# Evaluation of Spatial Distribution of Groundwater Fluoride Using Geo-statistical Technique in Unnao District Uttar Pradesh, India

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*Abstract-* Geo-statistical technique was used to study the spatial variability of fluoride (F) in the ground water in Unnao District, Uttar Pradesh, India. The delineation and mapping of F were carried out using semi-variograms, based on sampling at random intersection of 5 km x 5 km of square grid from shallow and deep hand pumps during both pre-monsson and post-monsoon seasons. The F concentrations in both shallow and deep handpumps were found to be spatially distributed. The F was estimated by point kriging method at un-sampled site and the interpolated kriged maps prepared, which showed a clear regional spatial variations pattern of F with distinct loops. It was also revealed that the shallow handpumps are highly contaminated with F as compared to deep handpumps.

Key words- Geo-statistical; Spatial Variability; Delineation; Fluoride; Kriging

## I. INTRODUCTION

The occurrence of fluoride (F) in ground water and the associated disease 'fluorosis' have become a worldwide problem. It is estimated that around 200 million people, from 25 nations all over the world, are under the dreadful fate of fluorosis [1]. In India, the fluorosis was first detected in the Prakasam District, Andhra Pradesh [2], when the disease was prevalent in only 4 states, namely Andhra Pradesh, Tamil Nadu, Punjab and Uttar Pradesh. Now the fluorosis has been reported endemic in 20 out of 32 constituent states of India [3] and day by day more new areas have been engulfed by this problem. Estimation also finds that 65% of India's villages are exposed to fluoride risk [4]. The occurrence of dental, skeletal fluorosis and muscular fluorosis has been reported variously [5, 6, 7] in Unnao District of Uttar Pradesh and the cause ascribed to the consumption of fluoride contaminated ground water. However, no attention has been paid so far to the spatial distribution of F concentration in the drinking water sources primarily ground water. The Unnao District of Uttar Pradesh is geographically located in the central part of the state, lying in the Ganga-Gomti doab of Indo-Gangetic plain is one of the F contaminated area in the state. It is also known that the drinking water is the major source of fluoride, which is harnessed mainly from shallow handpumps and deep handpumps in the villages. Therefore, in order to have better understanding and management of the fluoride problem, a systematic survey, delineation, sampling, analysis, mapping, and monitoring of various ground water sources are essentially needed. The occurrence of fluoride in the ground water and its spatial variability can be studied using geo-statistical techniques. However, delineation and mapping of the parameter could also be done using geographical information system (GIS) techniques. The geo-statistical techniques have been increasingly applied to even hydrological, geo-hydrological and climatic studies [8, 9, 10]. Mapping the spatial distribution of fluoride is important for ground water management decisions and is required as a tool for assessing the extent of fluoride problem in a particular area.

As in the past, no systematic attempts have been made in Unnao District of Uttar Pradesh for the proper delineation and mapping of the fluoride occurrence in the ground water. Thus an attempt was made in this study for a systematic survey, analysis of fluoride content and its spatial variability in ground water and mapping of fluoride using geo-statistical technique in Hasanganj Tehsil of Unnao District, Uttar Pradesh.

### II. MATERIAL AND METHODS

### A. Study Area

The study area lies between  $26^{\circ}32' 52"$  to  $27^{\circ} 0' 49"$  N latitude and  $80^{\circ}24' 27"$  to  $80^{\circ} 50' 33"$  E longitude in Hasanganj tehsil of Unnao District, Uttar Pradesh, India (Fig. 1), in the central Indo-Gangetic plain. The climate of the district is characterized by a hot dry summer and pleasant winter. Geologically, the area consists of quaternary sediments differentiated into older alluvium of middle to late Pleistocene age and newer alluvium of Holocene age. The older alluvium lithology is represented by a polycyclic sequence of brownish-yellowish silt clay with kankar layer and subordinate micaceous sand horizon. The newer alluvium differentiated into terrace is developed along the Sai river [11]. The land and water resource is a part of Ganga-Gomati drainage basin. The surface water mostly from Sarda Sahayak canal system and ground water meets the

irrigation and domestic water requirements, respectively. The ground water occurs in a four tier aquifer systems in confined condition. The ground water occurs in the pore spaces of unconsolidated alluvial material in the zone of saturation. The near surface clay and beds of  $CaCO_3$  concretions (locally called kankar) supports many open wells where ground water occurs under shallow water table condition. The concretions occurring at shallow depth also yield sufficient water to sustain moderate capacity of tube wells and hand pumps besides dug wells. Most of the shallow tube wells and hand pumps, harness water from these kankar beds and serve the drinking water needs of the local population.

