Physio-chemical and EDXRF Analysis of Water Samples from District Kurukshetra, Haryana, India

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Abstract: The analysis of physiochemical parameters of groundwater from nineteen locations of District Kurukshetra, Haryana was carried out. Each parameter was compared with the standard desirable limits prescribed by World Health Organization (WHO), Bureau of Indian Standard (BIS) and Indian Council of Medical Research (ICMR) to assess the quality of ground water. The physiochemical parameters namely pH, electrical conductivity, Total Dissolved Solids, Total Alkalinity, Total Hardness, Chloride, Calcium, Magnesium, and dissolved oxygen were determined. Systematic calculation was made to determine the correlation coefficient 'r' amongst the parameters. Significant value of the observed correlation coefficients between the parameters was also carried out. The results showed significant variations in water quality parameters in the study areas. Elemental analysis of different samples was carried out using the EDXRF technique. It is concluded that the water quality of water supply systems in different locations of Kurukshetra is of medium quality and can be used for domestic use after suitable treatment. Suitable suggestions were made to improve the quality of water.

1. Introduction

Water is the most important natural resource, available on the earth, for the welfare of the society. Water is essential for human being, all other living organisms, ecological systems, food production and economic development. The main applications of water are domestic uses, irrigation, commercial uses, industrial uses and for the production of hydropower. The safety of drinking water is affected by various chemical and microbiological contaminants and these contaminants cause serious health problems. Due to these contaminants, the quality of the drinking water is deteriorating day by day, which causes many diseases in the humans. The domestic sewage and industrial waste are the leading causes of ground water pollution (Singh *et al*, 2010, Singh *et al*, 2012; Garg *et al*, 1999 and Muthulakshmi *et al*, 2015). The physiological and energy dispersive x-ray fluorescence (EDXRF) analysis is, therefore, beneficial and provide valuable information for the water quality parameters.

Quality of ground water is the resultant of all processes and reactions that act on the water from the moment it is condensed in the atmosphere to the time it is discharged by a well or a spring and varies from place to place and with the depth of the water table (Jain *et al*, 1994). Many diseases are caused by the inability of the environment to supply the mineral needs of man and animals in adequate. Sometimes these nutritional abnormalities occur as simple deficiencies or excesses. Many investigations have found a correlation between cardiovascular deaths and water composition (Pitt et al, 1995). The disorder of teeth and bones is due to consumption of fluoride-rich water (Susheela, 1999). Atomic Absorption Spectro-photometry has been used to analyze soils from Ketaren Gwari area of Minna for possible heavy metal contamination due to dumping of refuse and mechanic activities (Dauda *et al,* 2011). The objective of the scientific investigations is to determine the hydrochemistry of the ground water in Kurukshetra, Haryana and to classify the water in order to evaluate the water suitability for drinking, domestic and irrigation uses and its suitability for municipal, agricultural and industrial use. The social relevance of the problem has encouraged us in carrying out this work.

Kurukshetra is the holy city of the state of Haryana and it is situated 160 km north of Delhi on the National Highway NH1. The Kurukshetra district lies between latitude 29º52' to 30º12' and longitude 76º26' to 77º04' in the North Eastern part of Haryana State. The district has a total of 419 villages. In Kurukshetra District, Markanda, Saraswati (since dried up before 1900BCE) and Ghaggar are the important rivers. Kurukshetra is a place of great

historical and religious importance, revered all over the country for its sacred associations. The battle of Mahabharata was fought in Kurukshetra and Lord Krishna preached His Philosophy of "Karma" as enshrined in the Holy Shrimad Bhagwad Geeta to Arjuna at Jyotisar. In Shrimad Bhagwad Gita, Kurukshetra is described as Dharamkshetra, i.e., field of righteousness.

