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Spectrophotometric Measurements of Some Inorganic Contaminants in Ground Water Samples

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Abstract:

The aim of this study was to measure the concentrations of some acid radicals in ground water samples, obtained from, boreholes, hand-dug wells, and pump wells, within Bara basin (Sudan). The measured parameters include sulphate, nitrate, nitrite, carbonate, bicarbonate, chloride, fluoride, and sulphide ions as well as ammonia nitrogen. The samples were spectrophotometrically analyzed using HACH method. Bicarbonates and chloride contents were measured titrimetricaly. The analysis showed high nitrate content in all samples. Some samples showed high sulphate and chloride contents, whereas others had higher bicarbonate content. The obtained results were statistically analyzed using SPSS program. The means of the measured values were correlated with some cations concentrations (means) for the same water sources to predict the probable geological background of the measured contaminants.

Key words: Acid radicals, HACH method, Geo-indicators, Semi arid, Correlation

1. INTRODUCTION

Water as a liquid is the most essential component of life, in the sense, that, life without it is not possible. On global scale there

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is enough abundance of water, but water is not always available in the right place at the right time and the right form (V. M. Ahluwalia, 2008). Over 90% of the fresh water in the world is groundwater (V. M. Ahluwalia, 2013). In Sudan about 85% of the population depends on groundwater (Abdeen. M. O., 2013; Gibla, O. A et al, 2016).

Natural water normally penetrate top soil layer, sub-soil layer and different rock formations to reach the aquifers as ground water reservoirs. When travelling downwards, water can dissolve a variety of compounds, ranging from simple salts to complex minerals and rocks. Rocks may contain a mixture of minerals such as silicates, carbonate, sulphate, chloride, fluoride, and nitrate. Natural water quality therefore may be affected by the prolonged and continuous water-rock interaction. Water stagnation in certain water bearing rocks may give chance, to more solubility of solids. The water soluble solids originate the main chemical properties that determine drinking water quality and suitability of ground water sources for human use. The high concentration of water- soluble substances leads to ground water salinity as one of the main properties that determine drinking water quality. According to Edmunds (1980, 2004) salinity build of ground water in semi arid regions has several origins. The most important ones are atmospheric aerosol, sea water of various generations and evaporite sequences. Salinity distribution may be due to natural geological and climatic factors, such as oxidizing and reducing conditions and the prolonged residence times (W. M. Edmunds, 2004).

In this study groundwater samples were collected from different sources including boreholes, hand dug wells and pump wells. The depths of the wells differ from 10 to 40meters for hand dug and pump wells. The bore holes are normally very deep. The samples were grouped into four classes described as section A, B, C, and D. Samples of section A and C are from fresh water sources. Samples of section B and D were from two areas characterized as high salinity zones known as Elga'ah and Sharshar. The studied areas are within Bara locality boundaries, in northern kordofan state. Groundwater here is directly used for human drink, animal watering and irrigation purposes without any pretreatment. This study was first aimed to find an explanation to the question that, why fresh water from some bore holes is corrosive to metallic reservoirs and tanks in many water yards. The study therefore conducted to perform qualitative and quantitative measurements, for the main anions that may cause natural water salinity as inorganic contaminants and as geoindicators. The obtained results were statistically analyzed using SPSS program. The mean concentrations of the measured parameters for section (A) samples were then correlated with mean concentrations of some cations obtained by atomic absorption spectrometric analysis.

2. MATERIALS AND METHODS

Samples were collected from forty five different sources. The chemicals used were all of analytical grade. Spectrophotometric analysis was carried for the determination of nitrate, nitrite, sulphate, sulphide, fluoride ions, and ammonia-N using HACH method, where specific readings were observed at the specific wavelengths. Chlorides, carbonate, hydrogen carbonate, and Hydroxide contents were determined titrimetrically.

3. RESULTS AND DISCUSSION

Nitrate (NO_3^-)

Nitrate concentrations were found to be significantly high in all sections (A, B, C, and D). Samples 1, 2 and 10 of section (A) show relatively low concentrations; (13.0, 18.0 and 29 ppm). (figure. 2) All the other samples, have nitrate concentrations higher than the standard permissible value (10- 40 mg/l), with the highest value in sample (No.4) which was 490 ppm. The mean value is 215.0 ppm nitrate. This may indicate high nitrate contamination. Such water samples are not suitable for human use especially for drinking.

