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NITRATES AND OTHER MAJOR IONS CONCENTRATION IN THE GROUNDWATER OF MARDAN CITY AND ITS VICINITY

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Abstract: Ground water quality of Mardan city and about 25 villages along the Kalpani stream for human consumption, domestic and irrigation purposes has been analyzed. Various Physico-chemical parameters, major ions namely Ca, Mg, Na, K, SO_4 and NO_3 have been determined. Standard methods were used for the assessment of Physico-chemical parameters. Na, Ca, Mg, K were analyzed by using atomic absorption spectrometry (AAS). The Physico-Chemical parameters range in concentration as follows: pH 6.88-7.04, EC 289-1468µS/cm, Turbidity 1.1-127.5 NTU, TDS 157-783mg/l and DO 2.96-3.99 mg/l. Na, Ca, Mg, K, values in the study area vary as follows: 2.53-7.04, 1.10-7.04, 9.55-127.95, 19-61.8 mg/l respectively. Nitrates in most samples are above the safe drinking limits for drinking purposes and varies from 7.92-80.08 mg/l. Sulfates concentrations are well within the guidelines developed for drinking water. Based on the high levels of Nitrates in the drinking water, local populations are at risk of adverse health effects.

Keywords: Ground water quality, water pollution, major ions, mardan city, nitarates.

Introduction

Groundwater quality and quantity, both are important aspects for suitabile water use. Knowledge of water quality and regular monitoring are important issues in groundwater studies. Variation of groundwater quality is always expected cused by geological formations and anthropogenic activities (Subramani, *et al*, 2005). Groundwater quality depends on aquifer properties, such as soil type, groundwater retention time, and its interaction with the surrounding water bodies. Human activities, either because they produce great amount of wastes or cause modifications in the hydrological cycle, often pollute these fragile systems by modifying their quality to such an extent that their subsequent use becomes more restricted (Helena, *et al*, 1999). There are various natural and anthropogenic sources that add pollutants to the groundwater e.g. erosion, agriculture run-off, solid wastes, municipal waste and industrial effluents (Spalding and Exner, 1993).

Among the various physical and chemical contaminants, heavy metals had got critical role in human health related studies (Soylak, *et al*, 2002). Further, drinking water is also used for cooking food, which contains a considerable amount of elements of water. Indirectly elements reach the body through drinking water when it is use for animals, which provide milk and meat.

Nitrate is the most widely found contaminant in the groundwater aquifers in the world. Mostly attributed to man-made sources like agricultural activities, animal husbandry and the use of fertilizers, changes in land use patterns, the concentration of

nitrates is reported to be increasing (Sapek, 2005). Human infants are the most vulnerable to excess amounts of nitrates, in babies of less than six months of age, excess amount of nitrates may cause a disease called methemoglobinemia or blue baby syndrome which can prove fatal and result in mortality.

It is estimated that about one third of the people of the world use groundwater for drinking purposes (UNEP, 1999). Groundwater obtained from bore wells, hand pumps and dug wells is extensively used for irrigation, drinking and other domestic purposes in Mardan city and its vicinity. The purpose of this study was to determine the concentration of nitrate concentration in the groundwater samples of the study areaand the resultant health concerns faced by the local population.

Materials and Methods

Physical parameters like pH, EC and TDS of drinking water samples were determined using Consort electrochemical analyser (Model C931T). DO and Turbidity of the samples were determined by using Jenco DO meter (Model 9173) and Jenway Turbidimeter (Model 6035) respectively. Na, Ca, K, Mg using Perkinelmer AAnalyst 700, atomic absorption spectrometer. All these instruments were calibrated prior to examination according to manufacturer's recommendations.

