

TEMPORAL VARIATION OF INORGANIC ARSENIC IN GROUND-WATER OF TWO CONTAMINATED TUBEWELLS.

M. Alauddin¹, M. Nazibur Rahman², A.K.M. Munir^{2,3}, Golam Mahiyuddin³ and B. Belal Hossin³

¹Department of Applied Chemistry and Chemical Technology, Islamic University, Kushtia 7003, Bangladesh

²Department of Applied Nutrition and Food Science, Islamic University, Kushtia 7003, Bangladesh.

³Sono Diagnostic Center Environment Initiative, Courtpara, Kushtia, Bangladesh.

ABSTRACT

A study on the temporal variation of the inorganic arsenic concentrations, As(III) and As(V), in two selected tubewells in Kushtia municipality area was carried out over a period of one year, May, 1999 to April, 2000 (TW-A) in one case and August, 1999 to July, 2000 in another (TW-B). In this period, the initial total arsenic concentration was about 185 µg/L in TW-A and that in TW-B was 1276 µg/L. The range of variation was from 920 to 1581 µg/L in the Kalishankarpur, TW-B. In the Courtpara area, in TW-A, this range was 151-246 µg/L for the total arsenic concentration. In both the cases, the maximum fluctuations were observed during July-November in Courtpara and August-December in the Kalishankarpur area. Groundwater geochemistry may be considered responsible for these variations in two tubewells water located at a distance of about 1.5 km apart from the depths of 110-130 feet. In this case study, the ratio of As(III)/As(V) was found to vary between 50-70%. Similar observations have been reported for West Bengal, India.

INTRODUCTION

Groundwater is the main source of drinking water for millions of people of Bangladesh, particularly in the rural areas. In recent years arsenic contamination of this vital natural resource, exceeding the maximum contamination level (MCL) of 50 µg/L in the Bengal basin has been widely reported by different study groups¹⁻³. The contaminated water is widely hand pumped from a depth of 30-200 feet and there are about 2.5 million tube wells according to WHO estimate⁴, although the unofficial estimate is about 10 million. It is estimated that of the 125 million people of Bangladesh, between 35-77 million are drinking groundwater containing more than 50 µg/L MCL⁵. Although the cause of this reported contamination has not yet been definitely unfolded, the groundwater geochemical conditions are considered to be the factor for the mobilization of the soluble arsenic species in groundwater.

Most of the studies so far carried out in Bangladesh to assess the extent of the problem is concerned with the measurement of the total content of arsenic in water, determined mostly by field Kits, SDDC spectrophotometry and partly by FI-HGAAS methods without any

repetitive measurements as case studies. The present study was undertaken at this background to have a better understanding of the nature of the contamination problem. Previously, we reported speciation of arsenic by an electrochemical technique^{6,8} and also the evaluation of a simple arsenic removal method for groundwater purification by the same technique⁷. Because the electrochemical technique is extremely selective in the measurement of As(III) which is far more toxic than As(V) and both of which are the oxidation states of major arsenic species in groundwater, monitoring of these toxicants in groundwater supplies is an important issue related to public health hazards from drinking water. In this communication, we report the results of a limited case study on the temporal variation of As(III) and As(V) in two selected tubewells in Kushtia, contaminated with arsenic at the level of about 200 and 1200 µg/L of total arsenic, having average pH 6.7 and 6.8 respectively. The study was carried out for one year during 1999-2000 (May-April and August-July) for two cases.

* To whom correspondence should be made

STUDY AREAS AND NATURE OF TUBEWELLS

It is known that Kushtia is one of the most affected areas of Bangladesh where 30-60% of tubewells are contaminated with more than the maximum contamination level of total arsenic.^{3,8,9} In order to understand the temporal variation of inorganic arsenic in groundwater, two arsenic contaminated tubewells were selected at two different geographical locations, namely, Courtpara(TW-A) and Kalishankarpur (TW-B) in Kushtia municipality, having 15.9 sq. km. area, with a population of about 1,50,000, and there are about 3200 Tubewells in the municipality area (Source: Department of Engineering and Sanitation, Kushtia municipality). The depth of the tubewells are 110 and 130 ft. respectively. Both are in regular use for 10 years and representative of thousands of tubewells in this area.

