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ARSENIC CONTAMINATION IN GROUNDWATER: A STATISTICAL MODELING

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Abstract: High arsenic in natural groundwater in most of the tubewells of the Purbasthali- Block II area of Burdwan district (W.B, India) has recently been focused as a serious environmental concern. This paper is intending to illustrate the statistical modeling of the arsenic contaminated groundwater to identify the interrelation of that arsenic contain with other participating groundwater parameters so that the arsenic contamination level can easily be predicted by analyzing only such parameters. Multivariate data analysis was done with the collected groundwater samples from the 132 tubewells of this contaminated region shows that three variable parameters are significantly related with the arsenic. Based on these relationships, a multiple linear regression model has been developed that estimated the arsenic contamination by measuring such three predictor parameters of the groundwater variables in the contaminated aquifer. This model could also be a suggestive tool while designing the arsenic removal scheme for any affected groundwater.

Keywords: Arsenic; groundwater; statistical modeling; multivariate analysis.

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INTRODUCTION

Arsenic contamination of groundwater is a major public health concern in West Bengal and elsewhere (Rahman *et al.,* 2005). Millions of people have been exposed arsenic through drinking water that comes majorly from ground water (Duker *et al.,* 2005). Chronic toxicity of arsenic in human from arsenic contaminated drinking water occurs in 3417 villages over 111 blocks, primarily within 12 districts of this state (Mondal *et al.,* 2011), affecting more than 1.5 million of people (De, 2008) of which 25% are suffering arsenical skin lesions. The maximum permissible level of arsenic in drinking water recommended by World Health Organization (WHO) 0.01 mg/liter and in West Bengal it has been adjusted to 0.05 mg/liter by the local authorities. Drinking water arsenic concentration in West Bengal ranged from 0.05 to 3.5 mg/liter are reported on those affected zones which are in the vicinity of river Ganga (Das, 2008) and confined within the member delta zone of the upper delta plain. It has been reported by Nag *et al.* (1996) that water of the intermediate (second) aquifer is polluted with arsenic; though in some areas deep (third) aquifer has been detected where there is no clay partition between the second and third aquifer.

Drinking water arsenic contamination is originated from the natural release of arsenic through aquifer and sedimentary rocks (Zandsalimi *et al.,* 2011). The element is fundamental constitute of sulphide minerals of which pyrite like, arseniopyrite, FeAsS, (McGurie *et al.,* 2001) is the most abundant. Arsenopyrite is highly insoluble in water but due to anthropogenic activities (Aktar & Ali, 2011) it dissolved via oxygenation with formation of soluble arsenate and arsenite. In West Bengal arsenic species in contaminated drinking water were found to be arsenate and arsenite in 1:1 ratio (De, 2008). Pyrite oxidation has been proven to be the most acceptable hypothesis to explain the occurrence of arsenic in ground level water (Fazal *et al.,* 2001). Therefore, the occurrence of arsenic might be coupled with the presence of iron (Fe) in water. Analysis of such groundwater in arsenic bearing zones also indicated the presence of high contain of Fe (Nag *et al.,* 1996). This would strengthen the correlation between arsenic and iron concentration of ground water more rational. Though several authors also reported an interrelation of groundwater arsenic concentration with Static water level (SWL) (Welch & Stollenwerk, 2003), Depth (Chakraborti *et al.,* 2009), pH (Saxena *et al.,* 2004) and Age (time) of the wells (Fazal *et al.,* 2001) at a regional level.

Now a day, interest has been also grown in determining of antimony (Sb) in groundwater due to its similar chemio-toxicological properties (Gibel, 1997) with arsenic though Sb-induced toxicity is more violent vomiting in accompanied with watery diarrhea and sever weakness (Das, 2008). Antimony occurs with sulfur bed as same as arsenic, generally in the form of antimonite (Sb_2S_3) (Siepak *et al.,* 2004). The unstable Sb_2S_3 decomposed via atmospheric oxygenation with formation of soluble oxide minerals of antimony and migrated into groundwater (Ashley *et al.,* 2003) as a similar way of arsenic. In comparison to other toxic metals very little information exists on antimony in environmental sample, probably as a result of its low groundwater concentration, normally range from 0.1 to 0.2 µg/liter (WHO).

Then, for our present interest, a regional level groundwater quality survey in the Purbasthali- Block II area of Burdwan district (W.B, India) was conducted, which is identified as an arsenic polluted area (Biswas, 2010; Mondal *et al.,* 2011). Groundwater samples from different tube wells were collected from 33 affected villages of the study area (Mondal *et al.,* 2011). The purpose of this article is also to ascertain the possible interrelation of Arsenic, Sb, Fe, pH, Depth, SWL and Age of the tubewells through statistical modeling on the basic on such water samples.

