and AAN Kits Compared with Continuous Hydride Generation AAS from ITC Laboratory, Dhaka (Reported by BRAC, Bangladesh). An independent report which compared two field kits with a continuous hydride generation AAS assay was published by BRAC, Bangladesh (22) in August 2000 utilizing 240 groundwater samples from Panisara Union of Jikargachha police station, Jessore district. Merck (doubling method) and AAN kits were used, and the results of these two field kits were compared with continuous hydride generation AAS from Intronics Technology Center (ITC) laboratory, Dhaka, Bangladesh and the results published in tabular form (22). With the permission of BRAC, we made a statistical evaluation of the analytical results of 240 samples.

Validation of AIH&PH Field Kit Used in Arsenic Affected Villages of Murshidabad and Malda (an UNICEF Project) of West Bengal, India. We then compared the AIH&PH field kit with our FiaHG—AAS system. Three groups collected 394 samples from arsenic affected districts of Murshidabad (Group A, 192 samples) and Malda (Group B, 104 samples and Group C, 98 samples) as having arsenic below 50 μg/L and above 50 μg/L. We utilized FiaHG—AAS analysis to test the accuracy of the information generated by the field kit.
Results and Discussion

We have reported elsewhere (32) the effects of various parameters (time, temperature, preservative, types of bottle, etc.) on arsenic assays. If the samples are collected in pre-washed (overnight with 1:1 HNO₃) plastic bottles (10 mL capacity) adding one drop of concentrated HNO₃ as preservative to 10 mL of water then the samples do not show any significant variation in total arsenic content when measured within 7 days. The correlation between the output of the spectrophotometric and FI-HG-AAS methods was defined by the least-squares technique to calculate the regression equation and correlation coefficient ($r^2 = 0.983$) as diagrammed in Figure 4a. The correlation ($r = 0.985$) of 10 samples from arsenic affected villages of Nepal analyzed by FI-HG-AAS by ENPHO laboratory (30) and our laboratory are shown in Figure 4b.

Statistical Analysis of 290 Hand Tube Wells Measured by 3 Field Kits and FI-HG-AAS. For comparison all the values of FI-HG-AAS corresponding to the values at particular level obtained by field kits were processed to find out the minimum, mean, maximum and standard deviation (SD) to have an idea about the degree of deviation. Minimum, mean minus SD, mean, mean plus SD and maximum values obtained by FI-HG-AAS were plotted against the corresponding value of field kits (NIPSOM and GPL kits). Figure 5a,b shows a wide variation at each level of both NIPSOM and GPL field kits. Based on SD it may be mentioned that some of the values (calculated) will be negative even if we consider the mean minus one sigma as shown in Figure 5a,b. The values less than zero have no physical entity.

Since the minimum detection limit of the Merck kit is 100 µg/L, we limited the comparison to values above this minimum. By FI-HG-AAS, arsenic in the range of 100 µg/L and above was found in 127 of 290 samples. The Merck kit identified 113 (89%) with an 11% failure rate. Figure 5c shows the wide variation at each level of the Merck kit.

The false positives and false negatives of the field test kits were calculated for each category: (a) 3 µg/L to 50 µg/L, (b) 50.1 µg/L to 100 µg/L and (c) >100 µg/L.
minimum arsenic concentration determined with 95% confidence by our FI-HG-AAS system.) as shown in Table 2. At arsenic concentrations below 50 \(\mu g/L\) (Table 2), false positive values were 6.2% for NIPSOM and 2.7% for GPL kits, supporting use of either kit to categorize wells as safe. In the range of 50.1–100 \(\mu g/L\), we found 56.9% and 68.6% false negatives and 35.3% and 17.7% false positives for NIPSOM and GPL, respectively. As a result, unsafe tube wells will be colored green i.e., safe. Although false positives at concentrations above 100 \(\mu g/L\) are not negligible for either kit, this will have no effect on the decision to color the tube well red.

For the Merck kit, at concentrations <50 \(\mu g/L\), it was found that only 3 of 113 were false negative plus one sample between 50.1 and 100 \(\mu g/L\). Thus, false negatives were not significant. On comparison of Merck kit results with 127 samples where FI-HG-AAS found arsenic above 100 \(\mu g/L\), then 18 samples (14.1%) tested by Merck kit as below 100 \(\mu g/L\). Although the variation of Merck kit from FI-HG-AAS is not significant, the Merck kit cannot be used for field testing of hand tube wells for arsenic below 100 \(\mu g/L\).

