

## Metal contents in the groundwater of Sahebgunj district, Jharkhand, India, with special reference to arsenic

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### Abstract

A detailed study has been presented on groundwater metal contents of Sahebgunj district in the state of Jharkhand, India with special reference to arsenic. Both tubewell and well waters have been studied separately with greater emphasis on tubewell waters. Groundwaters of all the nine blocks of Sahebgunj district have been surveyed for iron, manganese, calcium, magnesium, copper and zinc in addition to arsenic. Normal distribution statistic, exploratory data analysis and robust Z-score analysis have been employed to find out the distribution pattern, localisation of data, outliers and other related information. Groundwaters of three blocks of Sahebgunj, namely, Sahebgunj, Rajmahal and Udhawa have been found to be alarmingly contaminated with arsenic present at or above 10 ppb. Arsenic distribution patterns in these blocks are highly asymmetric in nature with the common feature of increasing width from first to fourth quartile. A very broad fourth quartile in each case represents a long asymmetric tail on the right of the median. Tubewell waters of at least two more blocks require regular monitoring to identify the outbreak of arsenic at the onset. Groundwaters of Sahebgunj district in general contain high iron and manganese. It is by and large soft in nature. Well waters have been found to be better with regard to arsenic but iron and manganese contents do not vary significantly. Normal distribution analysis (NDA), box and whisker (BW) plot and Z-score analysis together can provide a reasonably complete statistical picture of metal contents in Sahebgunj district groundwaters.

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### 1. Introduction

Groundwater arsenic contamination in West Bengal, India and adjoining Bangladesh is well publicised and perhaps one of the most grotesque natural calamities

of the world related to drinking water. An isolated observation in the mid eighties confined to a few families from one village of 24 Parganas district in West Bengal (Garai et al., 1984) snowballed into an international crisis involving two countries and endangering millions of people. The spread and depth of groundwater arsenic contamination in India and Bangladesh may be gauged from the following statistics. According to a recent survey carried out by School of Environmental Studies (SOES), Jadavpur University, Kolkata, groundwaters of 2700 villages in 9 districts out of a total of 18 in

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West Bengal are arsenic contaminated (arsenic content  $\geq 50$  ppb). About six million people from these districts having a total population of 42 million are consuming arsenic contaminated water and about 30000 of them are threatened with visible symptoms of arsenic poisoning. In Bangladesh, groundwaters of 2000 villages in 50 out of a total of 64 districts have been identified as containing arsenic above permissible level of 50 ppb (Chakraborti et al., 2002).

Recently Chakraborti et al. (2003) surveyed groundwaters of a village in Bhojpur district in Bihar, India situated in the middle Ganga plain of upstream Ganga. Integrated investigations on water quality, pathological and neurological manifestations established the presence of very high concentration of arsenic in tubewell waters of the particular village and its adverse impact on health. Based on these observations combined with an earlier report (Datta and Kaul, 1976) and some additional recent findings by other researchers (Tandukar et al., 2001), Chakraborti and co-workers tried to sensitise about the possible future danger of more arsenic outbreaks. According to them this arsenic belt may stretch over the entire upper, middle and lower Ganga plain.

Sahebgunj is one of the 22 districts in the state of Jharkhand situated on the western bank of river Ganges, facing Maldah district in the eastern bank. Maldah is one of the nine arsenic affected districts of West Bengal and perhaps one of the worst hit. While Maldah came into limelight during nineties in connection with groundwater arsenic contamination, Sahebgunj remained unnoticed. During 1998, a group of researchers from National Metallurgical Laboratory, Jamshedpur visited Sahebgunj for a field survey in a limited scale. The terms of reference were water quality with focus on arsenic, probable epidemiological evidence and people's feedback on water quality and health. Based on that study a more rigorous survey was undertaken to assess the groundwater quality of Sahebgunj district during 1999–2000 with special reference to arsenic.

Metal contents in the groundwaters of Sahebgunj district with focus on arsenic have been presented in this communication. The inferences presented are based on statistical analyses of the raw data. Statistical tools included normal distribution analysis (NDA), exploratory data analysis (EDA) and robust Z-score analysis. Outliers in statistical analysis have been accorded special significance in the present study. These are the values different from the rest of the group but are not necessarily due to erroneous measurements. On the contrary they represent the samples where maximum intervention may be required. The primary objective of this study was to present a statistically meaningful water quality database of Sahebgunj district with focus on arsenic and the secondary objective was to identify an appropriate statistical tool for this job.

## 2. Methodology

### 2.1. Study area

Sahebgunj is one of the 22 districts in the state of Jharkhand. It is located on the western bank of river Ganges facing Maldah district on the eastern bank in West Bengal. Fig. 1 shows the political boundary of Sahebgunj district. Sahebgunj shares land border with Bihar and river border with Bihar and West Bengal. Total area of Sahebgunj district is 160000 hectares and its population is less than one million. Sahebgunj district is divided into nine community development blocks, namely, Sahebgunj, Rajmahal, Taljhari, Udhawa, Barharwa, Pathna, Barhait, Borio and Mandro. Positions of these blocks have also been shown in Fig. 1. Tubewell and well samples were collected from each of these blocks and water quality data presented in this paper cover all these nine community developed blocks. This may be noted that the Sahebgunj district also has a community development block named Sahebgunj. To avoid confusion Sahebgunj district will be referred as Sahebgunj(D) and Sahebgunj block as Sahebgunj(B) in the text.

Sahebgunj(D) constitutes a part of the vast expanse of Gangetic plains and its morphology and surficial geology bear characteristic signatures of Gangetic delta. It consists of silts, clays and sands in the form of river

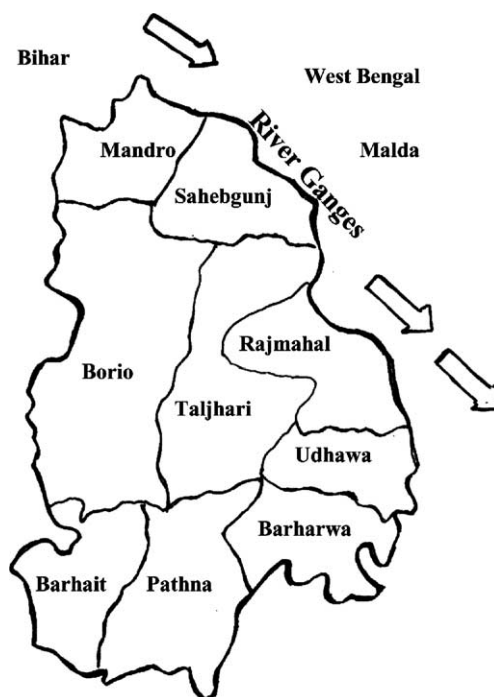


Fig. 1. Political boundary of Sahebgunj(D) district.

terraces and extends some thousands of metres below the surface. The age of these sediments range from Pleistocene to recent and they are believed to have been derived from the Himalayas and higher peninsular up-lands. It is also believed that Rajmahal trap rocks of upper jurassic to early cretaceous age, which are exposed further east and south of Sahebgunj, could have contributed significantly towards the sedimentation of this area (Krishnan, 1982; Kumar, 1985).

### 3. Sampling methodology

Samples were collected from each of the nine blocks. Emphasis was paid on tubewell samples but well samples were also collected. Sampling was based on an earlier survey carried out by the present group of investigators as mentioned in the introduction and also on the feedback received from local inhabitants regarding water quality and health. Each sample was stabilised with 1–2 drops of  $\text{HNO}_3$  immediately after collection.

### 4. Arsenic and other elemental analysis

Arsenic was the focal point in this study. However, in addition to arsenic all water samples were also analysed for Fe, Mn, Ca, Mg, Cu and Zn.

### 5. Instrumental

Arsenic was analysed by HG-AAS technique (Maity et al., 2004) using a GBC 908AA atomic absorption spectrometer. Same equipment was used for estimating Fe, Mn, Ca, Mg, Cu and Zn.

### 6. Statistical analysis

Sample data were subjected to statistical treatment using normal distribution statistic, exploratory data analysis (EDA) and robust Z-score statistic. Details of these may be found in standard books on statistics and software packages. Given below are some of the important features of these techniques that were used in the present study.