MATERIALS AND METHODS

Water Sampling

One hundred and thirty-two tubewell water samples were collected from different locations of Purbasthali Block-II in Burdwan district, West Bengal, India, in the month of September to October, 2011. The samples were collected in pre-cleaned sterilized polyethylene bottles of one liter capacity following standard protocol. To avoid any contamination at the source, the samples were taken by holding the bottles at the bottom and drawn directly from the tubewell after water was allow running at least fifteen (15) minutes (Karthikeyan *et al.,* 2010). The water samples were immediately refrigerated after collection and brought to the laboratory with extreme care and preserved for further analysis.

Reagents and standards

Chemical of analytical grade were procured from M/S, Merck India Ltd; and used through the study without further purification. To prepare all reagents and standards, double distilled water was used. All glassware was cleaned by being soaked in 15% HNO_3 and rinsed with double distilled water. Each sample was analyzed three times and the results were found reproducible within ± 3 error limit.

Methodology

The sets of water samples were analyzed in the Departmental laboratory of Environmental Science, University of Burdwan (India). The total arsenic contain analysis were estimated by using of atomic absorption spectrophotometer (Model No. GBC HG 3000) into Ar-H_2 flame at 193.7 nm wavelength (De, 2008).

A UV-visible spectrophotometer (Systronics, Vis double beem Spectro 1203) with 1 cm quartz cell was used for spectrophotometric determination of Sb and Fe metals in water. The metal contains were estimated using N-phenylbeziumidylthiourea and Phenanthroline methods for Sb (Shrivas *et al.*, 2008) and Fe (De, 2008) respectively. The pH values of the water samples were examined at the site of sample collection with a portable pH meter (Eutech, pH Tester 30).

Other parameters of these samples like SWL, Depth and lowering year of the tubewells have been downloaded, as secondary data, from the official website of Public Health Engineering Department of West Bengal Government (WBPHED) web site, http://www.wbphed.gov.in/main/Static_pages/ArsenicReport/bardhaman.pdf. The lowering year of the tubewells help us to determine the Age of the tubewell with respect to the date of arsenic detection.

Statistical analysis of data

The analytical data was statically analyzed with the help of SPSS 7.5 and Minitab 15 (trial) software. The Minitab 15 was performed for modeling Principal Component and Cluster analysis along with the factor analysis of Scree plotting. SPSS 7.5 was only exploring to develop multi linear regression model.

RESULTS AND DISCUSSIONS

Analysis was preformed against 132 tubewell water samples collected from the study area with varied depths of 15, 27, 28, 30, 34, 35, 37, 43, 55, 71, 83 and 85 meter. The maximum arsenic concentration was found on that depths are 0.085, 0.027, 0.205, 0.012, 0.091, 0.019, 0.095, 0.076, 0.261, 0.191, 0.120 and 0.001 mg/liter, respectively. Out of 132 samples the concentration of arsenic in twenty-two samples and Sb in thirty-nine samples was recorded below detection limit. The pH values of the water samples shows that it is more or less neutral. The maximum Sb concentration was found 0.0651 μg/liter in 43 meter depth aquifer whereas maximum of Fe was reported in the 71 meter depth layer as 11.45 mg/ liter. The SWL of the tubewells are ranged from 6.00 to 24.54 meter. On the basis of the results of the various parameters, the following statistical modeling of ground water on the contaminated region is performed.

Loading Plot of Principal Component Analysis

The loading plot displays the relation among the variables. The loading are the weight combining of the original variable to from the scorer. The loading plot shows the orientation of the obtained plane in relation to the original variable. Hence the loading plot of the principal component analysis based on two principal components may explain notably the variances of the nature and influences of the selected variables. The loading plot of the principal component analysis portrays very well with the correlations of the water parameters in **Fig. 1**. The parameters are symbolized by vectors which have only been indicated for a few variables to avoid cluttering the plot. Variables that are most important for the model are found on the periphery of the loading plot. Conversely, non-influential variables are encountered around the origin of plot (0,0). Parameters having significant influences on arsenic have noticeably been found to make clusters among themselves. This strong relationship of Arsenic with other parameters such as Fe and SWL can explicitly be visualized in the lower right quadrant of the graph plot (**Fig. 1**). Similar observations have also been reported by other investigators Chakraborti *et al.* (2009) and Mondal *et al.* (2011), respectively.