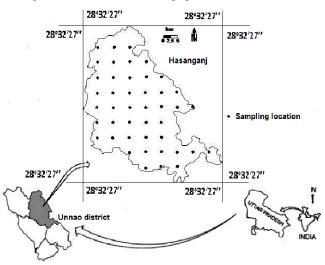


Fig. 1 Location of the study area showing sampling points

### B. Sampling and Analysis

The groundwater samples were collected at random intersection of 5 km x 5 km of square grid from privately owned shallow hand pumps and public deep hand pumps during both pre-monsoon and post-monsoon seasons. The water samples were collected in pre-cleaned polythene bottles with 1 litre capacity and transported to the laboratory. The fluoride in water was analyzed by the method adopted by [12]. Twenty-five ml of water sample was mixed with total ion strength adjuster buffer (TISAB) (4 g cyclohaxane diammnine tetra acetic acid (CDTA), 58 g NaCl and 57 ml glacial acetic acid in 1 litre of distilled water adjusted to pH 5.0–5.5 by 6 N NaOH) in 1:1 ratio and the fluoride concentration was measured directly by using fluoride ion selective electrode with the help of ORION ion analyzer 5 star series.

#### C. Classical Statistics

The measured fluoride concentration in water sources was analyzed using classical statistical method to obtain maximum, minimum, mean, median, first quartile, third quartile, skewness, variance and standard deviation (SD). The frequency distribution of F concentrations in shallow and deep hand pumps was determined. The normality of the measurement was established by simple frequency distribution diagram [13] and by statistical evaluation of the goodness of fits of the theoretical distribution to the measured data by using Kolmogorov statistics (D), where

$$D = Max_{X} | Fn(X) - F(X) |$$

F(X)= hypothetical theoretical distribution function, Fn(X)= Empirical distribution function of n measurements estimated from the samples. The *D* statistics was chosen because of its simple structure and intuitive appeal [14].

## D. Geostatistics

The spatial distribution of F concentration in shallow and deep handpumps was determined by geo-statistical method using semi-variogram analysis and kriging. The semi-variograms of F was computed [15] to determine any spatial dependent variance within the sites. The semi-variogram was calculated by taking all pairs of observations at a lag distance h apart and averaging the square of their difference. This is done for all possible lag distance, *h*. The resulting  $\gamma$  (*h*) function

$$\gamma(h) = \frac{1}{2} n(h) \sum_{i=1}^{n(h)} [Z_i - Z_{i+h}]^2$$

Where *n* (*h*) is the pair of observations at a separation distance *h*,  $Z_i$  and  $Z_{i+h}$  are the measured values of the regionalized variables *Z* at sampled locations  $X_i$  and  $X_{i+h}$ . The semi-variograms were plotted with *h* on abscissa and  $\gamma$  (*h*) i.e. semi-variance on the ordinate and the resulting experimental semi-variogram functions were fitted to linear, spherical and exponential theoretical models. Characteristics of the semi-variogram such as nugget, sill and range calculated for F and provided the basis for interpretation. Using the appropriate semi-variogram, the field grid points were kriged to estimate the values between the

sampling points. The plots of F concentration in shallow hand pumps and deep hand pumps were made from these kriged values by using surfer version 8.02 for windows [16].