#### 6.1. Normal distribution analysis (NDA)

A univariate data set may be represented as,

$$\{x_1, x_2, \dots, x_i, \dots, x_n\}$$

$x_i$  in the present context means a parameter  $x$  for the  $i$ th water sample.  $x_i$  may be arsenic, iron or any other element in the scope of the present study. This univariate data set may be expressed by the normal distribution function,

$$y = f(x, \mu, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\left[\frac{(x-\mu)^2}{2\sigma^2}\right]} \quad (1)$$

$\mu$  and  $\sigma$  are known as sample mean and standard deviation respectively and are expressed as,

$$\mu = \bar{x} = \frac{1}{n} \sum_i x_i \quad (2)$$

$$\sigma = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{(n-1)}} \quad (3)$$

Some more statistical estimates derived from the normal distribution mentioned above (Eq. (1)) were also made in the present study for analysing water quality data and have been shown below.

#### 6.1.1. Sample variance ( $\sigma^2$ )

Sample variance is given as the square of the standard deviation.

#### 6.1.2. Kurtosis

Kurtosis is an indicator of the relative sharpness or flatness of the peak compared to normal distribution. Positive kurtosis indicates a sharp distribution while negative kurtosis indicates a flat one. Kurtosis may be calculated as

$$\text{Kurtosis} = \left[ \frac{n(n+1)}{(n-1)(n-2)(n-3)} \sum_i \left( \frac{x_i - \bar{x}}{\sigma} \right)^4 - \frac{3(n-1)^2}{(n-2)(n-3)} \right] \quad (4)$$

#### 6.1.3. Skewness

Skewness typifies level of asymmetry of a distribution around its mean. Positive skew indicates an asymmetric tail extending towards higher values while a negative skew is a pointer towards an asymmetric tail extending towards lower values. Skewness may be calculated as

$$\text{Skewness} = \frac{n}{(n-1)(n-2)} \sum_i \left( \frac{x_i - \bar{x}}{\sigma} \right)^3 \quad (5)$$

#### 6.2. Exploratory data analysis (EDA) (Meloun et al., 1992)

Exploratory data analysis is a first contact tool that helps in identifying basic statistical features of the data set, some of which may not be apparent otherwise, especially for a large data set. EDA also helps in extracting dormant and not so obvious features through visual displays. These may be conformance to or deviation from normal distribution, localisation or scattering of data, a typical distribution kernel etc.

### 6.2.1. Order statistics, quantiles and letter values

An exploratory data analysis (EDA) for a univariate data set commences with its ordering, normally in ascending order. The data set  $\{x_1, x_2, \dots, x_n\}$  may be sorted in ascending order and the order statistics is,

$$\{x_{(1)} < x_{(2)} < x_{(3)} \dots < x_{(n)}\}$$

$P_i$ th sample quantile (or percentile) is the value of  $x$  below or at which  $100 \times P_i\%$  of the sample values lie.  $P_i$ th quantile is given as

$$x_{P_i} = x_{(j)} \quad \text{where } j = (n+1)P_i \quad (6)$$

$j$  may also be a non-integer lying between two integers  $m$  and  $m+1$ .  $P_i$ th quantile,  $x_{P_i}$  in that case may be interpolated between  $x_{(m)}$  and  $x_{(m+1)}$  by the formula,

$$x_{P_i} = x_{(m)} + (j-m)(x_{(m+1)} - x_{(m)}) \quad (7)$$

In the present study,  $P_i$  is calculated as,

$$P_i = \frac{i}{n+1} \quad (8)$$

$P_i$  at 25% is called first quartile, at 50% second quartile and at 75% third quartile.  $P_i$  is also known as the cumulative probability function which lies in the range  $0 < P_i < 1$  for  $i = 1, \dots, n$ .

### 6.2.2. Letter values

Letter values are used to mark different points in the ordered statistic axis based on quartile values. Fig. 2 shows some of the conventional letter values. Acceptability/rejection of any data may be based on their relative position with the letter values.

### 6.2.3. Dot and jittered dot diagram

Dot diagram is a one-dimensional scatter plot of univariate data on  $X$ -axis. Letter values superimposed on

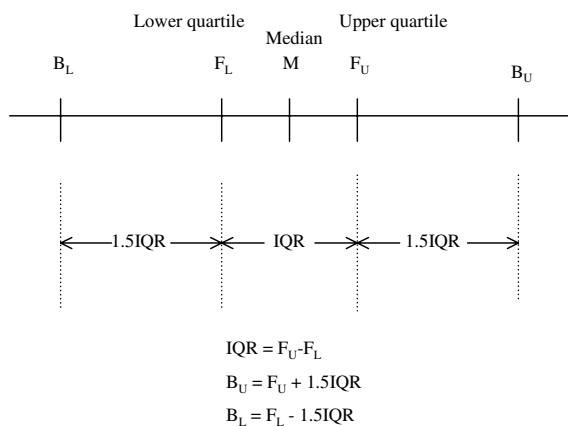


Fig. 2. Schematic representation of letter values.

dot diagrams indicate local concentrations of data, outliers and extremes. Two dimensional dot diagrams with a small interval of random members along  $Y$ -axis represents a jittered dot diagram.

### 6.2.4. Box and whisker (BW) plot

Box and whisker (BW) plot is a variation of dot diagram drawn as a box and two whiskers on two sides of the median based on five letter values,  $M$ ,  $F_L$ ,  $F_U$ ,  $B_L$  and  $B_U$ . BW plot helps in visual representation of spread and skewness of sample data, identification of outliers and illustration of asymmetric distribution tails on either side of the distribution.

### 6.2.5. Quantile plot

Plot of order statistics  $x_{(i)}$  against cumulative probability function,  $P_i$  is known as quantile plot and the function describing it is called quantile function  $Q(P)$ . For any value  $\alpha$  in the interval  $[0, 1]$ ,  $100\alpha$ th quantile  $x_\alpha$  may be calculated by linear interpolation.

$$x_\alpha = x_{(i)} + (n+1) \left[ \alpha - \frac{i}{n+1} \right] (x_{(i+1)} - x_{(i)}) \quad (9)$$

$$\text{where } \frac{i}{n+1} \leq \alpha \leq \frac{i+1}{n+1}.$$

A quantile plot helps in making a quick comparison of the sample distribution with a normal one. A normal distribution should yield a symmetric S-type quantile plot.

### 6.2.6. Midsum plot

Midsum of a dataset may be calculated as,

$$MS_i = ((x_{(n+1-i)} + x_i)/2) \quad (10)$$

Plot of  $MS_i$  against the ordered statistic  $x_{(i)}$  gives the midsum plot. Midsum plot of a symmetric distribution should yield a horizontal line  $y = M$  (median). Midsum helps in identifying the deviation of data from normal distribution.

### 6.3. Robust Z-score analysis (NATA, 2002)

Robust Z-score statistic is normally employed to a data set that has wide variations within. This does not get greatly influenced by extreme values. On the contrary, it serves as an efficient and robust filter for acceptable values, leaving behind the outliers.

In robust Z-score statistic each data point is ascribed a normalised score, a Z-score, which indicates the deviation of the data point from the median value. Z-score of a data point beyond a critical value entails the point as an outlier.

Robust Z-score analysis has proved to be a very efficient tool in proficiency testing programmes involving inter and intra laboratory collaborations (NATA,

2002). Z-score analysis was also exploited in a different context to ascertain endogenic mineral element compositions of eight common spices (Gupta et al., 2003) and a tropical medicinal plant (Bhattacharjee et al., 2004).

Z-score analysis starts with order statistic and identification of median ( $M$ ), quartile values ( $F_U$  and  $F_L$ ) and interquartile range  $IQR(F_U - F_L)$ .

Interquartile range is further normalised and a normalised IQR (NIQR) is defined as,

$$NIQR = 0.7413 \cdot IQR \quad (11)$$

The factor 0.7413 comes from the standard normal distribution, which has a zero mean and standard deviation equal to 1. The width of IQR of such a distribution is 1.34898 and  $1/1.34898 = 0.7413$ .  $Z_i$ , the Z-score for the  $i$ th data point in the ordered statistics may be calculated as,

$$Z_i = (x_{(i)} - M)/NIQR \quad (12)$$

Conventionally any  $Z_i$  greater than 3 or less than  $-3$  is classified as an outlier. This, however, is a flexible criterion and may be redefined by the user. The data set may be pruned by excluding the outliers and a fresh pair of mean and median may be calculated.