For section (C) the mean concentration of nitrate was 57.0 ppm. The maximum readings were 130 ppm and 139.0 ppm, The lowest nitrate (NO_3^-) concentration in this section is 10 ppm, other samples with acceptable nitrate range in section (C) were No. (26), (27), (30), (31), (33) and (34) with (27, 20, 23, 29, 13 and 16) ppm nitrate respectively. The minimum acceptable nitrate concentration is 10mg/l (figure. 4). For section (B) and to (D) the mean nitrate values were 245.2 and 67.5 ppm. Since the samples were from high salinity zones such high nitrate concentration ranges may be expected. Suitable water quality for live stock use should not contain more than 100 ppm as nitrate and nitrite (CCREM, 1978; FEPA, 1991; ECPRC, 1991) (figures.3, 6). Therefore we may conclude that the nitrate concentration is a real risk in the study area. Sudanese Standards and Metrology Organization (SSMO, 2002) consider 50 mg/l nitrate as a maximum admissible limit for drinking water. Although nitrate contamination, partially, may be, attributed to animal waste especially in the case of open shaft wells, where, people are using (Dalue) for water abstraction, the geological formations are expected to be the main source in the case of the Bore Holes.

Nitrite (NO_2^-)

In section (A) the nitrite concentration ranged from (0.03 to 0.6 ppm), with a mean value as 0.4944ppm (figure. 1). In section (C) samples nitrite content was ranging from (0.01 to 0.04 ppm), with a mean value of 0.0164ppm (figure. **5**). It is clear that the nitrite concentration in these two sections is proportional to that of nitrate, since the mean concentrations of nitrate ions for section (A) and (C) were found to be 215.8 and 57.07 ppm respectively. This may increase the indication of nitrate risk. For section (B) and (D) samples, the maximum concentration of nitrite was 10 ppm for (B) and 3.9 ppm for (D). The mean nitrite content for the two sections was 2.599 ppm for

(B) and 1.2473 for (D) (figures. 3 and 6). The concentration of nitrite here is not a direct problem, since the water is not used for human drinking or livestock watering. Such relatively high nitrite (NO_2^-) content may be expected in high salinity zones with high TDS values, including nitrate (NO_3^-) ions occurrence. The proposed guideline value for nitrite is 3ppm (WHO, 1993). Because of the possibility of simultaneous occurrence of nitrite and nitrate in drinking water, the sum of the ratios of the concentration of each ion to its guideline value should not exceed one (1). e. g. $CNO_2^-/GVNO_2^- + CNO_3^-/GVNO_3^- \leq 1$, where C is concentration, GV is guideline value.

Sudanese standards and meterology organization considered the admissible concentration of nitrite in drinking water as 2 mg/l. Accordingly the nitrite concentrations for samples of section (A) and (C) are far low from the maximum levels accepted by WHO (1993) and SSMO, (2002).

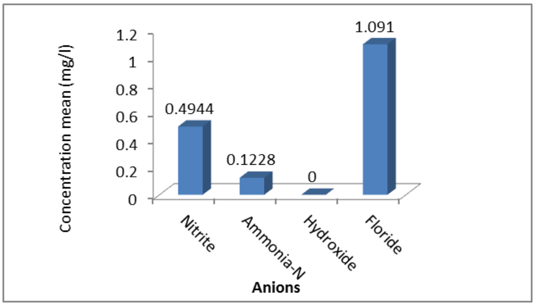

Fig. 1: Micro-anions mean concentration (mg/l) Section (A)

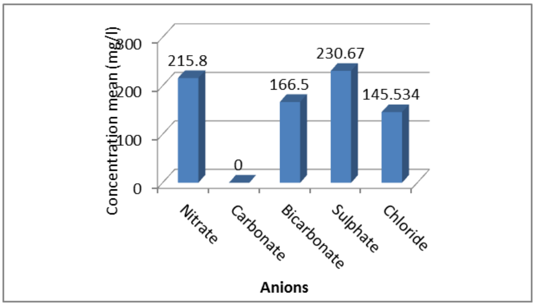

Fig. 2: Macro-anions mean concentration section (A) (mg/l)