EXPERIMENTAL

Apparatus: A Model HQ-2040G (Advanced Analytics, Virginia, USA) personal computer controlled electrochemical analyzer was used for the analytical measurements of arsenic. The functional details of instruments used in this study are described elsewhere.¹⁰⁻¹³ For arsenic analysis a staircase anodic stripping voltammetry (SASV) was used. Glass electrochemical cells with a Teflon top and Teflon magnetic stir bar were used throughout the experiment. The Teflon top also has provisions to insert a Teflon purging tube and micropipet tips for standard additions. A thin gold film coated glassy carbon (3.0 mm diameter) was used as the working electrode. The electrode preparation is discussed later. A platinum wire (53 mm long) directly immersed in test solution was used as the counter electrode. The reference electrode was a Ag/AgCl in saturated KCl isolated from the test solution by a porous Vycor junction. All electrode potentials mentioned here are referenced to this electrode.

Reagents and Chemicals: Primary standards of As(III) and As(V) were prepared from analaR grade As_2O_3 and $Na_2 HAsO_4$. All samples and reagents were prepared in distilled deionized water with trace metal grade HCl.

Metallic gold foil (purity 99.99%) was used for the preparation of Au^{3+} stock solution. AnalaR grade Na_2SO_3 (BDH), was used as the reductant for As(V). A 100 ppm ($\mu\text{g/mL}$) As(III) stock solution was prepared by dissolving As_2O_3 in a minimum volume 1.0 M NaOH solution and then diluted with 1.0 M HCl. Lower concentrations of standards, 50 ppm and 25 ppm As(III), were prepared by sequential dilution of the stock standard

Methods and Procedure: The method was similar to that of United States Environmental Protection Agency (USEPA) approved method no. 7063, based on anodic stripping voltammetry (ASV) for arsenic in water with improvements as follows.^{8,14} Au^{3+} solution prepared by dissolving 0.500 g Au in a minimum volume of aqua-regia (2.0 mL nitric acid and 6.0 mL HCl dropwise). The solution was carefully heated to reduce the volume to a minimum before spattering. Then 5 mL concentrated HCl was added and diluted to 100 mL in a volumetric flask. The solution was purged with water saturated nitrogen (99.99% pure) for 10 min. to remove the residual oxidizing impurities such as Cl_2 and NO_2 . The final solution was bright golden yellow in color.

The glassy carbon (GC) electrode was polished with 0.3 μ polishing grade alumina on a fine polishing pad to a mirror finish and rinsed for removing any adhering alumina particles. The gold deposition solution was prepared by adding 300.0 μL of gold stock solution into 12.0 mL. of 0.5 M HCl in the electrochemical cell. The solution was then purged with nitrogen for 10 minutes and a constant nitrogen flow was maintained above the solution. The gold film deposition was carried out at an initial deposition potential of -150 mV for 100 s without stirring. These conditions ensure steady-state reduction of Au^{3+} to metallic Au. The electrode potential was then returned to 500 mV and held there for a minute to ensure complete removal of trace metal impurities from the gold film. The procedure is generally repeated three times to obtain a shiny gold film on the GC electrode. A mirror underneath the cell was used to observe the bottom of the electrode without taking the electrode out of the solution. The

electrode was washed with 1.0 M HCl and stored hanging in an empty cell. The deposition solution was stored for future reuse. The gold electrode can be used for as many as 20 measurements before the response starts to diminish. Between analysis, the electrode was rinsed with a blank 6.0 M HCl solution to minimize carry over.

The groundwater samples from tubewells were collected in 250 mL high-density polyethylene bottles (treated overnight with distilled deionized water with HCl) containing 1.0 mL 32% HCl without a headspace. The tubewell was pressed for 10 minutes before the sample was collected. The sample collection and preservation procedure is very effective in retaining the As(III) and As(V) stable for months. Samples were collected and analyzed on the same day between 10 a.m. to 1 p.m. The measurement of total inorganic As was done by reducing As(V) to As(III) by Na_2SO_3 . For each 5.0 mL of 9.0 M HCl, 0.20 g of Na_2SO_3 was used. The solution was heated near boiling with occasional stirring unit all excess SO_2 fumes cleared. The accuracy of chemical reduction of As(V) to As(III) was found to be 5-20% at 10 ppb level. Blank experiment showed no detectable arsenic added in the reduction process.