By outlier one normally understands a data point, which is grossly odd in a set of otherwise conforming data. This may happen due to several reasons such as faulty instrumentation, non-representative sample, inaccurate measurement, to name a few. In the present context, however, the term outlier has a different connotation and a greater significance. Since care was taken to exclude instrumental or personal errors, outliers represented extreme values representing water samples containing the element under question present at an undesirable quantity.

## 7. Results and discussion

Table 1 gives a summary of the samples collected from each block. A total of 1535 water samples were collected of which about 1317 (~85.8%) were tubewell samples and 218 (~14.2%) were from wells.

Table 2 presents a comparison of different international drinking water norms with regard to As, Fe, Cu, Mn, Zn and hardness (WHO, 1971; HACH, 2003). WHO (1971) proposes two norms, namely, highest desirable and maximum permissible, based on which three levels were defined. Any parameter below highest desirable level was marked as 'Safe', between highest desirable and maximum permissible level as 'Alert' and above permissible level marked as 'Toxic'.

Based on these criteria, all collected Sahebgunj water samples (Table 1) were categorised as safe, alert or toxic with respect to each of the parameters mentioned in Table 2, a summary of which has been presented in Table 3.

Table 1  
Block wise sample collection summary

| Block name   | Number of samples | Sources  |      |
|--------------|-------------------|----------|------|
|              |                   | Tubewell | Well |
| Barhait      | 68                | 62       | 6    |
| Barharwa     | 331               | 300      | 31   |
| Borio        | 237               | 178      | 59   |
| Mandro       | 51                | 51       | 0    |
| Pathna       | 142               | 134      | 8    |
| Rajmahal     | 219               | 180      | 39   |
| Sahebgunj(B) | 169               | 151      | 18   |
| Taljhari     | 149               | 136      | 13   |
| Udhawa       | 169               | 125      | 44   |
| Total        | 1535              | 1317     | 218  |

Table 2  
Comparative drinking water guidelines<sup>a</sup>

| Parameter | USEPA,<br>Maximum<br>contaminant<br>level,<br>mg/l (ppm) | Canada,<br>Maximum<br>acceptable<br>concentration,<br>mg/l (ppm) | EEC,<br>Maximum<br>admissible<br>concentration,<br>mg/l (ppm) | Japan,<br>Maximum<br>admissible<br>concentration,<br>mg/l (ppm) | WHO<br>guideline<br>mg/l (ppm) | WHO guideline <sup>b</sup>          |                                       |
|-----------|----------------------------------------------------------|------------------------------------------------------------------|---------------------------------------------------------------|-----------------------------------------------------------------|--------------------------------|-------------------------------------|---------------------------------------|
|           |                                                          |                                                                  |                                                               |                                                                 |                                | Highest<br>desirable,<br>mg/l (ppm) | Maximum<br>permissible,<br>mg/l (ppm) |
| As        | 0.05                                                     | 0.025                                                            | 0.05                                                          | 0.01                                                            | 0.01                           | 0.01                                | 0.05                                  |
| Cu        | 1.3                                                      | 2.0                                                              | 2.0                                                           | 1.0                                                             | 1–2                            | 0.05                                | 1.0                                   |
| Fe        | 0.3                                                      | 0.2                                                              | 0.2                                                           | 0.3                                                             | 0.3                            | 0.1                                 | 1.0                                   |
| Mn        | 0.05                                                     | 0.05                                                             | 0.05                                                          | 0.01–0.05                                                       | 0.1–0.5                        | 0.05                                | 0.5                                   |
| Zn        | 5                                                        | 5.0                                                              | –                                                             | 1.0                                                             | 3.0                            | 5                                   | 15                                    |
| Ca        | –                                                        | –                                                                | –                                                             | –                                                               | –                              | 40                                  | 200                                   |
| Mg        | –                                                        | –                                                                | –                                                             | –                                                               | –                              | 30                                  | 150                                   |
| Hardness  | –                                                        | –                                                                | 50                                                            | 300                                                             | –                              | –                                   | –                                     |

<sup>a</sup> HACH (2003).

<sup>b</sup> WHO (1971).

Table 3

Summary of Safe (S), alert (A) and toxic (T) samples in Sahebgunj(D) district in percentage

| Element | Block        | Tubewells |      |      | Wells |      |      |
|---------|--------------|-----------|------|------|-------|------|------|
|         |              | S         | A    | T    | S     | A    | T    |
| As      | Barhait      | 100       | 0    | 0    | 100   | 0    | 0    |
|         | Barharwa     | 100       | 0    | 0    | 100   | 0    | 0    |
|         | Borio        | 100       | 0    | 0    | 100   | 0    | 0    |
|         | Mandro       | 100       | 0    | 0    | 0     | 0    | 0    |
|         | Pathna       | 99.3      | 0.7  | 0    | 100   | 0    | 0    |
|         | Rajmahal     | 82.3      | 13.9 | 3.8  | 84.6  | 2.8  | 2.6  |
|         | Sahebgunj(B) | 83.4      | 7.3  | 9.3  | 94.4  | 5.6  | 0    |
|         | Taljhari     | 99.3      | 0.7  | 0    | 100   | 0    | 0    |
| Fe      | Udhawa       | 83.2      | 14.4 | 2.4  | 86.4  | 13.6 | 0    |
|         | Barhait      | 8.0       | 22.6 | 69.4 | 16.7  | 33.3 | 50   |
|         | Barharwa     | 15.3      | 41.4 | 43.3 | 29    | 42   | 29   |
|         | Borio        | 18.5      | 48.9 | 32.6 | 27.1  | 47.5 | 25.4 |
|         | Mandro       | 31.4      | 35.3 | 33.3 | 0     | 0    | 0    |
|         | Pathna       | 31        | 43   | 26   | 12.5  | 62.5 | 25   |
|         | Rajmahal     | 21.6      | 47.8 | 31.6 | 30.8  | 33.3 | 35.9 |
|         | Sahebgunj(B) | 19.8      | 54.9 | 25.3 | 27.8  | 61.1 | 11.1 |
| Ca      | Taljhari     | 33.1      | 42.6 | 24.3 | 53.8  | 38.5 | 7.7  |
|         | Udhawa       | 22        | 54   | 24   | 13.6  | 54.6 | 31.8 |
|         | Barhait      | 95.2      | 4.8  | 0    | 100   | 0    | 0    |
|         | Barharwa     | 81        | 18   | 1    | 51.6  | 48.4 | 0    |
|         | Borio        | 80.3      | 19.7 | 0    | 84.7  | 15.3 | 0    |
|         | Mandro       | 68.6      | 31.4 | 0    | 0     | 0    | 0    |
|         | Pathna       | 73        | 25   | 2    | 75    | 25   | 0    |
|         | Rajmahal     | 41.5      | 56.5 | 2    | 53.8  | 41   | 5.2  |
| Mg      | Sahebgunj(B) | 35.1      | 60.9 | 4.0  | 38.9  | 44.5 | 16.6 |
|         | Taljhari     | 20.6      | 72   | 7.3  | 7.7   | 84.6 | 7.7  |
|         | Udhawa       | 15        | 81   | 4.0  | 6.8   | 88.6 | 4.6  |
|         | Barhait      | 98.4      | 1.6  | 0    | 83.3  | 16.7 | 0    |
|         | Barharwa     | 83.3      | 16   | 0.7  | 67.7  | 32.3 | 0    |
|         | Borio        | 84.3      | 15.7 | 0    | 89.8  | 10.2 | 0    |
|         | Mandro       | 72.5      | 27.5 | 0    | 0     | 0    | 0    |
|         | Pathna       | 76.1      | 23.9 | 0    | 62.5  | 37.5 | 0    |
| Mn      | Rajmahal     | 68.3      | 32.2 | 0.5  | 76.9  | 23.1 | 0    |
|         | Sahebgunj(B) | 56.9      | 43.1 | 0    | 38.9  | 61.1 | 0    |
|         | Taljhari     | 51.5      | 48.5 | 0    | 61.5  | 38.5 | 0    |
|         | Udhawa       | 54.4      | 45.6 | 0    | 34.1  | 65.9 | 0    |
|         | Barhait      | 20.9      | 50   | 29.1 | 16.7  | 66.7 | 16.6 |
|         | Barharwa     | 43        | 45.3 | 11.7 | 77.4  | 16.1 | 6.5  |
|         | Borio        | 56.7      | 33.2 | 10.1 | 50.8  | 40.7 | 16.5 |
|         | Mandro       | 45.1      | 47.1 | 7.8  | 0     | 0    | 0    |
| Zn      | Pathna       | 58.9      | 38.8 | 2.9  | 62.5  | 25   | 12.5 |
|         | Rajmahal     | 38.8      | 37.2 | 25   | 48.7  | 35.9 | 15.4 |
|         | Sahebgunj(B) | 51.6      | 38.4 | 10   | 38.9  | 33.3 | 27.8 |
|         | Taljhari     | 38.3      | 46.3 | 15.4 | 53.8  | 46.2 | 0    |
|         | Udhawa       | 42.4      | 38.4 | 20.2 | 34.1  | 34.1 | 31.8 |
|         | Barhait      | 100       | 0    | 0    | 100   | 0    | 0    |
|         | Barharwa     | 98.3      | 1.7  | 0    | 96.8  | 3.2  | 0    |
|         | Borio        | 100       | 0    | 0    | 100   | 0    | 0    |
|         | Mandro       | 100       | 0    | 0    | 0     | 0    | 0    |
|         | Pathna       | 100       | 0    | 0    | 100   | 0    | 0    |
|         | Rajmahal     | 98.9      | 1.1  | 0    | 100   | 0    | 0    |
|         | Sahebgunj(B) | 98.7      | 1.3  | 0    | 38.9  | 33.3 | 27.8 |
|         | Taljhari     | 98.5      | 1.5  | 0    | 100   | 0    | 0    |
|         | Udhawa       | 100       | 0    | 0    | 100   | 0    | 0    |