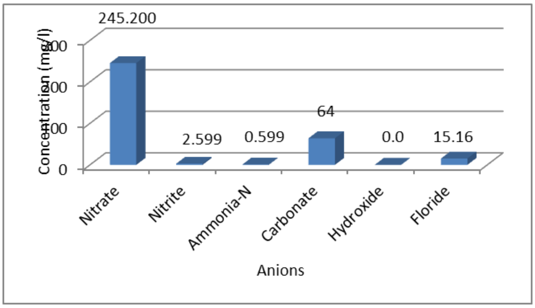

Fig. 3: Anions concentrations mean (mg/l) Section (B)

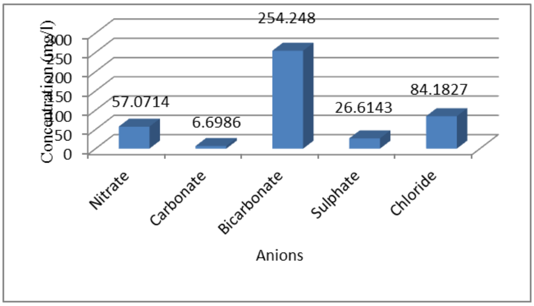

Fig.4: Macro-Anions concentrations mean (mg/l) Section (C)

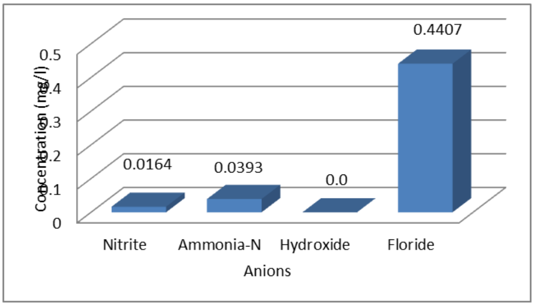

Fig.5: Micro-Anions concentrations mean (mg/l) Section (C)

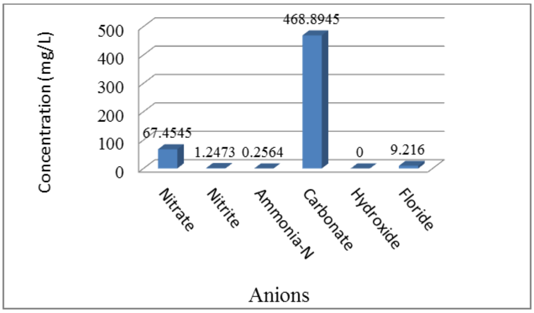

Fig.6: Anions means concentration (mg/l) section (D)

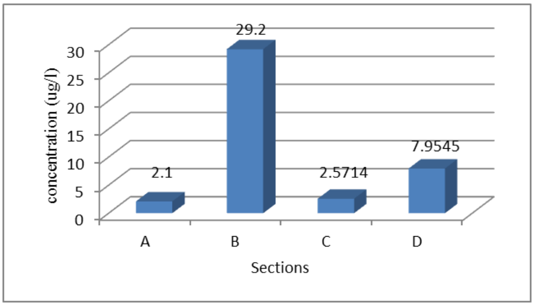

Fig.7: Sulphide means concentration (ug/l)

Ammonia Nitrogen (NH_3-N)

Ammonia Nitrogen has the mean values of 0.1228, 0.5994, 0.0393 and 0.2564 ppm for section A, B, C, and D respectively. According to WHO, (1993), the natural levels of ammonia in surface and ground water are usually below 0.2 mg/l. Ammonia in its non-ionized (NH_3) and the ionized form (NH_4^+) in drinking water is not of immediate health relevance. Aerobic ground water may contain up to 3mg/l. Ammonia contamination arising from bacterial, sewage and animal waste pollution has no, proposed, health based guideline value. Ammonia toxicological effects are observed only at exposures above 200 mg/kg of body weight (WHO 1993).

The measured NH_3-N values for section (A) and (C) are not problematic (figures. 1, 5). The few exceptions may be due to local environmental pollution (e.g. sample (No. 9)). Section (C) may be almost ammonia Nitrogen free. Brine samples of section (B and D) show higher concentrations in general with respect to the standard limit (0.2 ppm) (figures. 3, 6). SSMO level for drinking water is 1.5 mg/l which is greater than the mean concentration for the four sections covered by this study.