Furthermore, the direction and magnitude of each vector indicates its importance as a constituent of the samples lying in the direction in which the vector points. Adversely the parameters particularly Time and pH in the upper right and left quadrant are less correlated vector cluster of the graph which only enriching the plotting. Dissolved Sb and Depth vectors

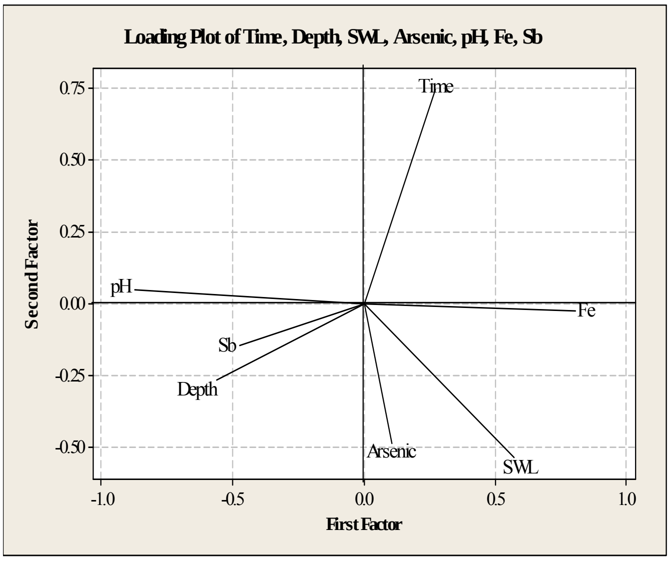

Fig. 1 Loading plot of the principal component analysis of the studied groundwater.

also point in the direction of the lower left quadrant in the plot. However, these variables do not directly correlated with Arsenic but indicating that the water samples contain more Sb at higher Depth. These findings are very much consistent with the hierarchical cluster analysis that can be found elsewhere.

Hierarchical Cluster Analysis

The purpose of the hierarchical cluster analysis was defined a cluster solution or small number of cluster solutions that could be analyzed by the hierarchical procedure to identify a single final cluster solution. The clustering algorithm in a hierarchical procedure determines how similarity is defined between multiple-member clusters in the clustering process. By using hierarchical cluster analysis, variable were interrelated to each other according to the maximum similarities. Ward's method is the most popular hierarchical algorithm and is recommended as distance measures of clustering. Plot of hierarchical cluster with Ward's linkage is portrayed in **Fig. 2**. The Ward's method of hierarchical cluster analysis which was used in this study has the advantage of not demanding any prior knowledge of the number of clusters which the non-hierarchical method does.

Cluster analysis suggests two groups in the dendrogram. The Group-I is composed by Time, SWL, Fe, Arsenic and reflected the stronger correlation that may exist among the parameter in the same cluster. The similarity level between SWL-Fe, Time–SWL, Time-Arsenic are displayed in the dendrogram. The position of SWL-Fe in the same cluster and Depth-pH in Group-II also reflected their very much distinguishable characteristics among the pair in compare too other parameters. Time here is seen to be linked with arsenic also indicate the oxidative dissolution of arsenic mineral which may again be consider to release of arsenic in ground water as a time variable parameter. The same phenomenon is endorsed by Fazal *et al.* (2001).

Group-II is represented by the stream of Depth, pH and Sb. The similarity level between Depth and Sb is 53.65, showing that the release of Sb is depth dependent. Cluster analysis strongly supports the observation that was found in the loading plot analysis.

Scree Plot of Factor Analysis

Factor analysis was used to determinate the relative relationship between arsenic and other water parameters. The main aim of factor analysis us to explain the variation in a multivariate data set by as few factors and also to detect the hidden structure of the multivariate data. Factor analysis when applied to the widely different set of sample data appears to be the moderately successful as a statistical tool for examining the relationship between the variables within a data set.

Scree plot of eigenvalues (**Fig. 3**) is the most acceptable method of this analysis. The Scree plot is a graph of each eigenvalue (Y axis) against the factor with which it is associated (X axis). Contribution of factor is said to be significant when the corresponding eigenvalue is greater than 0.8 (Keshavarzi *et al.*, 2010).