Table 1. Sample locations

Sample No.	Location	Sample No.	Location
1	Ghalader	**16**	Mohabbat Abad
2	Nawankilly	**17**	Koragh
3	Sowaryan	**18**	Shiekh Maltoon
4	Toru	**19**	Shiekh Maltoon
5	Toru	**20**	Mian Killay
6	Mayar	**21**	Sharif Abad
7	Mardan City	**22**	Dheray Baba
8	Mardan City	**23**	Katlang Chowk
9	Mardan City	**24**	Janday
10	Mardan City	**25**	Baghdada
11	Mardan City	**26**	Baghdada
12	Mardan City	**27**	Baghdada
13	Mardan City	**28**	Gari Kapura
14	Mardan City	**29**	Gari Kapura
15	Mrdan City	**30**	Gari Kapura

The groundwater samples (Table 1) were collected in clean 1 liter polyethylene bottles. Samples were preserved according to standard methods as recommended by APHA

(1998). The samples were obtained directly from the pumps after running it for 20 minutes. The major ions were determined within one week of sampling. The results were then compared with standards set by USEPA and World Health Organization.

Results and Discussion

Physico-Chemical Properties

The results of parameters studied are summarized in Table 2. pH ranges from 6.88-7.04, EC concentration in the study area shows great spatial variation (range = 289-1468 µS/cm, ave. 805.46) with the lowest value at Sowarian and the highest value was recorded at the village Toru. Turbidity values range from 1.1-127.5 NTU with the lowest recorded at village Mayar and the highest being recorded at Toru. About 3 samples from Khawokaly, Toru and Mardan City show values above the permissible limit of 5 NTU (WHO, 2004). DO levels were the lowest (2.96 mg/l) at village Toru and the highest (4.67 mg/l) at the sampling point near Hoti Bridge in Mardan city.

Based on the results for Total Hardness test, water can be classified in to four categories: soft water (0-60 mg/l), moderately hard water (60-120 mg/l), hard water (120-180 mg/l) and very had water (> 180 mg/l). Most water samples (24 samples out of 30) in the study area lie in the very hard category (Fig. 1). An inverse relationship has been reported between hardness and cardiovascular diseases however the available data is insignificant to indicate a causal relationship. Hence, World Health Organization holds no health based guideline value for hardness (WHO, 2004).

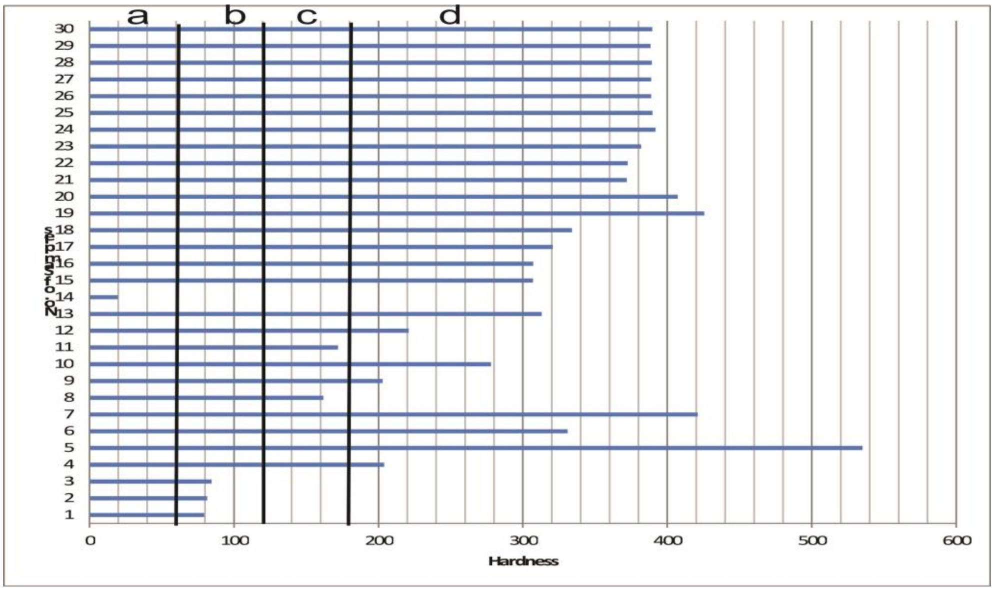

Fig.1. Categorization of Water Samples based on total hardness (TH) (mg/l) a. soft water (0-60 mg/l), b moderately hard water (60-120 mg/l), c. hard water (120-180 mg/l) and d. very hard water (>180 mg/l).