Table 3 (continued)

| Element | Block        | Tubewells |      |     | Wells |      |     |
|---------|--------------|-----------|------|-----|-------|------|-----|
|         |              | S         | A    | T   | S     | A    | T   |
| Cu      | Barhait      | 96.8      | 3.2  | 0   | 100   | 0    | 0   |
|         | Barharwa     | 93        | 6.7  | 0.3 | 93.5  | 6.5  | 0   |
|         | Borio        | 93.3      | 6.7  | 0   | 91.5  | 6.8  | 1.7 |
|         | Mandro       | 92.2      | 7.8  | 0   | 0     | 0    | 0   |
|         | Pathna       | 85.1      | 14.9 | 0   | 100   | 0    | 0   |
|         | Rajmahal     | 83.9      | 16.1 | 0   | 84.6  | 15.4 | 0   |
|         | Sahebgunj(B) | 93.4      | 6.6  | 0   | 100   | 0    | 0   |
|         | Taljhari     | 89        | 11   | 0   | 92.3  | 7.7  | 0   |
|         | Udhawa       | 88        | 12   | 0   | 93.2  | 4.5  | 2.3 |

### 7.1. Tubewell waters

#### 7.1.1. Arsenic

It may be seen from Table 3 that all tubewell water samples of Barhait, Barharwa, Borio and Mandro and well water samples of Barhait, Barharwa and Borio were found safe with regard to arsenic. In Pathna, one tubewell water out of a total of 134 had shown 20ppb arsenic, which by the present scale was in alert range. More importantly, however, 8 Pathna tubewell waters from an apparently safe category had shown arsenic very close to 10ppb. Similarly in Taljhari, though only one tubewell water out of a total of 136 was in alert category, 9 tubewell samples from safe category contained arsenic close to 10ppb. These observations are of concern as arsenic concentration in groundwater is prone to sharp fluctuation depending upon geochemical conditions. Groundwaters of Pathna and Taljhari should be regularly monitored to detect any possible outbreak of arsenic at the onset.

Groundwaters of Rajmahal, Sahebgunj(B) and Udhawa depict a different picture. 7.3% and 9.3% of collected tubewell samples of Sahebgunj fall under toxic and alert categories respectively. Corresponding figures are 3.8% and 13.7% for Rajmahal and 2.4% and 14.3% for Udhawa. This, however, is only the part story. In Sahebgunj(B), out of 126 supposed to be safe water samples, 23 (~18%) contain arsenic around 10ppb, the borderline value. Similarly in Rajmahal about 17% (out of a total of 148) and in Udhawa about 14% (out of a total of 105) safe waters contain arsenic around borderline value of 10ppb. This analysis clearly reveals that Sahebgunj(B), Rajmahal and Udhawa blocks of Sahebgunj district are alarmingly contaminated with arsenic.

To look into the trend and distribution patterns of arsenic occurrence, groundwaters of Sahebgunj(B), Rajmahal and Udhawa were exposed to several statistical treatments, which have been briefly discussed in Materials and Methods section. A conventional descriptive statistics based on normal distribution has been shown in Table 4 with regard to arsenic in the ground-

waters of Sahebgunj(B), Rajmahal and Udhawa blocks. Only those samples were considered for statistical treatment in which arsenic could be detected and determined. Large difference between mean and median in each case, high standard deviation and positive kurtosis indicate that the distribution is widely off normal. Wide data range in each case indicates the presence of extreme values, which are likely to bias the normal distribution statistic.

To understand distribution pattern of arsenic in tubewell water, Sahebgunj(B), Rajmahal and Udhawa arsenic data were subjected to preliminary EDA analysis. Fig. 3(a)–(d) show the jittered dot plot (JDP), quantile plot (QP), box and whisker plot (BW) and midsum plots (MSP) of arsenic containing groundwater (tubewell) samples of Sahebgunj(B), Rajmahal and Udhawa. Fig. 3 is revealing in many ways. From Fig. 3(a), one may find that in Rajmahal and Udhawa almost all samples are clustered within 0–100ppb arsenic while in Sahebgunj(B), a number of water samples contain arsenic even higher than 100ppb. Letter values calculated from Fig. 3(a) for three sets (Sahebgunj(B), Rajmahal and Udhawa) of water samples have been given in Table 5. Similarities as well as closeness between the letter values of Rajmahal and Udhawa clearly indicate that they have

Table 4  
Normal distribution statistic for arsenic in Sahebgunj(B), Rajmahal and Udhawa tubewell waters

| Statistic          | Sahebgunj | Rajmahal | Udhawa |
|--------------------|-----------|----------|--------|
| Mean (ppm)         | 0.063     | 0.027    | 0.026  |
| Median (ppm)       | 0.015     | 0.021    | 0.022  |
| Standard deviation | 0.109     | 0.022    | 0.023  |
| Sample variance    | 0.012     | 0.000    | 0.000  |
| Kurtosis           | 15.3      | 0.173    | 3.64   |
| Skewness           | 3.55      | 1.03     | 1.74   |
| Range              | 0.615     | 0.084    | 0.104  |
| Minimum            | 0.005     | 0.005    | 0.005  |
| Maximum            | 0.62      | 0.089    | 0.109  |
| Count              | 45        | 53       | 36     |