### III. RESULTS AND DISCUSSION

The classical statistics parameters such as minimum, maximum, mean, standard deviations etc. for F in the shallow and deep handpumps during pre-monsoon and post-monsoon season are summarized in Table 1. The F concentration in the shallow handpumps ranged from 0.28 to 4.92 mg  $\Gamma^1$  in the pre-monsoon with a mean of 1.02 mg  $\Gamma^1$  while in the post monsoon it ranged from 0.16 to 4.18 mg  $\Gamma^1$  with a mean of 0.83 mg  $\Gamma^1$ . It was found that in pre-monsoon period 36.36% of the sampled shallow handpump waters were contaminated with F exceeding the desirable limit of 1.0 mg  $\Gamma^1$ , as prescribed by Bureau of Indian Standards [17] whereas in the post-monsoon period it was found to be 22.72%. Generally, recharge water dilutes the chemical concentrations during post-monsoon seasons and tends to increase towards pre-monsoon periods because of the effect of evaporation [18]. In the deep handpumps the fluoride concentration ranged from 0.21 to 2.88 mg  $\Gamma^1$  in the pre-monsoon with a mean of 0.7 mg  $\Gamma^1$  while in the post-monsoon, it ranged from 0.19 to 1.35 mg  $\Gamma^1$  with a mean of 0.60 mg  $\Gamma^1$ . During pre-monsoon period 18.2% of the sampled water was found to be contaminated with fluoride exceeding the maximum desirable limits as prescribed by Bureau of Indian Standards [17] (BIS 1991) whereas in the post-monsoon, it was found to be only 13.6%.

TABLE 1 SUMMARY OF CLASSICAL STATISTICS OF FLUORIDE CONCENTRATION (MG/L) IN GROUNDWATERS OF THE STUDY AREA

Statistical	Shallow handpumps		Deep handpumps	
Parameters	Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon
Mean	1.02	0.83	0.70	0.80
Median	0.74	0.58	0.58	0.52
S.D.	0.83	0.72	0.46	0.30
Variance	0.69	0.51	0.21	0.09
Kurtosis	10.77	10.54	10.54	-0.18
Skewness	2.80	2.78	2.70	0.88
Minimum	0.28	0.16	0.21	0.19
Maximum	4.92	4.18	2.88	1.35
Lower quartile	0.49	0.39	0.44	0.36
Upper Quartile	1.18	0.94	0.86	0.81

There are quite a few techniques used to test the normality of the data, and some techniques are more powerful than others for detecting certain form of departure from normality [19]. Before the analysis of semi-variograms, the F in shallow handpumps, and deep handpumps were analysed for normality by different graphical methods such as frequency distribution diagram and fractile diagram and also by statistical method i.e. kolmogorov D statistics. The frequency distribution curves exhibited by F (Fig. 2) were found to be fairly normal. The normality of these distributions was reinforced by the fractile diagrams (Fig. 3) except for few point deviations from the line.

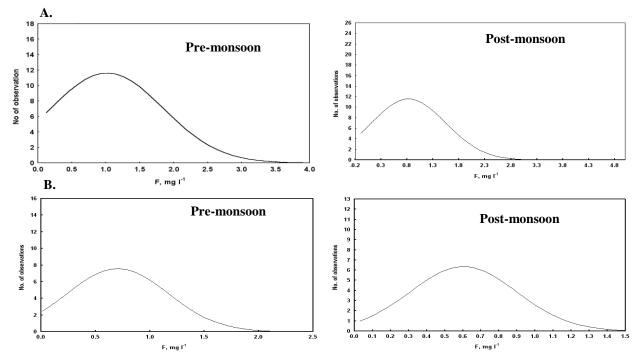


Fig. 2 Normal distribution of fluoride in (A) shallow handpumps and (B) deep handpumps of Hasanganj Tehsil during pre-monsoon and post-monsoon seasons

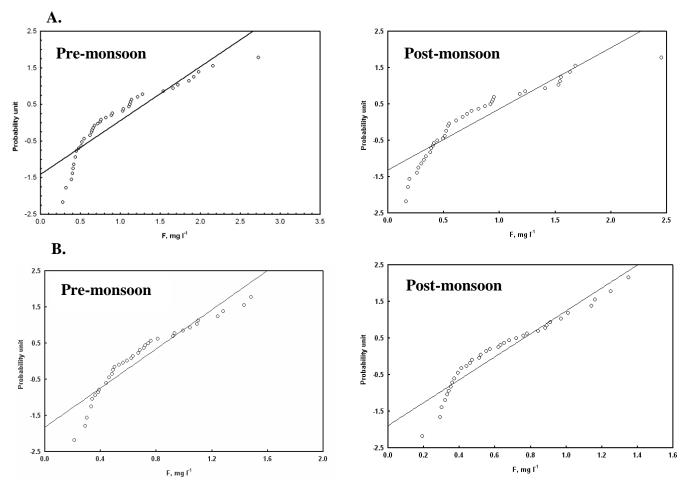


Fig. 3 Fractile diagram of fluoride in (A) shallow handpumps and (B) deep handpumps of the area during pre-monsoon and post-monsoon season

