

Original Research Article

Assessment concentration and non-carcinogen risk of arsenic in groundwater by spatial distribution model (Kriging method); Hasht Bandi of Minab, Iran

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A B S T R A C T

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The presence of metals such as Arsenic in drinking water resources can be dangerous for human due to toxicity and biological accumulation. The Arsenic concentration was measured by atomic absorption Spectrophotometer in model DR2800 during the years 2012-2013 from 17 wells in the region of Hasht Bandi of Minab. Also, using the spatial distribution model (kriging method) and the concentration of Arsenic in the groundwater and Hazard Quotient was evaluated. The mean and range concentration of Arsenic in the groundwater is $7.69 \pm 2.56 \mu\text{g/l}$ and $0-23.7 \mu\text{g/l}$, respectively. The concentration of Arsenic in the groundwater in autumn (North West Region), winter (North East), spring (North East, North West and Center) and in summer (Center and East), is in the unsafe range. Hazard Quotient and Chronic daily intake of population in the Hasht Bandi of Minab were calculated $0.28 \mu\text{g/kg-d}$ and 0.92 , respectively. The mean concentration of Arsenic and Hazard Quotient of population in Hasht Bandi is in a worrying and safe area, respectively. The Spatial distribution model prepared by kriging showed that in the North East, the highest concentration of Arsenic and in the South and West, the lowest concentration of Arsenic and subsequently, Hazard Quotient was observed. By increasing the number of samples and the sampling points, kriging method can be considered as a good method for evaluating the distribution of environmental pollution and non-carcinogen risk.

Introduction

More than 70 % of earth's surface is covered by water, but due to salinity, its use for many poor and developing countries is impossible. The 3% of the earth's surface has fresh water, of which only 0.6% (wells, canals, rivers and lakes) is applicable to humans and the rest cannot be currently used for human use due to being existed in poles.[1] In recent years, contamination of water supplies to heavy metal has been considered for environment researcher. The presence of heavy metals in water can be caused by natural processes (erosion) or caused by human activities (urban, industrial or agricultural waste water discharges) ,2] [3. Entry of heavy metals in water resources will reduce water quality for drinking or agricultural irrigation [4]. Heavy metals and metalloids have properties such as biological accumulation, toxicity and environmental sustainability [5, 6]. Some heavy metals (cadmium, chromium, manganese, lead, and nickel) and metalloids (Arsenic) in high concentrations can be hazardous to human health and other organisms.[8 ,7] Epidemiological studies show that there is a significant relationship between tooth decay, heart disease, kidney disorders, neurological disorders and cancer associated with heavy metals [10 ,9] . Also studies have shown that 35×10^6 kg/y Arsenic is entered into water, soil and atmosphere [11]. Despite the different ways Arsenic can enter humans body (eating, smoking) but the most important input source is the drinking of contaminated water .[12] Entry of Arsenic into body in the long term can cause cancer of the bladder, liver, kidneys and the skin lesions [15-13] One very important factor in the development of Blackfoot disease is the use of water contaminated with Arsenic ,16] [17. According to the WHO and EPA standard, the concentration of Arsenic in drinking water has been classified into Class 1 (safe); 0-5 $\mu\text{g/l}$, Class 2 (worrying); 5-10

$\mu\text{g/l}$, Class 3 (non- safe); $10 > \mu\text{g/l}$ [19 ,18]. Many studies have shown that arsenic can be entered soil and water resources through chemical fertilizer .[21 ,20] In this study, it was attempted to evaluate concentrations of Arsenic in groundwater as well as Non carcinogenic risk population in Hasht Bandi of Minab by using the spatial distribution model (kriging method) (Figure 1).

Materials and Methods

Study area

Hasht Bandi area with a population of 5 thousands and area of 20 km^2 is located in the north eastern city of Minab and 100 km from Bandar Abbas (Center of Hormozgan Province) and the coordinates of 27°07'19" N and 57°27'23" E (Figure 1) [22]. This region has a dry and hot climate and its population is increasing due to the growth of agricultural activity.

Sample collection

In this cross-sectional descriptive study, samples were collected from 17 wells over an area of 20 km^2 during one year of 2012-2013. During every season of every 27 sample wells were collected. Hence During one year 1836 water samples from 17 wells were collected. After 10 minutes of water withdrawal out of the tube pump, the sample was transferred into 1.5 liter polyethylene bottle [23]. Finally, samples were transferred to the chemical laboratory of Faculty of Health at Bandar Abbas city in the temperature of 4 °C [24].