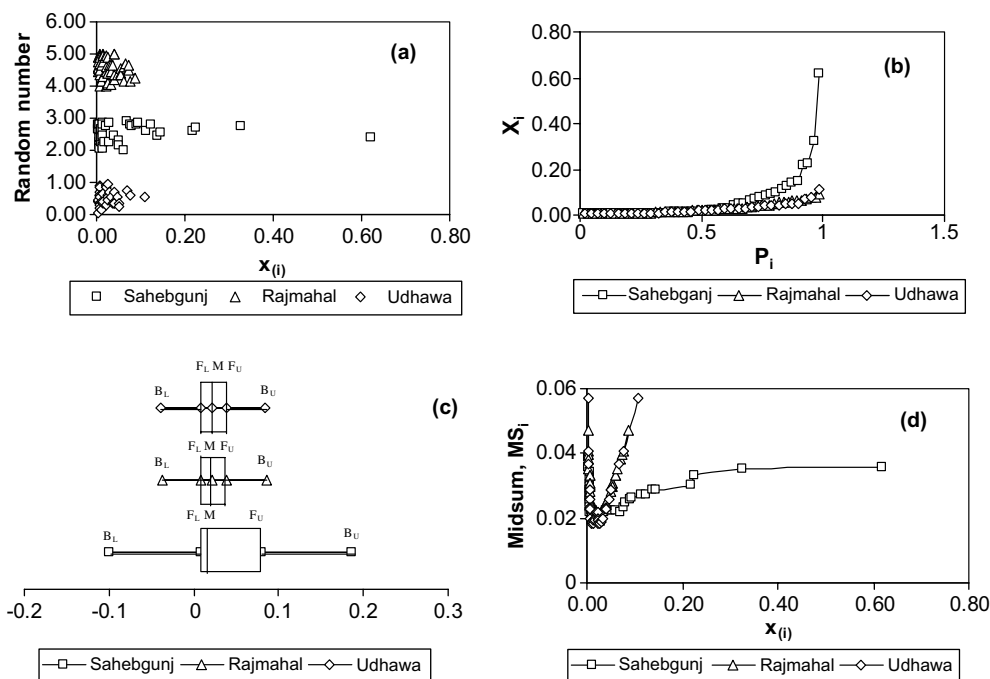


Fig. 3. (a) Jittered dot plot, (b) quantile plot, (c) box and whisker (BW) plot and (d) midsum plots of arsenic in tubewell waters of Sahebgunj(B), Rajmahal and Udhawa.

almost identical distribution pattern. In Sahebgunj(B) position of lower quartile is same as that of Rajmahal and Udhawa, but upper quartile is located far off indicating a comparatively larger spread as is also given by interquartile range,  $IQR(F_U - F_L)$  in Table 5. Interestingly Sahebgunj(B) data set has a smaller median as compared to Rajmahal and Udhawa.

BW plots in Fig. 3(b) visually represent distribution patterns of arsenic in Sahebgunj(B), Rajmahal and Udhawa tubewell waters. In Sahebgunj(B), median  $M$  being very close to the lower quartile,  $F_L$ , width of the second quartile is only 0.007 as opposed to the third quartile of 0.064. This indicates an asymmetric distribution, which may also be found in Rajmahal and Udhawa albeit to a lesser extent. This was interesting to note that in all three places samples in the first quartile clustered much

before  $B_L$  while in the fourth quartile they were spread even beyond  $B_U$ . This implied an extended asymmetric tail on the right of the median. It was interesting to find four samples in Sahebgunj(B) containing arsenic even beyond  $B_U$  indicating that they were definite outliers. Outliers have a different connotation in the present case as has already been explained in Materials and Method section. It is not an erroneous measurement as is the case under usual situations. On the contrary, these cases represent very high arsenic content and should be accorded maximum attention.

Quantile plots for Sahebgunj(B), Rajmahal and Udhawa in Fig. 3(c) provide a better comparison of distribution patterns. One may find that quantile plots of Rajmahal and Udhawa are almost superimposable. Quantile plot of Sahebgunj(B) follows Rajmahal and Udhawa upto cumulative probability ( $P_i$ ) of 0.5 after which it deviates from them. Asymmetric distribution patterns of Sahebganj(B), Rajmahal and Udhawa waters with regard to arsenic are also conspicuous from the quantile plots, as a symmetric distribution should exhibit an S-type quantile plot. Midsum plots of Sahebgunj(B) Rajmahal and Udhawa have been shown in Fig. 3(d). Asymmetric arsenic distribution pattern in Rajmahal and Udhawa are evident from their respective midsum plots which are almost parabolic and overlapping. A symmetric distribution is represented by a horizontal line parallel to  $X$ -axis where midsum is equal to

Table 5

Letter values in arsenic distribution in Sahebgunj(B), Rajmahal and Udhawa tubewell waters

| Letter values | Sahebgunj(B) | Rajmahal | Udhawa |
|---------------|--------------|----------|--------|
| $B_L$         | -0.099       | -0.037   | -0.038 |
| $F_L$         | 0.008        | 0.009    | 0.008  |
| $M$           | 0.015        | 0.021    | 0.022  |
| $F_U$         | 0.079        | 0.039    | 0.039  |
| $B_U$         | 0.187        | 0.085    | 0.085  |
| IQR           | 0.071        | 0.030    | 0.031  |

the median. Midsum plot for Sahebgunj(B) is also asymmetric in nature though distinctly different from Rajmahal and Udhawa. The first half of Sahebgunj(B) midsum plot overlaps with Rajmahal and Udhawa though the second half flattens albeit much above median (0.015).

Fig. 4(a)–(c) give the Z-score plots for arsenic in Sahebgunj(B), Rajmahal and Udhawa tubewell waters. Highly asymmetric Z in each case points towards a significant deviation from normal distribution, maximum being observed in the case of Sahebgunj(B). Almost non-existent left half of the Z in Sahebgunj(B) data is an indicator of the skewness. This was also manifested in the BW plot where median and lower quartile almost fell on each other. Considering a cut off Z-score of  $\pm 3$ , four outliers could be identified in Sahebgunj(B). Interestingly same set of outliers was also identified in the BW plot of Sahebgunj(B).

Information extracted with regard to arsenic distribution in tubewell waters of Sahebgunj(B), Rajmahal and Udhawa of Sahebgunj(D) district employing NDA, EDA and Z-score may be summarised as follows. From NDA it is apparent that the distributions are not normal as is evident from the large difference between

mean and median values. Positive kurtosis and skewness in each set of samples is indicative of the asymmetric nature of the distributions. EDA projects clustering of data points within a small bracket. Asymmetric nature of the distributions is conspicuous in all three underscored by a much greater width of the third quartile as opposed to the second. In Sahebgunj(B), median almost flushes with the lower quartile. EDA also predicts four outliers in Sahebgunj(B) lying beyond the extreme letter value  $B_U$ . Z-score has been found to be convenient in finding out the qualitative nature of the distribution and very reliable for predicting the outliers. It has been found to be especially useful in the present case where median is very close to the lower quartile,  $F_L$  which is not legible from BW plot. BW plot, on the other hand, succeeds in representing the asymmetric tails on either side of the median, which is not apparent from Z-score plot. Thus BW and Z-score plots have been found to be complementary to each other. In subsequent analyses of remaining elements the data were subjected to NDA, BW plot and Z-score analysis.

Iron, manganese, calcium, magnesium, copper and zinc in Sahebgunj(D) tubewells.

NDA with regard to Fe, Mn, Ca, Mg, Cu and Zn in each block as well as all 1317 tubewell water samples have been shown in Table 6. Z-score and BW plots for these elements for the entire Sahebgunj(D) district have been shown in Fig. 5(a, c, e, g, i, k) and (b, d, f, h, j, l) respectively.  $E_x$  in Fig. 5(b, d, f, h, j, l) represents extreme upper value in the ordered statistic.

#### 7.1.2. Iron

Iron is the next most important element in Sahebgunj(D) tubewell waters. This is underscored by the figures in Table 3 where 66–90% of the tubewell waters in all nine blocks belongs to alert and toxic category put together. The worst of the situations might be observed in Barhait block where out of a total of 62 tubewell waters only 8% were safe and about 70% were toxic. Even well waters of Barhait exhibited very high iron content (50% toxic). All these clearly indicated that occurrence of iron in Sahebgunj(D) tubewell waters was geogenic in nature.