Overall, there was no systematic bias toward under or over reporting, but random error led to false positives and

| Table 2. False Positive and False Negative Results Obtained by Field Kits Comparing with FI-HG-AAS |

<table>
<thead>
<tr>
<th>NIPSOM</th>
<th>GPL</th>
</tr>
</thead>
<tbody>
<tr>
<td>ranges</td>
<td>false (−)</td>
</tr>
<tr>
<td>3–50 (\mu g/L)</td>
<td>7 (6.2%)</td>
</tr>
<tr>
<td>50.1–100 (\mu g/L)</td>
<td>29 (56.9%)</td>
</tr>
<tr>
<td>&gt;100 (\mu g/L)</td>
<td>19* (26.0%)</td>
</tr>
</tbody>
</table>

*In terms of <50 \(\mu g/L\). *In terms of <100 \(\mu g/L\).
false negatives. Field kits are not only semiquantitative but also produce false values.

To review the status of false positives and false negatives we have graphically presented 51 samples from Table 2 in the range of 50.1–100 μg/L of arsenic tested by FI–HG–AAS. Values of FI–HG–AAS are plotted on the X-axis against the values of field kits on the Y-axis and shown in Figure 6a for the NIPSOM kit and Figure 6b for GPL kit. Slope and intercept are given in the form of an equation. The intercept and angle of slope in Figure 6a,b indicate a weak correlation (r = 0.294 for NIPSOM and r = 0.440 for GPL kit).

A vertical and a horizontal line at 50 μg/L and 100 μg/L are drawn to divide values below 50 μg/L and above 100 μg/L. 29 and 35 values of 51 are below 50.1 μg/L and 18 and 9 values of 51 are above 100 μg/L for the NIPSOM and GPL kits, respectively.

**Statistical Analysis of the Results of 240 Hand Tube Wells by the Merck (Doubling Method) and AAN Kits and Checked by Continuous Hydride Generation AAS as Reported by BRAC, Bangladesh.** The detection limit reported for both the Merck (doubling method) and AAN kits is 10 μg/L. The detection limit of continuous hydride generation AAS of ITSC is 1 μg/L (33), and the lowest value detected while analyzing 240 samples by ITSC was 1.8 μg/L.

The same procedure as adopted for NIPSOM and GPL kits (Figure 5a,b) was used to compare the analytical results of 240 water samples tested by the Merck (doubling method) kit and the AAN kit with the AAS value as the true value. A wide variation among the AAS values versus the kit values are shown in Figure 7a for the Merck (doubling method) kit and Figure 7b for the AAN kit grouped in 3 categories: 1–50 μg/L, 50.1–100 μg/L and above 100 μg/L. The minimum detection limit of continuous flow AAS of ITSC laboratory was reported to be 1 μg/L, so lowest value was 1 μg/L in the first group i.e., 1–50 μg/L. The number of false positives and false negatives are shown in Table 3.

In the range 1–50 μg/L, both the Merck (doubling method) and AAN kits have a false positive rate of 25.6%. That means 47 of 183 wells were erroneously colored red despite delivering safe water.

In the range of 50.1–100 μg/L, the Merck kit shows 46.7% false negatives i.e., 46.7% of the hand tube wells were colored green (safe) despite containing arsenic above 50 μg/L. For the AAN field kit, the false negative rate was 50%.

On analysis of the 27 samples containing more than 100 μg/L, 48.2% of the samples tested by the Merck kit were read as less than 50 μg/L falsely indicating safe water. The AAN kit reported 70.4% below 50 μg/L when the actual value was above 100 μg/L by AAS. For all samples above 100 μg/L by AAS, 85.2% samples were read as below 100 μg/L by the Merck kit and 92.6% by the AAN kit.

The graphical presentations in Figure 6a–d of two sets of results from Table 3i.e., (i) 30 samples in the range 50.1–100 μg/L and (ii) 27 samples above 100 μg/L of arsenic by AAS and the corresponding Merck (doubling method) kit and AAN kit values use parameters similar to Figure 6a,b. Figure 8a,b indicates that in the range of 50.1–100 μg/L, 14 and 15 of 30 values are below 50.1 μg/L while 5 and 4 values are above 100 μg/L for the Merck (doubling method) and AAN kits, respectively. At concentrations above 100 μg/L (Figure 8c,d) 13 and 19 values of 27 are below 50 μg/L while 23 and 25 values are below 100 μg/L by the Merck (doubling method) and AAN kits, respectively.