Measurement concentration of arsenic

Water samples were filtered through Watzman 42. Then to reach $\text{PH} < 2$, nitric acid (65 Merck) was added to preservation of heavy metals up to 28 days. Measurement concentration of Arsenic was done by

atomic absorption spectrophotometry model DR2800 in Method 8013 Silver Diethyl dithiocarbamate method [26,25].

Statistical analysis

For analysis different concentration of arsenic between seasons and regions with each other use pair sample T test. Also, statistical analysis was conducted by SPSS16 software with 5% error as significant level.

Calculating chronic daily intake and Hazard Quotient

Chronic daily intake was calculated by the equation proposed by EPA [27]:

Equation 1

$$CDI = C \times DI / BW$$

CDI; chronic daily intake (mg/kg-d), C; pollutant concentrations (concentration of Arsenic) in drinking water (mg/l), DI; daily water consumption (l/d) and BW; body weight (kg). Since there was no information on the mean water consumption and people's body weight of Hasht Bandi area, hence, according to DI and BW provided by EPA and WHO, chronic daily intake was calculated. DI for adults and BW were 2.723 l/d and 76 kg [29,28] Carcinogenic risk of heavy metals caused by eating or drinking is calculated by Equation 2 [30].

Hazard Quotient (HQ); for Non-carcinogenic risk of Arsenic caused by drinking, it was calculated by equation 2:

Equation 2

$$HQ = CDI / RfD$$

RfD; Contaminant Reference Dose is (mg/kg-d) and RfD for Arsenic is 0.0003

mg/kg-d [31] population is placed in a safe range if Hazard Quotient <1 [32]

Kriging method

Kriging method estimates the rate of regarded variable (concentrations of arsenic in groundwater) in other parts accurately through finding best line without error [33]

Equation 3

$$Z^*(x_p) = \sum_{i=1}^n \lambda_i Z(x_i)$$

To find best line without error, the following two equations must be solved simultaneously:

The general equation of Kriging method is as follows:

Equation 4

$$\sum_{i=1}^n \lambda_i \gamma(x_i, x_j) - \mu = \gamma(x_i, x_j)$$

$$\sum_{i=1}^n \lambda_i = 1$$

$Z^*(x_p)$, the estimated value of the variable in x_p , $Z(x_i)$; the estimated value of the variable in x_i , λ_i data weights, μ lagrange coefficient, $\gamma(x_i, x_j)$ Variogram value according to variable size in the point x_i and the final point of x_j [34]. In this study, spatial distribution models (Kriging surface) was prepared using the software Surfer12.

Results and Discussion

Mean annual ($M \pm SD$)¹ and concentrations range of groundwater are $7.69 \pm 2.56 \mu\text{g/l}$ and

¹ Mean \pm Standard deviation

0-23.7 µg/l, respectively. Annual mean concentration of Arsenic is located in class 2 (worrying class). According to the classification of Arsenic in drinking water, the mean concentration of Arsenic in autumn is (5.18±3.55 µg/l), winter (7.87±5.14 µg/l), spring (10.72±6.32 µg/l) and summer is (6.99±4.34 µg/l) are in classes 1 (secure), Class 2 (worrying), Class 3 (non-safe) and Class 2 (worrying) (Table 1). Order of seasons given the mean concentrations of arsenic is spring>winter>summer>autumn. Statistical analysis showed that there is a significant difference between the mean concentrations of arsenic in spring with other seasons (p value<0.05). Also, there is no significant difference in concentration of arsenic in winter, summer and autumn seasons (p value>0.05). Order of wells according to mean annual concentration of arsenic is W1> W6> W5> W11> W10> W13> W2> W3> W4> W14> W15> W9> W16> W8> W7> W12> W17. Annual mean concentration of arsenic in wells W8, W9, W13, W14 and W1 is in Class 3 (p value <0.05).

In contrast to our study, high concentrations of arsenic in much of the world in groundwater (10 µg/l<) is reported in the countries such as Bangladesh [37-35], India [38], Pakistan [39], and the United States [40]. This high concentration of arsenic in these areas could be the result of contamination of soil and water to industrial and agricultural wastewater or more of arsenic in the tissue layers of the earth and its dissolution in the water under the earth .[41] In the study done by Amin et.al, it has been indicated that the more the distance of sampling points and the number of samples from the area, the more the prediction accuracy of surface kriging map is increased .[42]

Chronic daily intake and Hazard Quotient population of Hasht Bandi region is 0.28