These statistical methods are not based on quantitative measures. Therefore, the objective statistical evaluation of the goodness of fit of the theoretical data could not be possible. Hence, the Kolmogorov D statistics was used for testing the normality for the variables as presented (Table 2). The data indicated that the values of D for F during pre and post monsoon at the significance level ( $\alpha$ =0.1) are not significant. This led to accepting the null hypothesis and concluded that the actual distribution of the variable was equal to the expected distribution i.e. variables were normally distributed.

TABLE 2 TEST OF NORMALITY AND KOLMOGOROV D STATISTICS OF FLUORIDE IN THE GROUNDWATERS OF THE STUDY ARI	EA
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Ground water type	K <sub>D</sub> value for F	P (0.1)	Distribution	
Pre-monsoon				
Shallow hand pump	0.116	NS	Normal	
Deep hand pump	0.145	NS	Normal	
Post monsoon				
Shallow hand pump	0.159	NS	Normal	
Deep hand pump	0.135	NS	Normal	

The spatial pattern of F concentration in shallow and deep handpumps in the study area (grid size 5 km x 5 km) were analysed by semi-variograms. In order to check the anisotropy, the conventional approach is to compare variograms in several directions [20]. In this study major angles of  $0^{\circ}$ ,  $45^{\circ}$ ,  $90^{\circ}$ , and  $135^{\circ}$  with an angle tolerance of  $\pm 22.5$  were used for detecting anisotropy. However, there were no distinct differences among the structures of the calculated variograms in the four directions. The parameters of the best fitted omni-directional variograms were obtained based on coefficient of determination i.e.  $R^2$ .

The experimental semi-variograms of F concentration in shallow and deep handpumps during pre- and post-monsoon revealed that the experimental variograms displayed an increase in semi-variance with increasing distance i.e. F concentration in these situations produced a valid variograms (Fig. 4). The F concentration in shallow handpumps and deep handpumps in the study area followed exponential model. The nugget value which represents the short distance variation smaller than the range, indicated that within a distance of 4 km, F concentration among the shallow handpumps during post monsoon and among the deep handpumps in pre-monsoon was uniform. The absence of nugget effect indicated that there was a good spatial continuity at a close distance between sampling points. The goodness of fit for the exponential model and small nugget

variance among the shallow handpumps during pre-monsoon and among the deep handpumps during post monsoon indicated that the local variance is continuous rather than abrupt. Low nugget effect and consequently low nugget-to-sill ratio generally can be used to classify the spatial dependence [21].

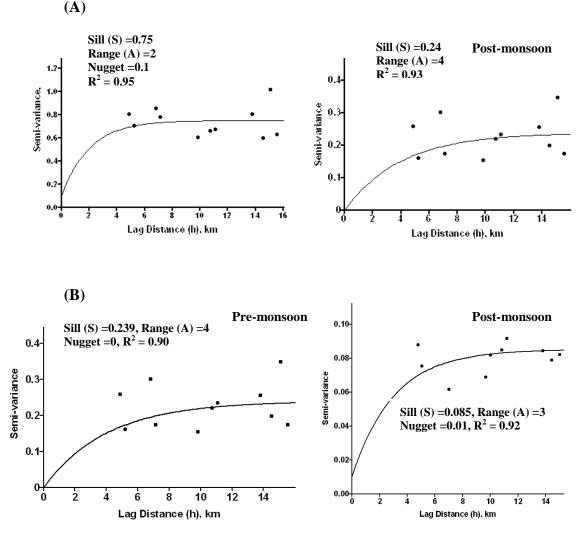


Fig. 4 Semi-variogram of Fluoride in (A) Shallow Handpumps and (B) Deep Handpumps of the Study Area During Pre-monsoon and Post-monsoon Seasons

With the help of appropriate semivariogram models geo-statistical interpolations by point kriging was carried out for fluoride concentrations. The mean and standard deviations of the variation of measured and the kriged values were given in Table 3. The average absolute difference between the kriged estimate and the measured values in the shallow handpumps in the area during both seasons i.e. pre and post-monsoon was found to be 0.002; in deep handpumps, it was 0.01 and 0.005 in pre-monsoon and post-monsoon, respectively. As the differences and their standard deviations were low, which means the kriged values were closer to the observed values. Kriging automatically led to a minimization of interpolation error because this minimization is a part of the solution in kriging system.