NDA on iron values in Sahebgunj(B) tubewell waters as shown in Table 6 reveals large difference between mean and median values indicating asymmetric distribution pattern and presence of extreme values in the form of outliers. It was interesting to note that mean and median values in different blocks enjoyed a reasonably linear correlation ( $r^2 = 0.9148$ ). It was also interesting to note that kurtosis and skewness were linearly correlated ( $r^2 = 0.9524$ ) though a cubic correlation was a better one ( $r^2 = 0.9961$ ). This, however, was only an observation and no definite reason could be attributed to it. All these were indicators of similar iron distribution in all nine blocks of Sahebgunj(D) district. It was

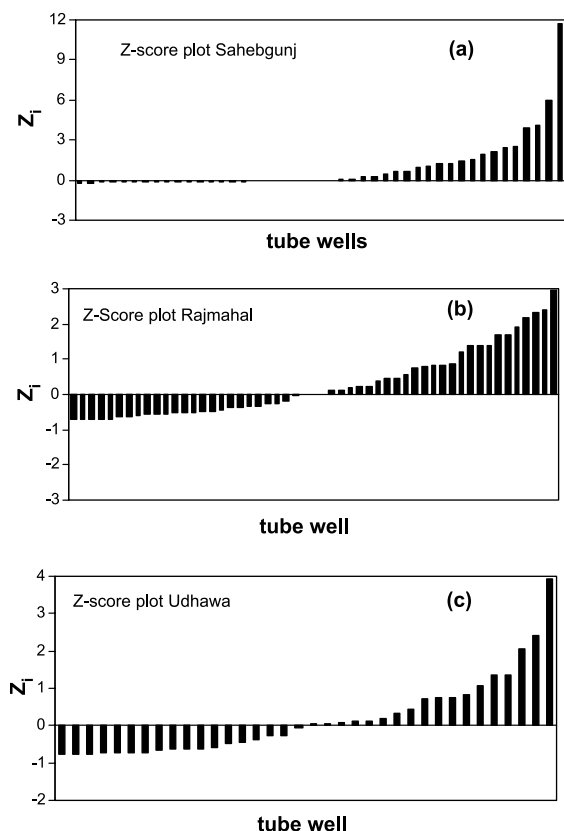


Fig. 4. Z-score plots of arsenic in tubewell waters of (a) Sahebgunj(B), (b) Rajmahal and (c) Udhawa.

Table 6

Normal distribution statistic for Fe, Mn, Ca, Mg, Cu and Zn in Sahebgunj(D) tubewell waters

| Block              | Statistics         | Fe    | Mn    | Ca     | Mg     | Cu    | Zn    |
|--------------------|--------------------|-------|-------|--------|--------|-------|-------|
| Barhait (62)       | Mean (ppm)         | 3.42  | 0.510 | 23.9   | 18.1   | 0.007 | 0.356 |
|                    | Median (ppm)       | 1.93  | 0.217 | 24.2   | 17.8   | 0.000 | 0.113 |
|                    | Standard deviation | 3.58  | 0.733 | 12.1   | 6.27   | 0.017 | 0.631 |
|                    | Sample variance    | 12.8  | 0.538 | 146    | 39.4   | 0.000 | 0.398 |
|                    | Kurtosis           | 1.21  | 6.38  | 4.34   | 0.234  | 5.63  | 9.22  |
|                    | Skewness           | 1.32  | 2.44  | 1.40   | −0.125 | 2.56  | 2.85  |
|                    | Range              | 13.8  | 3.73  | 68.9   | 32.0   | 0.071 | 3.40  |
| Barharwa (300)     | Mean (ppm)         | 1.69  | 0.320 | 33.6   | 22.3   | 0.013 | 0.733 |
|                    | Median (ppm)       | 0.790 | 0.076 | 27.5   | 19.0   | 0.000 | 0.162 |
|                    | Standard deviation | 2.52  | 0.934 | 34.3   | 18.7   | 0.025 | 1.54  |
|                    | Sample variance    | 6.35  | 0.872 | 1175   | 349    | 0.001 | 2.37  |
|                    | Kurtosis           | 14.3  | 84.5  | 17.6   | 34.9   | 25.0  | 29.0  |
|                    | Skewness           | 3.31  | 7.87  | 3.60   | 4.82   | 3.68  | 4.84  |
|                    | Range              | 19.1  | 11.9  | 282    | 193    | 0.250 | 12.7  |
| Borio (178)        | Mean (ppm)         | 1.14  | 0.174 | 27.9   | 20.9   | 0.017 | 0.142 |
|                    | Median (ppm)       | 0.445 | 0.030 | 25.2   | 18.6   | 0.004 | 0.053 |
|                    | Standard deviation | 2.06  | 0.395 | 25.8   | 13.7   | 0.042 | 0.239 |
|                    | Sample variance    | 4.25  | 0.156 | 667    | 189    | 0.002 | 0.057 |
|                    | Kurtosis           | 34.4  | 29.8  | 17.6   | 4.03   | 25.4  | 15.9  |
|                    | Skewness           | 4.93  | 4.74  | 3.49   | 1.57   | 4.63  | 3.60  |
|                    | Range              | 19.0  | 3.42  | 193    | 89.4   | 0.336 | 1.69  |
| Mandro (51)        | Mean (ppm)         | 1.49  | 0.194 | 29.5   | 21.3   | 0.018 | 0.127 |
|                    | Median (ppm)       | 0.322 | 0.062 | 26.4   | 18.0   | 0.000 | 0.042 |
|                    | Standard deviation | 3.03  | 0.426 | 22.1   | 16.2   | 0.043 | 0.252 |
|                    | Sample variance    | 9.20  | 0.182 | 490    | 263    | 0.002 | 0.064 |
|                    | Kurtosis           | 19.8  | 19.3  | −0.572 | −0.341 | 18.2  | 11.0  |
|                    | Skewness           | 4.05  | 4.12  | 0.560  | 0.789  | 3.93  | 3.28  |
|                    | Range              | 18.4  | 2.54  | 81.8   | 57.3   | 0.249 | 1.19  |
| Pathna (134)       | Mean (ppm)         | 1.32  | 0.086 | 39.0   | 22.5   | 0.020 | 0.287 |
|                    | Median (ppm)       | 0.392 | 0.039 | 25.9   | 19.4   | 0.000 | 0.074 |
|                    | Standard deviation | 2.58  | 0.137 | 70.8   | 15.4   | 0.033 | 0.825 |
|                    | Sample variance    | 6.68  | 0.019 | 5014   | 236    | 0.001 | 0.681 |
|                    | Kurtosis           | 14.7  | 7.64  | 70.9   | 3.31   | 4.86  | 61.7  |
|                    | Skewness           | 3.49  | 2.59  | 7.54   | 1.38   | 2.08  | 7.26  |
|                    | Range              | 17.3  | 0.787 | 734    | 96.0   | 0.182 | 7.99  |
| Rajmahal (180)     | Mean (ppm)         | 1.59  | 0.338 | 66.0   | 27.0   | 0.026 | 0.466 |
|                    | Median (ppm)       | 0.460 | 0.101 | 49.6   | 25.0   | 0.000 | 0.073 |
|                    | Standard deviation | 3.19  | 0.590 | 74.1   | 18.3   | 0.075 | 1.15  |
|                    | Sample variance    | 10.2  | 0.349 | 5489   | 334    | 0.006 | 1.33  |
|                    | Kurtosis           | 28.1  | 31.6  | 32.3   | 15.3   | 54.2  | 21.2  |
|                    | Skewness           | 4.67  | 4.47  | 4.82   | 3.01   | 6.93  | 4.31  |
|                    | Range              | 26.8  | 5.44  | 686    | 151    | 0.671 | 8.38  |
| Sahebgunj(B) (151) | Mean (ppm)         | 1.15  | 0.183 | 77.4   | 29.5   | 0.024 | 0.540 |
|                    | Median (ppm)       | 0.438 | 0.053 | 59.9   | 26.1   | 0.016 | 0.073 |
|                    | Standard deviation | 2.50  | 0.362 | 78.1   | 17.7   | 0.037 | 1.44  |
|                    | Sample variance    | 6.24  | 0.131 | 6104   | 315    | 0.001 | 2.08  |
|                    | Kurtosis           | 47.5  | 13.7  | 18.3   | 2.34   | 69.2  | 44.1  |
|                    | Skewness           | 6.11  | 3.51  | 3.32   | 0.946  | 7.22  | 6.01  |
|                    | Range              | 23.5  | 2.26  | 635    | 116    | 0.400 | 12.9  |
| Taljhari (136)     | Mean (ppm)         | 0.984 | 0.258 | 90.1   | 32.6   | 0.020 | 0.336 |
|                    | Median (ppm)       | 0.303 | 0.091 | 73.5   | 28.9   | 0.009 | 0.017 |
|                    | Standard deviation | 1.95  | 0.385 | 69.7   | 18.7   | 0.040 | 1.15  |
|                    | Sample variance    | 3.78  | 0.148 | 4853   | 349    | 0.002 | 1.31  |