Scree plot (**Fig. 3**) displayed that four (4) factors such as Time, SWL, Fe and Arsenic are very much significant contributor with eigenvalues 2.37, 1.17, 1.10 and 0.88 respectively. The solution using the eigenvalues in four components which represent

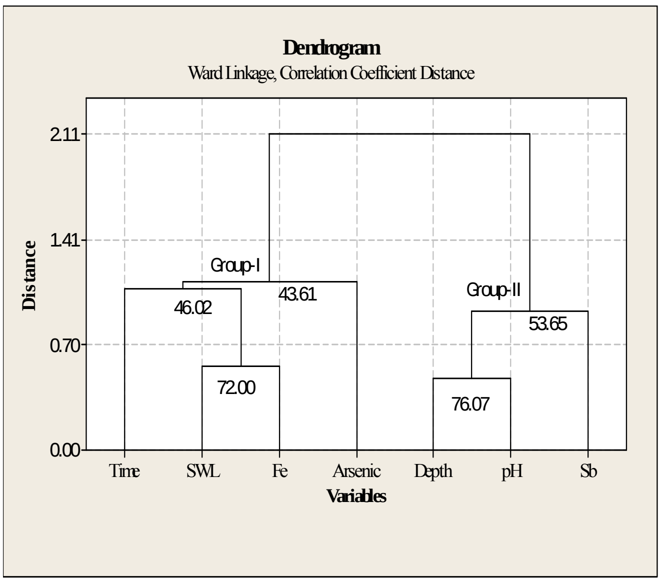

Fig. 2 Hierarchical cluster analysis of the studied groundwater.

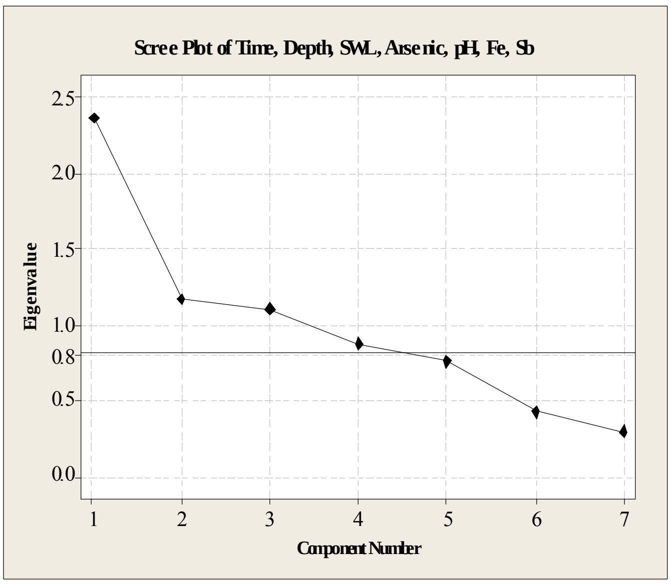

Fig. 3 Scree plot of factor analysis of the studied groundwater.

78.86% total cumulative variance shows that suitable factor analysis with scree plotting. This plot motivated us to also use the standard multiple regression analysis as to the effect of the other three independent variables on arsenic and to design a mathematical relation.

Multiple Linear Regression Model

Generally a multiple regression analysis attempts to fit the independent variables for predicting a single dependent variable. In our data 3 censor variables are observed from scree plot analysis (**Fig. 3**). This motivated us to also use the multiple regression analysis as to the effect of the independent variables on arsenic.

The multiple regression model has the general form:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \ldots\ldots.. + \varepsilon$$

where X_1, X_2, X_3 denote the independent variables, Y stands for the dependent variable, β_0, β_1, β_2, β_3 represent the correlation coefficients, and ε designates the error term.

The final fitted model based on the multiple regression approach is

$$\text{Arsenic} = 9.528\times10^{-2} - 5.93\times10^{-4}\,\text{Fe} + 1.01\times10^{-4}\,\text{SWL} - 4.82\times10^{-4}\,\text{Age of the tubewells}$$

From this model it clearly results that Fe, SWL and the Age of the wells are very much significant for the arsenic contamination at groundwater level. This model may suggest the prediction of the arsenic contamination by measuring these thre predictor parameters of the groundwater variables in any contaminated aquifer. This model may also be a suggestive tool in predicting arsenic contamination level while designing the arsenic removal activities by the Environmental Scientists.

CONCLUSION

In this study three multivariate analyses (Principal Component, Cluster and Factor analysis) have been applied in order to study the effect of some groundwater parameters on arsenic contamination level. These models are found to be highly significant. From these models it clearly demonstrated that out of seven variables four of them like SWL, Fe, Arsenic and Age of the tubewells are closely interrelated with each other. Multiple regression model has been developed as a predictor model to perceive an estimation of the arsenic contamination level by measuring the three predictor parameters of the groundwater variables in any contaminated aquifer. Then, further research focusing on these variables will be helpful to guide the Environmental Scientists to design an efficient arsenic removal plan while treating the groundwater that may have contaminated badly with that.

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