µg/kg-d and 0.92, respectively. Mean non carcinogen risk of arsenic is less than 1. Also, the Hazard Quotient for W7, W8, W9, W12, W13, W14, W15 and W16 wells is less than 1. The highest and lowest Hazard Quotient is relates to W13 and W4, respectively (Table 3). Groundwater arsenic concentrations in autumn is located in the North West region (3.8% of total area), in winter in the North East (13.3% of total area), in the spring, North East, North West and Centre (55.6% of total area) and in summer in Central and East (12.8% of total area) in a non-safe area (Figure 2). Thus the seasons in terms of non-safe area is spring>winter>summer>autumn. Autumn and spring seasons are the lowest and highest non- safe area (p value<0.05). A source of water pollution with heavy metals is agricultural wastewater .[43] Since the region has a temperate climate in autumn and winter, the agriculture in the region began in the fall and reaches its peak in the spring. Dissemination of agricultural waste in the winter and spring seasons is far more than the other ones. Since the region lacks any industrial center and subsequently the industrial waste, hence, this increase of arsenic concentration of groundwater, especially in winter and spring can cause further dissemination of agricultural waste in the season (Figure 2). Of course, arsenic entry from earth layers to groundwater cannot be overlooked.

According to the annual mean concentration of arsenic, 2.55 km² of the area is in Class 3 (12.7% of total area). In general, the highest mean concentrations of arsenic is in the north-east (W16, W15, W14, W13) and the lowest one is in the south and southwest (W4, W2, W3 and W5) (Figure 3). Statistical analysis (pair sample t test) showed significant differences in the concentrations of arsenic of the two regions (p value<0.05). As noted above, this difference could be due to different

dissemination of agricultural waste, soil permeability or concentration of arsenic in the ground layer or hydrologic processes [46-44].

Given that 2.55 km² of the area has a higher concentration than the standard concentration of arsenic, but 9.58 km² of the area (47% of total area) are located within the non-safe range (Hazard Quotient >1). The highest Hazard Quotient was seen in the North East areas and the lowest Hazard Quotient was seen in the South and South West (Figure 4).

Conclusions

The annual mean concentration of arsenic and Hazard Quotient of population Hasht

Bandi are in worrying class and Safe range, respectively. But spatial distribution models prepared by the kriging method showed that 47% of the area is located in a non-safe range (Hazard Quotient>1). Also, the highest concentrations of arsenic and subsequently Hazard Quotient is in the North East and the lowest one is in the South and South West. By increasing the points and the number of sampling in kriging method, it can be a good way to monitor, assess and manage the quality of the groundwater. Using kriging method, the way of moving the various pollutants, pollution sources and extent of contamination can be identified and carefully evaluated.

Table.1 The mean, range and standard deviation of 17 wells in Hasht Bandi region of Minab (µg/l)

	Width (X)	Length (Y)	Autumn	Winter	Spring	Summer	Min	Max	Mean ²	SD ³
W1	572348	270724	⁴ 4.7	8.9	9.8	5.25	2.3	10.9	7.16	2.56
W2	572440	270730	0.45	1.85	1.27	0.9	0	2.1	1.12	0.59
W3	572437	270623	0.87	0.98	1.21	1.25	0	1.4	1.08	0.18
W4	572518	270811	0.3	0.8	1.4	0.75	0	1.46	0.81	0.45
W5	572639	270742	3.9	6.9	7.6	4.9	1.6	8.4	5.83	1.72
W6	572542	270842	4.8	2.9	8.6	11.5	2.4	12.7	6.95	3.85
W7	572723	270839	9.7	7.9	12.4	8.7	0	13.2	9.68	1.96
W8	572558	270918	9.1	9.8	11.6	11.9	2.6	12.6	10.60	1.36
W9	572738	270917	5.2	11.3	13.5	15.8	0	16.9	11.45	4.55
W10	572756	270947	3.8	4.9	6.3	3.7	0.6	7.2	4.68	1.21
W11	572609	271001	2.5	3.6	6.9	7.6	1.1	8.3	5.15	2.48
W12	572457	271001	11.3	8.1	13.4	5.9	2.9	14.1	9.68	3.33
W13	572806	271005	4.6	16.5	22.5	13.1	4.5	23.7	14.18	7.47
W14	572650	271031	10.9	10.8	17.9	8.1	5.5	19.1	11.93	4.19
W15	572719	271104	7.8	13.9	19.8	4.7	5.6	21.1	11.55	6.70
W16	572619	271052	1.8	17.8	16.3	8.6	5.3	18.2	11.13	7.41
W17	572623	271133	6.4	6.9	11.7	6.1	0	12.4	7.78	2.64
Mean			5.18	7.87	10.72	6.99			7.69	