Table 6 (continued)

| Block        | Statistics         | Fe    | Mn    | Ca      | Mg    | Cu    | Zn    |
|--------------|--------------------|-------|-------|---------|-------|-------|-------|
| Udhawa (125) | Kurtosis           | 25.6  | 7.03  | 3.00    | 5.92  | 44.7  | 39.6  |
|              | Skewness           | 4.33  | 2.44  | 1.40    | 1.90  | 5.65  | 5.93  |
|              | Range              | 15.7  | 2.30  | 411     | 114   | 0.370 | 9.13  |
|              | Mean (ppm)         | 0.844 | 0.259 | 95.4    | 31.0  | 0.028 | 0.165 |
|              | Median (ppm)       | 0.363 | 0.066 | 91.2    | 28.0  | 0.000 | 0.022 |
|              | Standard deviation | 1.32  | 0.398 | 57.8    | 17.3  | 0.105 | 0.358 |
|              | Sample variance    | 1.75  | 0.158 | 3337    | 299   | 0.011 | 0.128 |
|              | Kurtosis           | 8.06  | 9.82  | 0.901   | 8.63  | 54.2  | 13.3  |
|              | Skewness           | 2.76  | 2.65  | 0.660   | 1.800 | 7.23  | 3.45  |
|              | Range              | 7.40  | 2.61  | 317.160 | 133   | 0.871 | 2.14  |
| All (1317)   | Mean (ppm)         | 1.42  | 0.255 | 53.9    | 25.2  | 0.019 | 0.413 |
|              | Median (ppm)       | 0.473 | 0.067 | 32.5    | 21.4  | 0.000 | 0.067 |
|              | Standard deviation | 2.56  | 0.596 | 61.6    | 17.5  | 0.052 | 1.12  |
|              | Sample variance    | 6.56  | 0.355 | 3800    | 305   | 0.003 | 1.25  |
|              | Kurtosis           | 23.5  | 126   | 29.3    | 14.8  | 124   | 51.5  |
|              | Skewness           | 4.12  | 8.40  | 4.01    | 2.64  | 9.56  | 6.34  |
|              | Range              | 26.8  | 11.9  | 734     | 194   | 0.871 | 12.9  |

therefore thought to be prudent to carry out NDA on all surveyed tubewell water samples of Sahebgunj(D) district. NDA on iron and all remaining five elements for all 1317 tubewell water samples have been presented in Table 6. Simultaneous Z-score and BW plots of Fe, Mn, Ca, Mg, Cu and Zn in all 1317 tubewell waters of Sahebgunj(D) district have also been shown in Fig. 5(a)–(l).

One may find from the Z-score plot (Fig. 5(a)) that iron distribution in Sahebgunj(D) tubewell waters is highly asymmetric. There are 149 outliers on the right hand side out of a total of 1317. This implied approximately 11% of surveyed Sahebgunj(D) tubewell waters were severely contaminated with iron. Asymmetry in iron distribution is even more conspicuous from the BW plot (Fig. 5(b)). The width of second quartile is only 0.33 as opposed to third quartile of 1.05. A long fourth quartile of 25.27 is a clear indicator of the asymmetric tail. It was interesting to note that BW plot predicted 148 outliers which was one less than what was obtained from Z-score plot.

#### 7.1.3. Manganese

Manganese in Sahebgunj(D) tubewell waters is almost as important as iron. It may be seen from Table 3 that except for Borio and Pathna and marginally Sahebgunj(B), half of the surveyed tubewell waters in remaining blocks contain manganese either at toxic or alert level. NDA in Table 6 indicates Pathna waters to be the best with respect to Mn. Similar Mn distribution pattern in all nine blocks is testified by NDA on Mn for all 1317 tubewell water samples.

Z-score plot for Mn (Fig. 5(c)) comprising all tubewell waters of Sahebgunj(D) highlight the asymmetric

nature of the distribution. There are 179 outliers representing about 13.6% samples implying manganese contamination in Sahebgunj groundwaters to be more severe than iron. Asymmetric nature of Mn distribution is also apparent from the BW plot (Fig. 5(d)). The width of the third quartile (0.15) is greater than even twice the second quartile (0.06), which for a symmetric distribution should be equal. A long fourth quartile of 11.7 represents a long asymmetric tail. It was gratifying to note that number of outliers from BW plot was identical to what was obtained from Z-score plot.

#### 7.1.4. Calcium and magnesium

Sahebgunj(D) tubewell water samples appear to be reasonably soft with respect to calcium and magnesium. The distributions for both, however, appear to be asymmetric with the common feature of third quartile being wider than the second and a long fourth quartile indicating an asymmetric tail. Z-score plots for calcium (Fig. 5(e)) and magnesium (Fig. 5(g)) demonstrate that magnesium concentrations are more evenly distributed than calcium, which is also apparent from the BW plots (Fig. 5(f) for calcium and Fig. 5(h) for magnesium). It is conspicuous from the BW plots that the difference in width between third and second quartile is much smaller in the case of magnesium as compared to calcium. There are about 7.5% outliers in calcium and 2.6% in magnesium as obtained from Z-score plots.

#### 7.1.5. Copper

Sahebgunj(D) water samples seem to be reasonably safe with respect to copper. Only one water sample in Barharwa was found to be in the toxic range. Interestingly, however, a substantial number of samples in seven

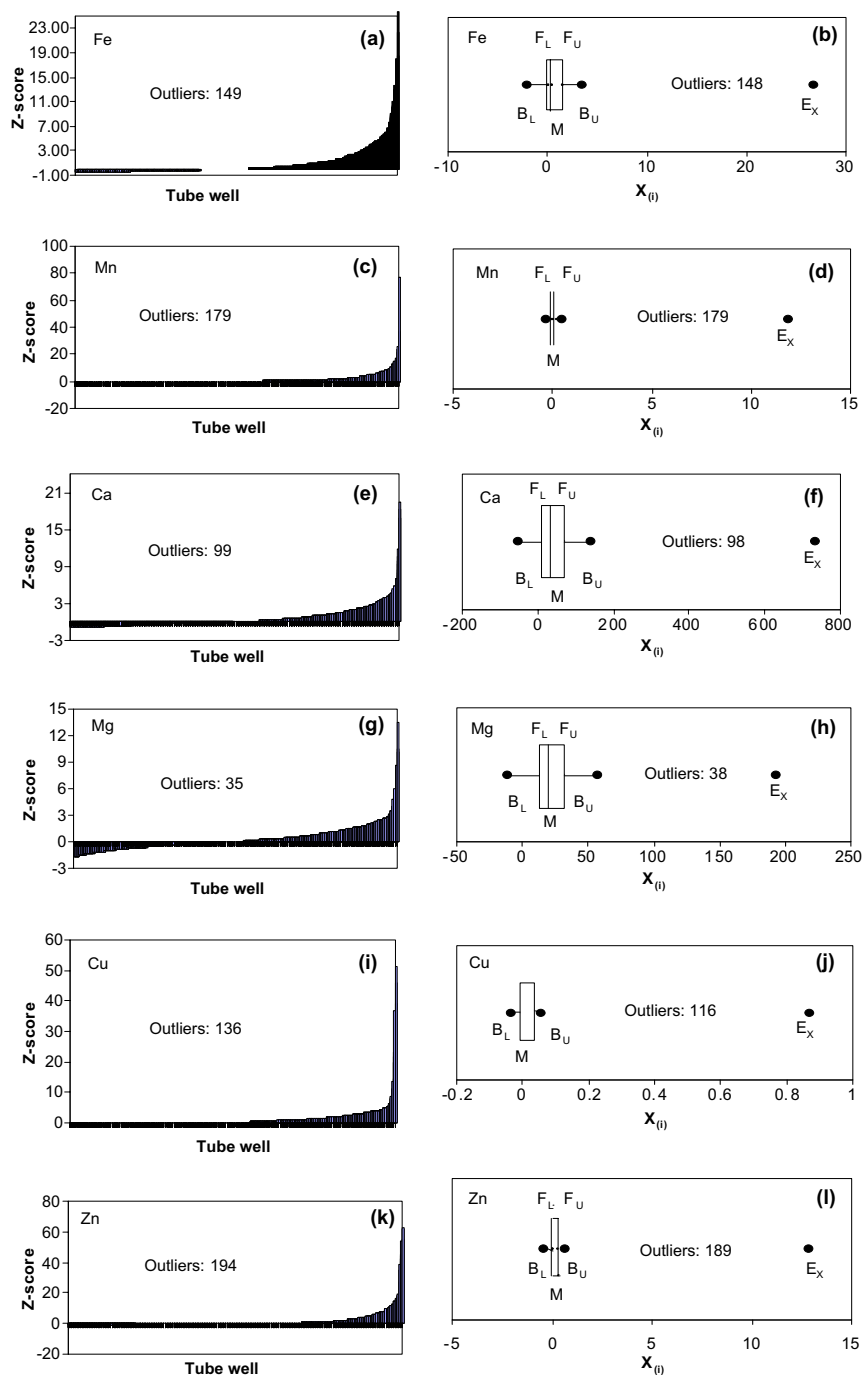


Fig. 5. Z-score (a, c, e, g, i, k) and box and whisker (BW) (b, d, f, h, j, l) plots of Fe, Mn, Ca, Mg, Cu and Zn in tubewell waters of Sahebgunj(D) district.