Table 2. Descriptive statistics of the Water Quality Parameters in the Study Area

	C°	pH	EC	TDS	Turbi dity	DO	TH	Ca	Mg	Na	K	SO_4	NO_3
			µS/c m	*mg/l*	*NTU*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*
WHO - 2004	-	-	-	***500***	***5***	-	-	-	-	***200***	***10***	***250***	***10***
Max	24	7.2	1945	880	127.5	4.67	535	7.152	128	7.047	61.8	94	80.08
Min	21	6.8	289	152	1.1	2.96	19.8	1.107	9.55	2.535	19	9	7.92
Median	22	6.9	1180	653.5	3.66	3.385	332.5	3.953	79.775	3.7365	26.17	38.035	41.07
Q1	22	6.9	766.5	404.75	1.9	3.2025	208.25	2.412	50.1325	3.45025	23.6275	30.865	23.24
Q3	24	7.1	1393.75	746.5	4.71	3.905	389.1	4.05575	92.165	4.32525	30.05	48.9625	47.63
St.Dev	1.18	0.078	424.13	208.36	22.71	0.41	125.25	1.381	29.575	1.091	7.935	19.729	17.95
Mean	22.8	6.96	1097.8	578.83	7.52	3.523	301.9	3.428	72.078	4.0016	28.027	42.73	37.64

High levels of TDS (Fig. 2) were found in the study area (range =152 to 783 mg/l, ave. 430.93). Most of the ground and surface water are rich in inorganic contents in the form of various salts. Organic contents are usually in small amount. The desirable limit for TDS is 500 mg/l; 18 samples in the study area exceed this limit. Water containing TDS more than 500 mg/l causes gastrointestinal irritation (BS, 1991), the presence of high levels of TDS (greater than 1200 mg/l) in drinking water is objectionable to consumers. Water with low levels of TDS is also not recommended because of its low nutrient quality and objectionable taste (WHO, 2003).The classification of groundwater on the basis of TDS (Freeze and Cherry, 1979) shows that all the samples in the study area can be classified as fresh water i.e. < 1000 (Table 3).

Table 3. Water Classification based on Freeze and Cherry (1979)

TDS (mg/l)	Nature of Water
<1000	Fresh water
1000–10000	Brackish water
10000–100000	Saline water
>100000	Brine water