Electrochemical Measurement Conditions :

For analysis, a 5.0 mL of tubewell water sample was mixed with 5.0 mL of 9.0 M HCl in the electrochemical cell and the solution was purged with nitrogen (99.99% from Bangladesh Oxygen Ltd.) for 10 minutes to remove dissolved oxygen from the solution. The nitrogen purge tube is placed near the top of cell and any bubbles adhering to the electrodes are tapped off. In the anodic stripping voltammetry (ASV), the following values for the experimental parameters are used; initial potential -150 mV, final potential 500 mV, step potential 5 mV, scan rate 50 mV/s, initial delay 120s, quiet time delay 30s. The deposited arsenic is stripped off the electrode by a linear potential ramp from -150 to 500 mV in the same solution while the oxidation current is recorded as a function of potential. The resulting staircase anodic stripping voltammogram (SASV) was used to measure the concentration of arsenic.

The method of standard addition was employed to eliminate matrix effect of solution. The electrochemical method can be used to measure As(III) in presence of As(V) at all concentrations. The analytical performance of the method can be summarized as follows: precision 1-10% relative standard deviation (rsd) of three replicate runs, accuracy 10% rsd (maximum) for 10 ppb at 95% confidence level for 120 s deposition time, dilution and aliquot addition errors 10% max, and sample carry over 0-4 ppb max. The analytical quality control of the method is maintained through quality control chart of analysis with the same method over a period, apart from independent method approach of analytical validation. Fig 1 (a, b) shows a typical stripping voltammograms and a standard additions plot. The sample was from TW-A.

RESULTS AND DISCUSSION

The temporal variation in arsenic contamination levels are reported in Table 1 and 2 for two locations in the Kushtia municipality area. The tubewells are located, at a distance of 1.5 km from each other and both of them are about 10 years old.

Table- 1: Analytical data for Arsenic contamination level of TW-A (study period: May 1999 to April 2000).

Month-Year	As(III) ppb	As(V) ppb	As(Total) ppb
May: 1999	78	107	185
Jun: 1999	95	115	210
Jul: 1999	101	104	205
Aug: 1999	83	93	176
Sep: 1999	65	86	151
Oct: 1999	110	114	224
Nov: 1999	98	114	212
Dec: 1999	89	121	210
Jan: 2000	92	98	190
Feb: 2000	114	121	235
Mar: 2000	96	99	195
Apr: 2000	116	130	246

In TW-B locality of Kalishankarpur, there are clinically identified arsenicosis patients and the use of the tubewell is discontinued. TW-A in Courtpara is located at the roadside is in regular use. Although both tubewells have water with 5 - 300 times the MCL, no case of arsenic

ical keratosis patient has been found in the locality of TW-A (Courtpara).

Table.2: Analytical data for Arsenic contamination level of TW-B (study period: August.1999 to July, 2000).

Month-Year	As(III) ppb	As(V) ppb	As(Total) ppb
Aug: 1999	670	606	1276
Sep: 1999	390	693	1083
Oct: 1999	308	942	1250
Nov: 1999	411	1170	1581
Dec: 1999	312	608	920
Jan: 2000	318	916	1234
Feb: 2000	381	755	1136
Mar: 2000	426	724	1150
Apr: 2000	418	801	1217
May: 2000	485	661	1146
Jun: 2000	413	526	939
Jul: 2000	449	844	1293

Tables 1 and 2 also show that the fluctuations on the total concentration of arsenic were maximum in TW- A during July - October and in TW-B during October - January. The ratio of As(III) to As(V) in both the tubewells varied between 50 and 70%. Similar results are also reported for the case of West Bengal, India.¹⁵

The presence of high proportions of As(III) in these groundwater is indicative of a reductive environment in the aquifer¹⁶. Whether the

As(III)- As(total) data could be used to characterize the geochemical condition of the aquifers is further explored in Figures 2 and 3.