Chloride (Cl^-)

Chloride concentrations for section (A) samples were, generally, lower than the maximum permissible value (250mg/l). The mean value concentration was (145.5 mg/l). Two exceptions were showed by samples No. (7) and No. (8), which were respectively 443.2 mg/l and 301.4 mg/l. IFAD analysis (2003) reported a 418.31 mg/l for the same sources. PRC Engineering consultant (1981) reported chloride concentration as 30 –160 mg/l at Bara. The results of this study were 35.453 mg/l and 106.359 mg/l at Bara, from an open shaft well and a borehole. (Figure. 2)

All section (C) samples have chloride content less than the admissible maximum limit, with a mean value of 84.18 mg/l. The lowest chloride concentrations in this study were at samples (No. 24, and 27) of section (C) which were (17.73, and 20.56 ppm) (figure. 4). In the high salinity zones of section (B) and (D), chloride content of ground water is very high, giving favorable conditions to salt production for commercial purposes by the local community. The highest chloride content is in sample (No. 12) which was 101.0 g/l.

Flouride (F-)

The maximum guideline value of fluoride is 1.5 mg/l (WHO, 1984, 1993; SSMO, 2002). Ground water may contain up to 10 mg/l (WHO, 1993). For section (A) and section (C) samples, the mean fluoride concentration is low than the maximum permissible value, it was 1.1 ppm for (A) and 0.447 mg/l for (C). In section (A), samples No. 2, 8, 6, and 7 show high fluoride concentrations of 1.54, 1.64, 1.93, and 2.0 mg/l respectively. IFAD (El-Obeid, 2003) reported 8.44 mg/l of fluoride at El-Murra. In this study samples No. 7 and 8 are from El-Murra. All ground water samples of section (C) could be described as fluoride deficient (Figure. 5). For section (B) and (D) (Figs. 3 and 6) the fluoride content is significantly high, with mean values of 15.16 mg/l for (B) and 9.21 mg/l for (D). Such high concentration may be expected as a part of dissolved ions in high salinity zones.

People of the area, who use ground water sources of section (A) and (C), may face a risk of increasing dental problems. PRC Engineering Consultants (1981) reported fluoride concentration of 1.16 mg/l at Bara and 0.7 mg/l at Um-Ruwaba.

Sulphide (S^{2-}) content

Sulphide concentrations of section (A) samples were ranging from (1.0 to 5.0µg/l) with a mean of (2.1 µg/l). In section (C) the values was also ranging from 1.0 to 5.0µg/l but with a mean value of (2.5714 µg/l). Occurrence of sulphide ions in water is mainly due to the presence of hydrogen sulphide, which is formed when sulphides were hydrolyzed in water. The level of hydrogen sulphide formed in drinking water, is usually low because sulphides are readily oxidized in good aerated water. In deep wells at semi arid zones, ground water contains dissolved hydrogen suphide as a source of (S^{2-}) ions, because oxygen content at such depths is generally low. With respect to (WHO. 1993) no health-based guideline value is proposed for sulphide in drinking water. Although oral toxicity data are lacking, it is unlikely that a person could consume, a harmful dose of H_2S. However, WHO (1993) recommended that hydrogen sulphide should not be detectable in drinking water by taste or odour. Sulphide contents of section (B) and (D) were relatively high with mean values of (29.2 and 7.95 µg/l) (figure. 7). These concentrations are low compared to TDS values in the two sections which were expressed as g/l (ppt) (Gibla, 2007).

Sulphate (SO_4^{2-})