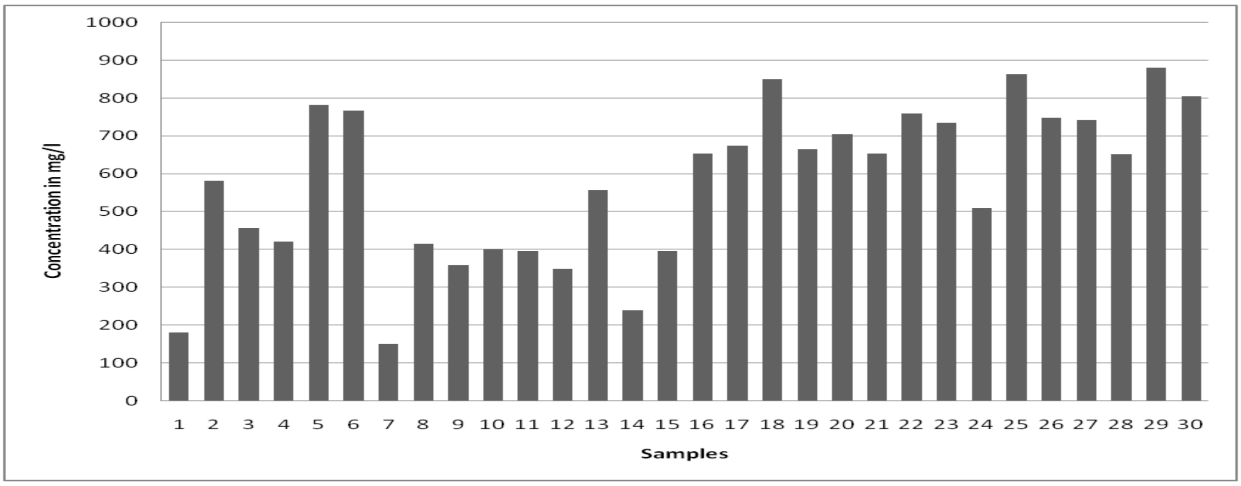

Fig.2. TDS (mg/l) in the groundwater samples of the study area

Major Ions

K concentration in all the samples from the study area is well above the permissible limit of 10 mg/l (WHO, 1984), while Ca, Mg and Na values were found within the permissible limits. The K content in groundwater samples range from 19-61.8 mg/l, with the lowest value determined at Khawokalay and the highest K concentration was recorded at Toru. Potassium is an essential element in human nutrition. Potassium concentrations in drinking water are generally low. Though some case studies have shown that high doses of K salt substitutes may cause stomach problems. World Health Organization has recently removed K from their health based guidelines and does not consider the evidence enough for formulating a health based guideline for drinking water intake (WHO, 2004; WHO, 2009).

The highest recorded value of Ca is 7.136 mg/l at Mardan City and the lowest value 1.104 mg/l was found at Sowarian. Mg values vary in range from 9.55-127.95 mg/l, with the lowest value in Katlang Chowk and the highest at Toru. Minimum Na value was recorded at Serai 2.535 and Maximum Na value 7.047 mg/l was recorded at Toru. Like K, Ca and Mg are also essential nutrients in human diet; the deficiency of both may cause health concerns. About 99 % of calcium in human body constitutes the structural element of the bones and teeth. Similarly, Magnesium is the fourth most abundant cation in the body and serves as a cofactor to about 350 enzymes Excess intake of calcium may cause osteoporosis, formation of kidney stones, hypertension and may also result in insulin resistance. Excess intakes of Mg may seldom result changing of bowel habits and may cause laxative effects (WHO, 2009).

Nitrates concentration (Fig. 3) in 28 samples from the study area show concentration above the maximum contamination level designated by the US EPA for drinking purposes (UNEP, 1999). Sulfate concentration in the study area ranged from 9 to 94 mg/l showing greater spatial variability. The main sources of nitrates in groundwater are agricultural activities, animal husbandry and changes in land use (Sapek, 2005). Globally mineral fertilizers and

cultivated soils are considered the major sources for nitrogen fixation (Pacyna and Gradael, 1995). Nitrate is not a natural component of the rocks or soil mineral matrix; instead it's a byproduct of nitrogen turnover in the soils. A defined portion of nitrates depending on the rainfall in a specific region may leach down to the aquifers (Sapek, 2005). Human use of fertilizers for agricultural purposes may further add to the concentration of nitrates in the groundwater. "High levels of nitrates in drinking water may blue baby syndrome in infants especially less than six months of age and is also associated with hyperthyroidism" (Maanen, 1994; WHO, 2004).

Sulfates in all the samples from the study area are well within the permissible limits of 200 mg/l assigned by WHO based on aesthetic reasons (WHO, 2004). Figure 4 compares the concentration of all the major ions studied, using a box plot. Mg appears as the most dominant ion in the study area followed by nitrate in a sequence: Mg>NO3>SO4>K>Na=Ca. Jochen (1992) studied the hydrochemistry of groundwater of the Peshawar Basin and classified the groundwater chemically in to three groups based on the concentration of major ions. He reported high concentrations of sulfates, chlorides and sodium from Mardan area. Further, he suggested the drilling of deep wells in the study area and clean water supply through pipe lines for the local population as remedial measure. In an earlier study Ali *et al.,* (2009) reported high levels of Pb, Cr, Ni and Cd in the drinking water obtained from water supply i.e. tap and hand pump sources. They attributed the higher amounts of heavy metals in the water samples from Mardan and its vicinity to plubosolvency resulting from the corrosive and aggressive chemical behavior of the water in the study area.