² Mean of 108 samples

³ Standard deviation

⁴ Mean of 27 samples

Table.3 The Chronic daily intake and Hazard Quotient population of Hasht Bandi region of Minab in 17 wells

	Mean ($\mu\text{g/l}$)	CDI ($\mu\text{g/kg-d}$)	HQ
W1	7.16	0.26	0.85
W2	1.12	0.04	0.13
W3	1.08	0.04	0.13
W4	0.81	0.03	0.1
W5	5.83	0.21	0.71
W6	6.95	0.25	0.83
W7	9.68	0.35	1.16
W8	10.60	0.38	1.27
W9	11.45	0.41	1.37
W10	4.68	0.17	0.56
W11	5.15	0.19	0.62
W12	9.68	0.35	1.16
W13	14.18	0.51	1.69
W14	11.93	0.43	1.42
W15	11.55	0.41	1.38
W16	11.13	0.4	1.33
W17	7.78	0.29	0.93
Mean	7.69	0.28	0.92

Figure.1 Hasht Bandi region in the northeastern city of Minab pre-province, Iran

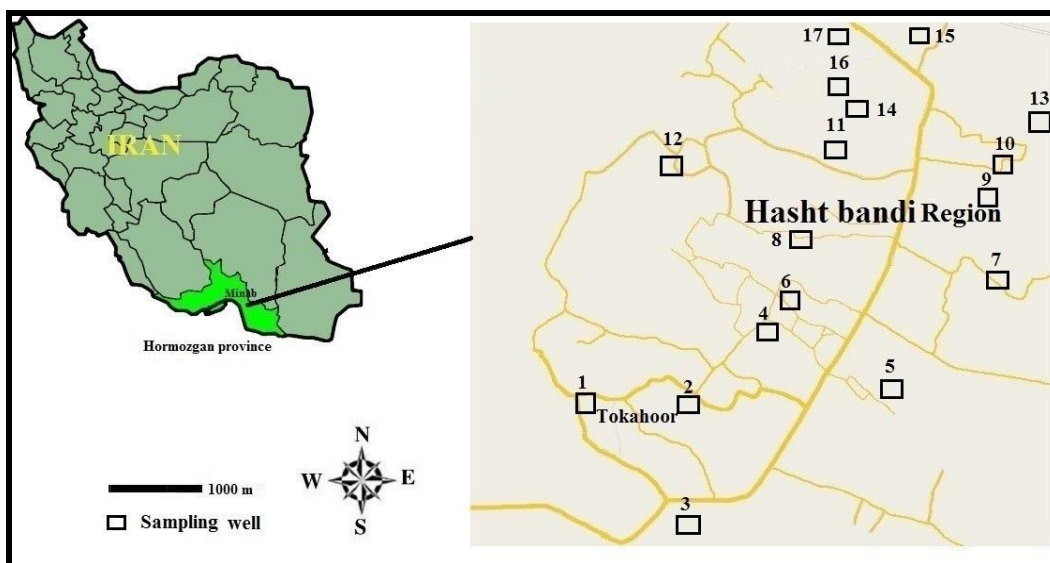


Figure.2 The spatial distribution model concentrations of arsenic in Hasht Bandi of Minab