The mean concentration of sulphate for section (A) and (C) is generally below the permissible limit. For section (A), it is 230.67 ppm with minimum values in sample (No.1) 25.0 ppm and maximum in sample (No. 8) which was 645 ppm. Samples (4), (6) and (7) showed sulfate concentrations of 319, 355 and 375 mg/l respectively (figure. 2). For section (C) the mean concentration was (26.61ppm), with lowest values of 0.5 ppm in sample No. 27 and 0.6 ppm in samples No. 22 and 24 (figure. 4). The highest sulphate concentration was at sample (No. 32) 18000 mg/l. The local communities use this water source for live stock watering only. For saline zone samples of section (B) and (D), the mean concentration is 80.2 g/l for (B) and 56 g/l for (D). IFAD, (1993) described the salinity zones in Bara basin to be characterized by very high sulphate and chlorides. They suggested that such salinity may be due to the presence of thick evaporite layer deposited under lacustrine conditions. They reported high sulphate and chloride concentrations over 1000 ppm Near Jebel Koan. The report described the ground water quality in basement rocks as a function of basement composition and annual recharges. Mukhtar (2001- 2002) reported that, the northern part of Mahlliat Taiba is under lained by basement rocks and form saline aquifers zones. Such high concentrations of sulphates and chlorides were reported by Sandia National Laboratories (SN labs) on evaluating ground water at Tularosa Basin of New Mexico (2002), concluding that "a wide range of water chemistry including sodium chloride, carbonate, and sulphate based, brackish water exist in that basin. This is nearly to be the case of the high salinity pockets for section (B and D) at Bara basin.

In this study the results may indicate, that, the main salinity sources in the area are bicarbonate, sulphate and chloride.

Table.1: Correlations of the measured anions and some cations of section (A) samples

Cations	**Anions**						
	NO_3^-	NO_2^-	CO_3^{--}	HCO_3^-	SO_4^{--}	Cl^-	F^-
Sodium (Na+)	-0.293 p = 0.411	-0.2423 p = 0.5	- -	- 0.0608 p = 0.868	-0.1745 p = 0.548	-0.3384 P = 0.373	*0.4566 p = 0.255
Potassium (K+)	0.2598 P = 0.469	0.1118 P = 0.759	- - - -	0.128 P = 0.724	0.3856 P = 0.271	*0.5145 P = 0.156	-0.2488 P = 0.552
Magnesium (Mg++)	*0.6962 P = 0.037	*0.7352 P = 0.024	- - - -	*0.7137 P = 0.031	**0.9049 P = 0.001	*0.5411 P = 0.166	*-0.6002 P = 0.154
Calcium (Ca++)	**0.8478 P = 0.002	*0.5836 P = 0.077	- - - -	0.3661 P = 0.298	*0.6357 P = 0.048	0.389 P = 0.266	*0.454 P = 0.187
Iron (Fe)	-0.0489 P = 0.893	-0.2894 P = 0.417	- - - -	*-0.6329 P = 0.050	-0.14444 P = 0.198	-0.3148 P = 0.368	0.1154 P = 0.786
Mangenese (Mn++)	-0.4139 P =0.234	-0.0622 P = 0.864	- - - -	-0.22 P = 0.541	-0.285 P = 0.425	-0.104 P = 0.774	-0.092 P = 0.801
Barium (Ba++)	0.129 P = 0.721	-0.100 P = 0.783	- - - -	*-0.512 P = 0.130	-0.199 P = 0.582	-0.306 P = 0.389	*-0.598 P = 0.068
Lead (Pb)	0.331 P = 0.350	0.302 P = 0.396	- - -	0.492 P = 0.148	0.335 P = 0.344	0.424 P = 0.222	*0.513 P = 0.129

For more investigation about, the most probable source of the measured parameters, the mean concentrations were correlated with mean concentrations of some cations obtained by atomic absorption spectrometric analysis for the same samples. (Table. 1)

The results showed strong positive correlation between calcium ions and nitrate and nitrite ions. Magnesium ions also show relatively strong positive correlation with nitrate and nitrite ions. Magnesium also shows positive correlation with sulphate and bicarbonate. Magnessium and potassium have almost the same positive correlations strength with chloride. These two elements are known to be found in earth crust in one ore ($KCl.MgCl_2.6H_2O$).

The reliability of the obtained results may be enhanced by the positive correlation of sodium and calcium with fluoride ions, as well as the negative correlation of magnesium and fluoride. MgF_2 is known to be insoluble in water; CaF_2 is partially soluble whereas NaF is expected to be of high solubility. Calcium fluoride is one of the known calcium ores in earth crust, therefore groundwater quality in the area may be influenced by local geological formations, which are expected to be dominated by calcium and magnesium nitrate and nitrite, magnesium carbonate, magnesium and calcium sulphate, magnesium and potassium chloride as well as sodium and calcium fluoride. In addition the higher nitrate concentration may be due to geological formation rather than biological contamination. Animal waste contamination may be fairly indicated by ammonia nitrogen concentrations.

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