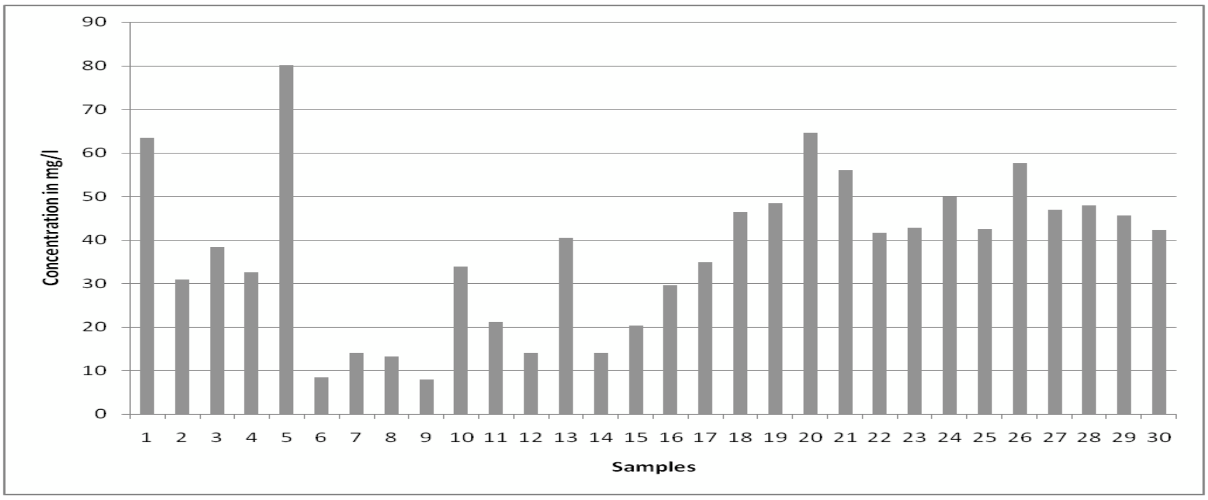

Fig.3. Nitrates (mg/l) in the groundwater samples of the study area

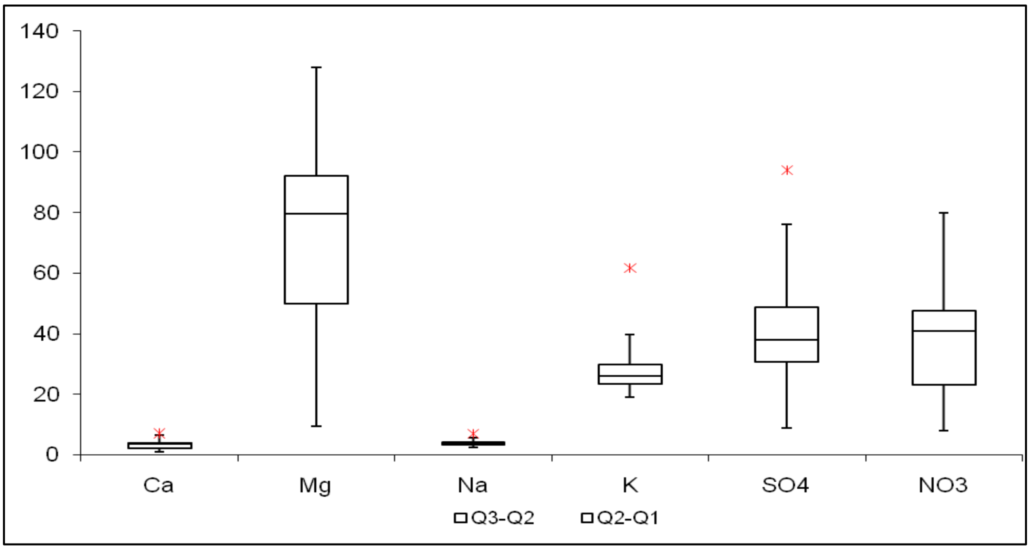

Fig.4. Box plot showing a comparison of major ion concentration in the groundwater samples of the study

Conclusion

Among all the major ions studied Magnesium shows highest concentration followed by Nitrates in the study area. Magnesium is not considered as a health threat and the concentrations found in the study area are not of a concern, similarly other major ions except nitrate are within the range of safety limits for drinking water. However, high levels of nitrates in the study area can pose serious health threats to the local population especially to infants below six months of age. Turbidity does not appear as a major source of concern in the study area. Only three samples in the study area show Turbidity above the permissible limits. On the other hand, TDS in half of the samples show concentration above the permissible limits. Proper treatment of drinking water prior to use and digging of deep wells is recommended, further awareness of the local population regarding the high concentration of nitrates in their drinking water sources is needed.

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