**Validation of AIIH&PH Field Kit Results by FI–HG–AAS.** The field kit of AIIH&PH has a ‘Yes’/’No’ system. A color on the bromide paper means the water sample contains arsenic above 50 μg/L (‘Yes’) while ‘No’ means no visible color i.e., the sample contains less than 50 μg/L.

UNICEF, Calcutta sent us 394 samples from Murshidabad and Malda, two arsenic affected districts of West Bengal. Three separate groups worked in the field to generate field data utilizing the AIIH&PH kit. Group A sent us 192 samples marked red (above 50 μg/L) and blue (< 50 μg/L). Group B sent us 104 samples reporting Yes/No and Group C sent us 85 samples marked ‘Yes’/’No samples marked ‘Uncertain’ which were excluded with statistical analysis of 85 samples. Table 4 compares the results with the FI–HG–AAS values.

Each of the 3 groups had been trained separately in use of the AIIH&PH field kit, worked independently, and had no connection with the other groups. As shown in Table 4, group A generated 89.6% reliable data, whereas group B and group C generated 55.8% and 80% reliable data. It appears that the performance of field kit is not the only factor affecting accuracy. UNICEF, Calcutta no longer uses the AIIH&PH field kit to color hand tube wells safe or unsafe in the villages of West Bengal.

**Operation of Field Kit by Skilled and Trained Person.** The ANOVA technique was applied to breakdown the total precision into its component e.g. between replicates and between persons trained for using field kits. These two components have an influence on the performance characteristics. These are considered as the optimization criterion.
in evaluating the performance of field kits. The two field kits (NIPSOM and GPL) were considered.

Table 5 reveals that there is no significant variation among the analysts whereas variation is significant among the replicates in most of the cases. The analyst variability defined in the UNICEF samples utilizing the A11HSP kit by groups trained under variable conditions was not confirmed in the NIPSOM and GPL results obtained by skilled analysts but inconsistency of the test kits was found in each group.

Analysis of 2866 Hand Tube Wells by FI-HG-AAS Previously Colored Red (Unsafe)/Green (Safe) after Field Kit Testing by Various Organizations in Bangladesh. To judge the accuracy of well markings, SOES, jointly with DCH, Bangladesh, went to the field and collected water samples from 2,866 hand tube-wells previously colored red or green on the basis of kit testing by field workers. FI-HG-AAS analysis of 1,143 tube wells colored green by field kits confirmed that 1,058 tube wells had arsenic concentrations below 50 μg/L but found that 85 (7.5%) were unsafe. Of 1,723 tube wells colored red by field kits, only 861 were found unsafe (<50 μg/L) and the remaining 862 were safe (<50 μg/L) by our FI-HG-AAS system. The field kits had mislabeled 862 + 85 = 947 (33.04%) of 2,866 hand tube wells. Given the scarcity of uncontaminated water the mislabeling of 50% of safe wells has a major socioeconomic impact.

The FI-HG-AAS results for 2,866 samples were compared with the status (green or red) of tube wells measured by field kits at concentrations ranging from <3 μg/L to <600 μg/L. Table 6 indicates that 1,920 tube wells were safe, although the kits had mislabeled 862 (44.9%) as unsafe. The overall results of 2,866 field sample analyses (Table 6) show that at arsenic concentrations <3 μg/L to <70 μg/L, field kits are not reliable. However from 70 μg/L to <600 μg/L the false detection by field kits is only 4.17% to 9.59%.

From Table 6, it appears that field kit results are mainly unreliable up to <70 μg/L of arsenic. British Geological Survey has analyzed from Bangladesh 3,534 hand tube wells (14) by reliable instrumental system in the laboratory. We have calculated from BGS result that 2,804 (79.3%) out of 3,534 samples contain arsenic <70 μg/L. We have also analyzed 34,000 hand tube well water samples by FI-HG-AAS from 64 districts of Bangladesh. Out of these 34,000 samples, 22,000 samples were from 31 districts where we have found arsenic patients and 65.1% samples contain out of 34,000 arsenic <70 μg/L. From West Bengal, we have so far analyzed more than 100,000 samples by the same FI-HG-AAS method and 79.2% contain arsenic <70 μg/L. The average of these results indicated that 74.5% of the total hand tube wells in Bangladesh and West Bengal together contain arsenic <70 μg/L.

If the total number of hand tube wells in Bangladesh are between 6 and 11 million (14) and that of 9 arsenic affected districts of West Bengal are 1.5–2.0 million (34), then according to Table 6, 74.5% of hand tube wells are in critical level according to field kit assessment.