Figure 2 shows that the tubewells are characterized by two clusters of data with significantly disparate As(III) even when they are measured at different months of the year. This is particularly true for TW-A. TW-A shows 50% of the total arsenic in the form of As(III) and TW-B has less than 50% of the same with less pronounced clustering. This is possibly an indication of two different processes of arsenic mobilization in groundwater. This is further explored in Figure 4 by the temporal variation plot of the ratio As(III)/As(total). The ratio indicates fraction of the total arsenic in the form of more toxic As(III). Here the months are counted incrementally starting from June 99. It clearly shows the oscillatory nature of the fluctuation of As(III)/As(V) with a cycle time of 4-5 months for TW-A with a constant average and a nearly constant amplitude.

A less regular oscillation is apparent for TW-B with the highest percent of As(III) concentration in January 2000. In comparison to TW-A, because TW-B is not in regular use, the As(III)/As(total) data may be influenced by usage history. Further studies are needed to

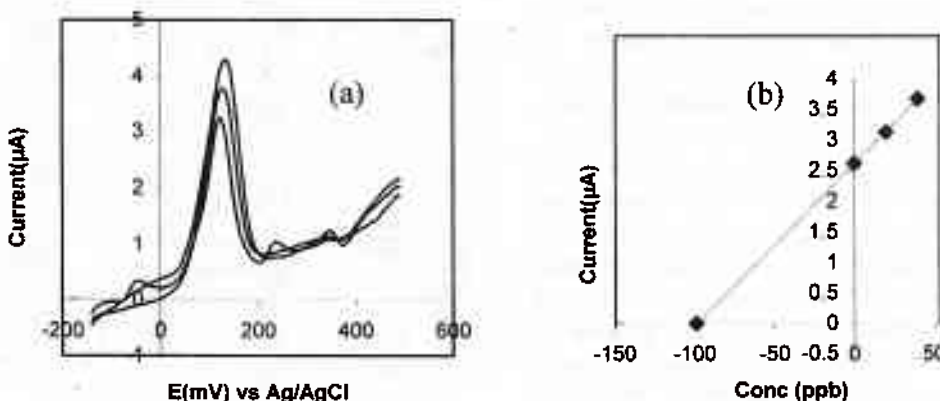


Fig 1. Plot showing (a) typical linear scan anodic stripping voltammograms of As(III) on a thin gold film coated glassy carbon electrode and (b) a standard addition plot for As(III) quantitation (sample was from TW-A collected on April 2000).

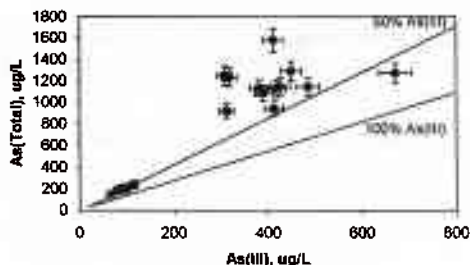


Fig 2 Speciation and abundance of As(III) as a function of As(total) for data in Table 1 and 2

seasonal water table depth, the water level of the nearby Ghorai river (branch of the Ganges) and the fluctuation of iron reducing bacteria.^{18,19} In particular, the presence of unusually high fraction of As(III) and high soluble iron Fe(II)⁷ in such samples could be indicative of the role of iron reducing bacteria in the reduction of arsenate to arsenite. This process may enhance the mobilization of arsenite in the groundwater because arsenite is less strongly bound to soil minerals such as hydrous ferric oxides¹⁷. The present study also demonstrates the utility of modern electrochemical technique in the study of arsenic measurement and speciation in a decentralized way which is not possible by other more expensive techniques such as FI-HGAAS, Furnace AAS and ICP-AES.

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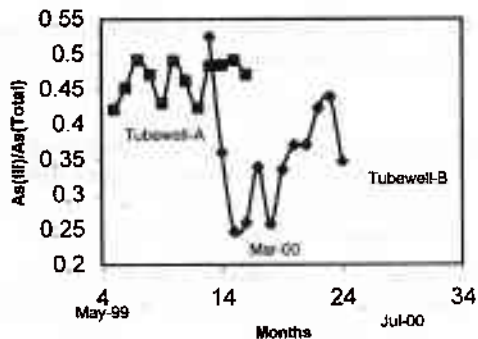


Fig 3 Monthly variation of As(III)/As(total) for tubewell-A and Tubewell-B

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