blocks (barring Barhait and Mandro showed presence of copper at alert level. This was also the reason for a large number of Z-score and BW plot outliers. Copper distribution was asymmetric and similar to those observed for

earlier elements. Number of outliers predicted from Z-score plot was more than BW plot. Source of copper in Sahebgunj(D) waters is not known and needs to be investigated.

#### 7.1.6. Zinc

Sahebgunj groundwaters are by and large safe with regard to zinc as may be seen from Table 3. Even then there are 194 and 189 outliers from Z-score plot and BW plot respectively. This is indication of the fact that about 14% samples have Zn values on the border of Safe (S) and Alert (A) in Table 3. Z-score and BW plots (Fig. 5(k) and (l)) confirm the asymmetric nature of zinc distribution in Sahebgunj tubewell waters.

Statistical observations on Fe, Mn, Ca, Mg, Cu and Zn in Sahebgunj(D) tubewell waters may be summarised as follows. All these elements exhibit an asymmetric distribution with a long asymmetric tail on the right of the median. The width of the third quartile was consistently found to be more than the second quartile for each element. A long fourth quartile represented the asymmetric tail. In the case of Mn, Cu and Zn, median almost coalesced with  $F_L$ , the lower quartile value. Except for Ca and Mg remaining elements showed large number of outliers implying a significant number of tubewell water samples might contain at least one of these elements present at an undesirable level. The number of outliers observed statistically in each case was more than the total number of samples in toxic level. This implied at least some of the alert samples and in some cases a few safe samples were also adjudged outliers. Sahebgunj(D) waters have in general high iron content but intriguingly they also contain high manganese in a significant number of samples with more severity. A sizeable number of tubewell water samples in seven blocks out of a total of nine contain copper at alert level. Number of outliers predicted from Z-score plot and BW plot, essentially two different techniques, match well thus strengthening the reliability of extracted statistical information.

#### 7.2. Well waters

A number of Sahebgunj well waters were also examined for As contents along with Fe, Mn, Ca, Mg, Cu and Zn though less rigorously than tubewell waters. One may observe from Table 3 that well waters are definitely safer with respect to arsenic as compared to tubewell waters. This should prove to be a very vital lead in the mitigation programme. Well waters are also definitely softer in comparison to tubewell waters. However, with regard to Fe and Mn they appear to be as contaminated as tubewell waters though the mean value was less in well waters. Cu and Zn seem to be present in well waters in insignificant quantity.

In the absence of reliable data no study could be carried out to correlate metal contamination with depth. However, absence of arsenic in well waters strongly points towards a depth correlation with the occurrence of arsenic.

#### 7.3. Mobilisation of arsenic in Sahebgunj(D) tubewell waters

Mobilisation of arsenic in Sahebgunj(D) tubewell waters is expected to follow a similar course as observed in the Gangetic delta of West Bengal, India and Bangladesh. Adjacency of Sahebgunj(D) with Maldah, one of the arsenic affected areas of West Bengal on the other side of river Ganges, further supports this. Though this study was not originally designed to address the issue of arsenic mobilisation in the tubewell waters of Sahebgunj(D) district, present observations will be used to comment qualitatively on arsenic mobilisation in the groundwaters of Sahebgunj(D).

Presently there are two prevalent theories on the mobilisation of arsenic in Gangetic delta. According to the first, oxidative dissolution of arsenic bearing pyrite minerals, caused due to overwithdrawl of groundwater, is the reason for contamination of the groundwater with arsenic oxyanionic species (Das et al., 1996). This theory, however, has been strongly contested based on groundwater quality data. Bhattacharya et al. (1997) forwarded the argument of reductive dissolution of iron coated sand as the more likely arsenic mobilisation scheme in the Gangetic plane of West Bengal and Bangladesh as opposed to the oxidative dissolution of arsenopyrite phase which was supported by others (Nickson et al., 1998; Acharyya et al., 1999; Roy Chowdhury et al., 1999). Since then some more publications have also appeared in support of this theory. Reduction of oxyhydroxide phase presumably takes place due to microbial oxidation of sedimentary carbon (Nicksson et al., 2000; Stuben et al., 2003).

Tubewell waters of Sahebgunj(D) have, in general (statistically), been found to contain high iron and manganese though no specific correlation could be observed with arsenic. This observation supports the reductive dissolution of iron/manganese oxyhydroxide theory. An estimation of dissolved oxygen,  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  in tubewell waters and carbon in the borehole sediment perhaps could have further consolidated this opinion. Presence of high manganese in tubewell waters of Sahebgunj(D) is also instructive, indicating reductive dissolution of oxyhydroxide of manganese as one of the factors of arsenic mobilisation. Presence of oxyhydroxide phase of manganese in the borehole sediments could corroborate this view. It was also interesting to note that, though Sahebgunj(D) as a whole was not a big territory, only those blocks which were adjacent to river Ganges, namely, Sahebgunj(B), Rajmahal, Udhawa, Taljhari and Pathna reported arsenic in tubewell waters. This indicated that there was marked difference in sedimentary compositions even within a small territory. Appreciable difference in arsenic contents in well and tubewell waters indicated a depth correlation with arsenic content, which, however could not be carried out in the absence of reliable well and tubewell depth data. Distribution pattern of As(III)

and As(V) species in tubewell waters and their variation with depth should be crucially important in establishing a mobilisation scheme.

Based on this study, it has been planned to undertake a detailed investigation on arsenic mobilisation scheme in Sahebgunj(D) district wherein a complete profiling of the tubewell groundwaters will be carried out with regard to cationic and anionic components including As(III) and As(V) species. Borehole sediments will also be comprehensively studied for the constituent mineral phases and organic carbon.

## 8. Conclusion

The conclusions of the present study may be listed as follows:

- A comprehensive statistical analysis of metal contents in tubewell waters of nine blocks in Sahebgunj(D) district has been carried out with special reference to arsenic.
- A significant portion of tubewell waters of three blocks in the Sahebgunj(D) district, namely, Sahebgunj(B), Rajmahal and Udhawa contain arsenic above the permissible level of 0.01 mg/l.
- Two more blocks, namely, Taljhari and Pathna are likely places where future arsenic outbreaks may take place. Tubewell waters of these places must be regularly monitored to detect any arsenic occurrence at the onset.
- Sahebgunj tubewell waters in general contain high iron and manganese.
- Arsenic mobilisation in tubewell waters of Sahebgunj(D) district follows reductive dissolution of oxyhydroxides of iron and manganese through oxidation of sedimentary organic carbon.
- Well waters of Sahebgunj(D) district contain much less arsenic than tubewell water.
- Sporadic occurrence of copper has been observed in some of the tubewell waters of Sahebgunj(D) district.
- A rigorous survey of the water quality comprising inorganic (cationic and anionic species including As(III) and As(V)), organic and biological parameter of all the tubewell waters of Sahebgunj(B), Rajmahal and Udhawa and mineralogical characterisation of borehole sediments are being planned for a comprehensive risk assessment and elucidation of arsenic mobilisation mechanism.

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