### Significance of the Results

The weak correlation’s between the kits and laboratory methods (Table 2 with Figure 6a,b and Table 3 with Figure 8a–d) indicates the random behavior of the kits. Though negative values are the indication of inverse correlation but at this level it does not bear any significance. The random behavior of the kits is also reflected in Table 6, where performance of kit was appreciably improved above 70 μg/L but finding that 85 (7.5%) were unsafe. At this level it does not bear any significance. The random behavior of the kits, it may be confidently mentioned that the kit is not at all quantitative and at best qualitative.

The most important limitation of using these field kits is visual identification of the color in the lower range. The identification of color or judgment in the lower range as varies from man to man. The persons with developed expertise through practice may not be engaged later on for estimation. As a result, the accuracy of the results suffers when the estimation is done by new hands as is generally the case. Several attempts have been made to develop different field kits by different manufacturers to quantify arsenic concentration even up to 10 μg/L levels. However none of the field kits manufacturer reported their field kit efficiency on different arsenic concentration level after comparing with large number of field samples measured by highly sensitive instrumental techniques. Quantification as needed in the lower range was not checked.

Cost is an important consideration but requires comparison with the even higher cost of falsely labeling a well as unsafe. The average cost of each field kit is around U.S. $40 for 100 determinations. The salary and maintenance expenses of the field analysts increases the cost of kit testing to U.S. $2 plus organizational and training expenses and data analyses. Our experience of around 2 000 000 water and biological samples analyzed for arsenic by FI-HG-AAS has established (35) that a totally reliable assay can be completed in 30–40 s at a cost even lower than that of the field kit. The amount of chemicals to be used for testing kits is not also

| TABLE 5. Study of Variation among Analysts and among Replicates |
|-------------------|-----------------|-----------------|-----------------|
| **true value** (μg/L) | **mean** (μg/L) | **SD** | **level of significance** |
| GPL | NIPSOM | GPL | NIPSOM | GPL | NIPSOM |
| 67 | 34 | 34 | 56 | 63 | 83 |
| 50 | 30 | 75 | 50 or less | 110 | 50 |
| 0 | 0 | 15 | 0 | 26 | 0 |
| NS | NS | S | NS | S | S |
| TABLE 6. Comparative Study of Field Kit with FI—HG—AAS from 2866 Field Samples | **range in μg/L** | **samples analyzed by FI-HG—AAS** | **no. of samples below 50 μg/L** | **no. of samples above 50 μg/L** | **false detection (%)** |
| <3 | 665 | 267 | 398 | 59.85 |
| 3—10 | 508 | 417 | 91 | 17.91 |
| 10—20 | 259 | 178 | 73 | 30.12 |
| 20—30 | 210 | 121 | 89 | 42.38 |
| 30—40 | 168 | 51 | 117 | 69.64 |
| 40—50 | 110 | 21 | 89 | 80.91 |
| below 50 | 1920 | 1058 | 862 | 44.90 |
| 50—60 | 95 | 15 | 80 | 15.79 |
| 60—70 | 87 | 20 | 67 | 22.99 |
| 70—80 | 73 | 7 | 66 | 9.59 |
| 80—90 | 73 | 7 | 66 | 9.59 |
| 90—100 | 67 | 5 | 72 | 6.42 |
| 100—200 | 358 | 23 | 335 | 6.42 |
| 200—300 | 97 | 3 | 94 | 3.09 |
| 300—400 | 51 | 1 | 50 | 7.89 |
| 400—500 | 21 | 1 | 20 | 4.76 |
| 500—600 | 24 | 1 | 23 | 4.17 |
negligible. For testing of 100 samples by field kits (average of NIPSOM, GPL and Merck), the amount of concentrated HCl required will be 150 mL and the mixture of Zn, KI and SnCl₂ is about 65 g (Table 1), whereas by FI-HG-AAS, the amount of chemicals required will be about 50 mL of acid and a mixture of 2.0 g of NaBH₄ and NaOH. If 10 million tube wells are to be tested by field kits, this will be a huge amount compared to FI-HG-AAS. The environmental contamination of the field kits is a real concern not evoked by FI-HG-AAS: in a micro-assay waste chemicals are minimal and the laboratory personnel are not exposed to arsine gas. Any field kit used in arsenic affected areas must be more reliable and sensitive than existing methods, otherwise the ‘bad’ kit data mixed with ‘good’ instrumental data contaminates the entire data pool for meaningful policy decision. No cost benefit can be attributed to field kits that waste water resources and fail to eliminate real hazards.