Four interpolated maps of F i.e. for shallow handpumps and deep handpumps during pre- and post-monsoon for the area using the kriged values were prepared and presented in Fig. 5. These maps remarkably indicated a clear regional spatial variation pattern of F with distinct loops. Four distinct loops of F having concentration between 1.0-1.5 mg  $\Gamma^1$  in the waters were observed in the shallow hand pumps during pre-monsoon season. In the post monsoon too, some loops of shrinked size of higher concentration of F were observed in the kriged map. This may be due to the dilution effects from the ground water recharge during post-monsoon period. The F concentration > 1.5 mg  $\Gamma^1$  was observed as circular loops and is prominent in west direction in both pre- and post-monsoon period located mainly near Rasulabad and Mirzapur. Smaller circular loops of high F were also observed during pre-monsoon which extended from S-E to S-W direction, particularly in the Nawabganj block. The mapping of F concentration of deep handpumps revealed that the concentration > 1.5 mg  $\Gamma^1$  was mostly found towards west direction only in pre-monsoon whereas no distinct loops were observed in the post monsoon season.

TABLE 3 COMPARISON OF STATISTICAL PARAMETERS FOR MEASURED AND KRIGED VALUES	
OF FLUORIDE (MG/L) IN DIFFERENT SOURCES OF WATER IN THE AREA	

Types of water sources	Parameters	Measured value	Estimated value	Difference
Shallow hand pumps	Mean	1.02	1.022	0.002
(Pre-monsoon)	S.D.	0.83	0.108	0.865
	Variance	0.69	0.012	0.748
Shallow hand pumps	Mean	0.83	0.828	0.002
(post -monsoon)	S.D.	0.72	0.168	0.765
	Variance	0.51	0.028	0.586
Deep hand pumps	Mean	0.70	0.710	0.01
(Pre-monsoon)	S.D.	0.46	0.166	0.504
	Variance	0.21	0.028	0.254
Deep hand pumps	Mean	0.60	0.605	0.005
(post monsoon)	S.D.	0.30	0.086	0.304
	Variance	0.09	0.007	0.093

Shallow Handpumps

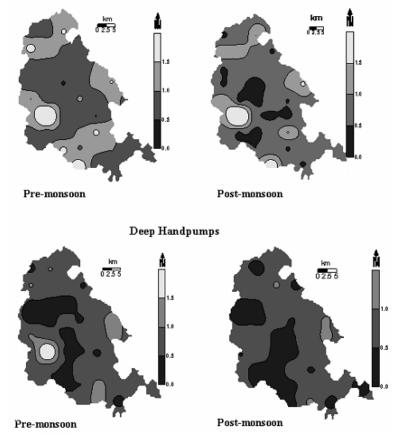


Fig. 5 Kriged map of the study area showing fluoride distribution in shallow and deep handpumps during pre and post monsoon season

# IV. CONCLUSIONS

The F concentrations in both shallow and deep handpumps were found to be spatially distributed. The kriged map prepared showed a clear regional spatial variations pattern of fluoride with distinct loops. The results indicated that the shallow handpumps were highly contaminated with the fluoride as compared to deep handpumps. Therefore, it is suggested that in these areas the waters from deep handpumps should be only used as drinking purposes and shallow handpumps should be avoided as far as possible. Further, the hydrology of the area and geogenic mineral source of F contamination in shallow hand pumps need to be investigated in order to come forward with some remedial measures. Also a continuous F monitoring programme should be designed in the zone of high fluoride and a smaller scale mapping (i.e. smaller grid size) may prove for even better identification of the fluoride endemic areas.

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