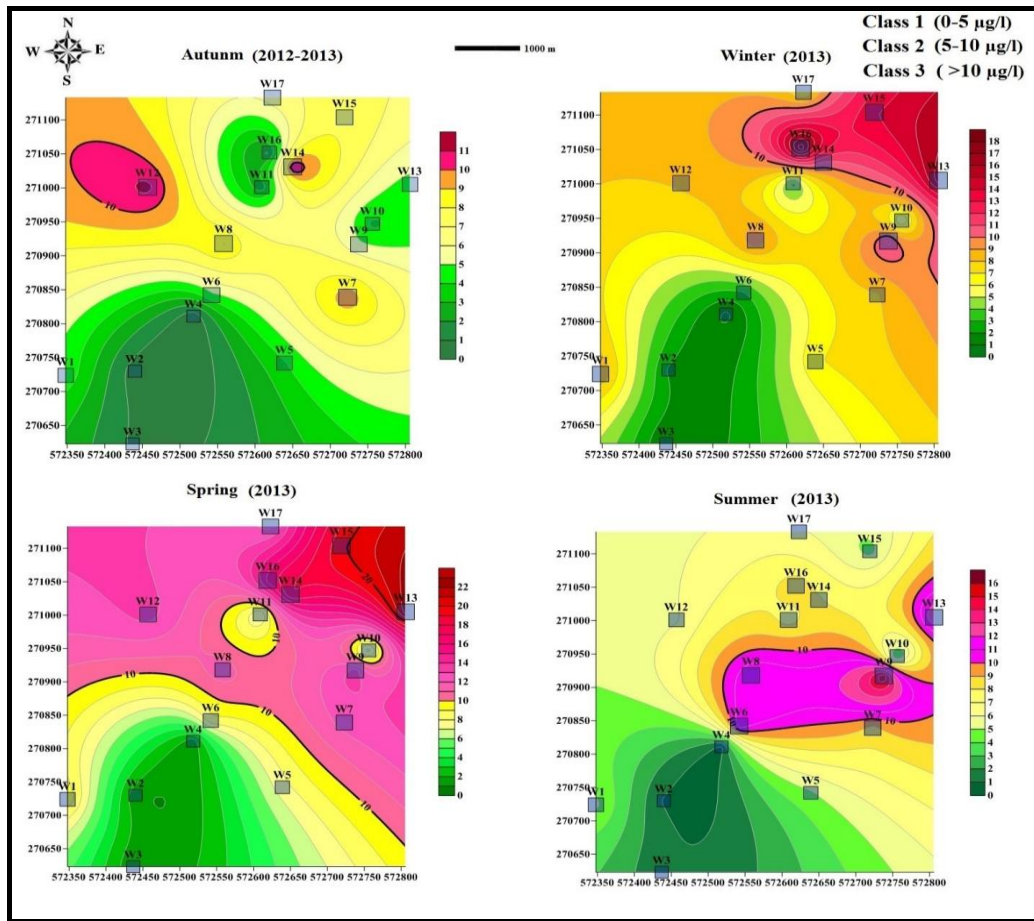


Figure.3 The Spatial distribution model the mean concentration of arsenic in groundwater of Hasht Bandi of Minab

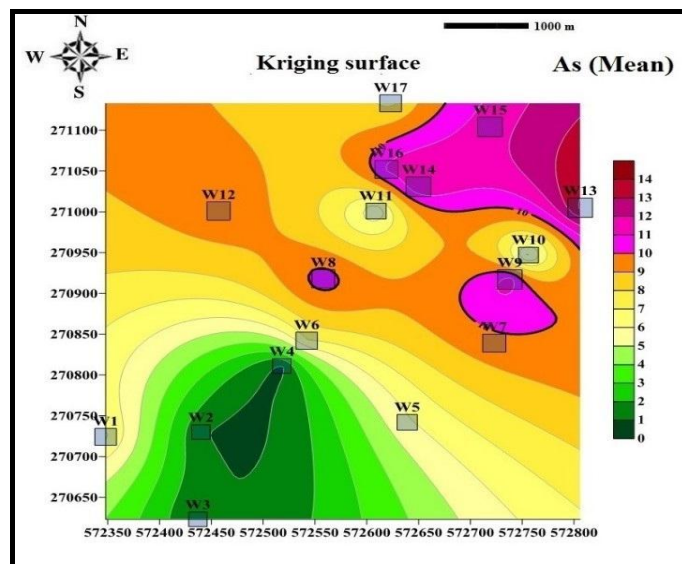
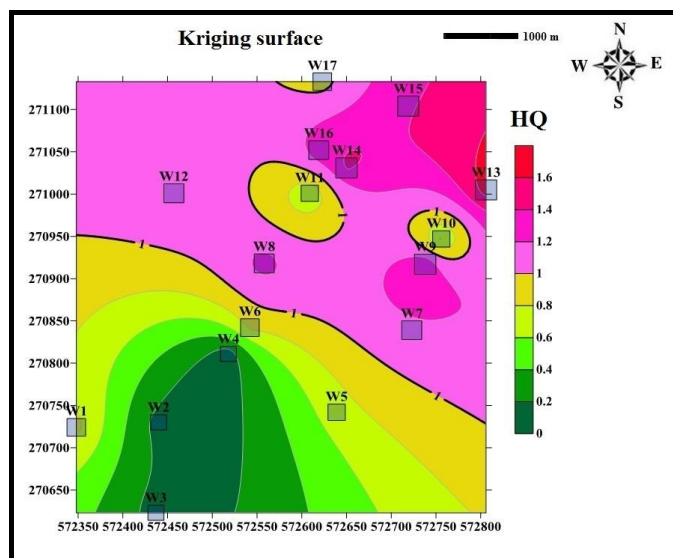


Figure.4 The Spatial distribution model for Hazard Quotient of arsenic in Hasht Bandi of Minab



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