**Acknowledgments**

We thank to BRAC, Bangladesh for permission to use their comparative study of field kits and continuous hydride generation AAS data for statistical analysis. Thanks to UNICEF, Calcutta for sending their field kit samples to us for validation.

**Literature Cited**


Sengupta, M. K.; Lodh, D.; Chanda, C. R.; Saha, K. K.; Mukherjee,

Mukherjee, S. C.; Roy, S.; Das, R.; Kaies, I.; Barua, A. K.; Palit,
S. K.; Quamruzzaman, Q.; Chakraborti, D. Environ. Sci. 2001;
8(5), 393–415.

(9) Roy Chowdhury, T.; Basu, G. K.; Mandal, B. K.; Biswas, B. K.;
Samanta, G.; Chowdhury, U.K.; Chanda, C. R.; Lodh, D.; Roy,

(10) Mandal, B. K.; Roy Chowdhury, T.; Samanta, G.; Mukherjee, D.

(11) Economic and Social Commission for Asia and the Pacific;
Geology and Health: Solving the Arsenic Crisis in the Asia Pacific
Region; ESCAP−UNICEF−WHO Expert Group Meeting, Bangkok,

(12) Tandukar, N. Abstracts; International Conference on Arsenic in
the Asia-Pacific Region: Managing Arsenic for our Future,

(13) Berg, M.; Tran, H. C.; Nguyen, T. C.; Pham, M. V.; Schertenleib,

(14) Arsenic Contamination of Groundwater in Bangladesh; BGS
Technical Report WC/00/19; British Geological Survey: Key-

(15) International Conference on Arsenic Pollution of Groundwater in
Bangladesh: Causes, Effects and Remedies, LGED Auditorium,
Dhaka, Bangladesh, February 8–12, 1998.


(17) Chowdhury, A. Q. Abstracts; International workshop on Arsenic
Mitigation, Local Government Division, Ministry of Local
Government, Rural development and Cooperatives, Government
of Bangladesh: Dhaka, Bangladesh, January 14–16, 2002,
Paper 50–53.

(18) DPHE-UNICEF Monthly Progress Report, Dhaka, Bangladesh,

(19) Das, R.; Rahman, M.; Quamruzzaman, Q.; Yusuf, J.; Mostafa, M.
G.; Mohonta, R.; Basu, S. M.; Mannan, M. A. Dhaka Community

(20) Half Yearly Report, NGO Forum for Drinking Water Supply &

(21) Fact Sheet 12 on Arsenic: A Disaster Forum Publication, Dhaka,
Bangladesh (e-mail: df@bangla.net).

(22) Combating a Deadly Menace: Early Experiences with a Commu-

nity-Based Arsenic Mitigation Project in Bangladesh, June
1999-June 2000, BRAC Research Monograph, Series No. 16,
August 2000.

(23) Joint Plan of Action: Arsenic Contamination of Drinking
Water: Government of West Bengal and UNICEF, Nodal
Department: Public Health Engineering Department, 1999.

(24) Arsenic exposure and health effects, Abernathy, C. O., Calderon,
1997.

(25) Hussam, A.; Alauddin, M.; Khan, A. H.; Raul, S. B.; Munir, A.

H-17, 31–41.

(27) Chatterjee, A.; Das, D.; Mandal, B. K.; Chowdhury, T. R.; Samanta,

(28) Samanta, G.; Roy Chowdhury, T.; Mandal, B. K.; Biswas, B. K.;

(29) Das, D.; Chatterjee, A.; Mandal, B. K.; Samanta, G., Chanda, B.;


(7), 827–832.

(32) Roy Chowdhury, T. Groundwater Arsenic Contamination in West
Bengal, India: Characterisation and Chemical Analysis of Bore-
hole Sediment Samples, Rotoevaporated Arsenic Rich Water
Residues and Present Status of Three Arsenic Affected Blocks
of 24-Parganas (North), Doctoral Dissertation, Jadavpur Uni-
vity, Calcutta, India, February 1999.

(33) Personal Communication, Alauddin, M. Chemistry Department,
Wagner College, City University of New York, USA.

(34) Groundwater Arsenic Contamination Status of Kalyani Mu-
unicipal Area, Nadia. A report by School of Environmental Studies,
Jadavpur University, Calcutta-700 032, India, September 1999.

(35) Comparative Study of Field Testing Kits with Field−AAS. A
report by School of Environmental Studies, Jadavpur University,
Calcutta-700 032, India, September 1999.

Received for review February 12, 2002. Revised manuscript
received September 23, 2002. Accepted September 25, 2002.
ES020591O