2.   Materials and Methods

Physio-Chemical Analysis was carried out for various water quality parameters such pH, Total dissolved solids (TDS), Total Hardness, Total alkalinity, Calcium, Magnesium, Chloride, fluoride, Dissolved oxygen, as per standard procedure described in standard methods for the examination of water and waste water (American public Health Association, 1992). The physical parameter pH was determined using the digital pH meter (LT-10, Labtronics, Panchkula, India) and EC was determined using the digital conductivity meter (LT-16, Labtronics, Panchkula, India). The water samples have been analyzed using the EDXRF setup available at EDXRF Laboratory, Physics Department, Panjab University, Chandigarh. This technique uses proportional characteristics of the multichannel semi-conductor detectors, to produce a distribution of voltage pulses proportional to the spectrum of photon energies from the target. Interactions of photons with matter permit analysis of the sample constituents using excited x-rays. These samples were analyzed without any chemical pre-treatment. In the EDXRF method, the ionization cross-section for an atomic level is greatest when the exciting x-ray energy just exceeds the binding energy of the electron in that level, and falls off drastically with an increasing difference between the excitation energy and the electron binding energy. The pellets were mounted into a target holder specially made for irradiation of thin target. The energies of the characteristic x-rays were used to identify the elements present in the water samples. All the calculations were done using $_{42}$Mo $K_{\alpha\beta}$ incident photon energy from intense Mo anode x-ray tube (Panalytical X-ray generator, model PW 3830 4kW). The tube voltage was kept at 29 kV and current 12 mA. The spectra were recorded using a Low Energy Germanium LE(Ge) detector coupled to a PC based multichannel analyzer (MCA) through a spectroscopy amplifier. The resolution of the LE(Ge) detector is about 143 eV at 5.89 keV. Measurements were carried out in vacuum of 10^{-2} Torr for optimum detection of elements. The standard samples of the elements present in the samples were also run to compare and to find the concentration. The EDXRF technique has proven to be a useful tool for elemental analysis of water samples. The strength of the technique relies on simple preparation of the samples, a reasonable time of measurement, and a non-complicated data analysis. Besides, the calculated concentrations are accurate and reliable.

3.   Study Area

The water samples were collected from nineteen locations of District Kurukshetra for their physio-chemical and from seventeen locations for EDXRF analysis. The different sampling locations are given in Table 1. Samples were collected in good quality polythene bottles of one-liter capacity. Sampling of water is truly representative of any aquatic environment. Once a sample has been taken it should have no possibility of transporting trace elements either to or from the sampling container walls. Natural water in its different forms has been interesting material of study. Sampling was carried out without adding any preservative. For the energy dispersive x-ray fluorescence (EDXRF) study, the samples were collected in clean polyethylene bottles five liter capacity without any air bubbles. The bottles were well rinsed before sampling and tightly sealed after collection and labeled in the field. For EDXRF analysis, each sample was passed through a coarse 2mm screen to remove the organic debris and then through a 250 lm nylon screen into a pre-cleaned plastic container. Each sample was dried in the oven at constant temperature of 150˚C. After drying, each sample was ground using a freezer-mill. The thin samples were prepared in pellet form by mixing and pressing the powder. To be sure that the sample holder was not going to introduce analytical errors, blanks were previously checked. The samples were scanned thoroughly to reduce the risk of analytical error and non-uniformity of the samples.

4.   Results and Discussions
4.1 Physio-Chemical Studies

Characterization of the physiochemical parameters of groundwater from nineteen different locations in Kurukshetra, Haryana are reported in Table 2. Each parameter was compared with the standard desirable limits prescribed by Bureau of Indian Standard (Specification for drinking water, 1991) and World Health Organization (WHO) (Guidelines for Drinking water Quality, 1984) and Indian Council of Medical Research (ICMR) to assess the quality of ground water. The physiochemical parameters namely pH, electrical conductivity, Total Dissolved Solids, Total Alkalinity, Total Hardness, Chloride, Calcium, Magnesium, and dissolved oxygen were determined. Systematic calculation was made to determine the correlation coefficient 'r' amongst the parameters. The desirable limit of pH value for drinking water is specified as 6.5 to 8.5. Measured pH

value of the water samples ranges from 7.45 to 8.53. pH values show a slightly alkaline trend. The electrical conductivity of the samples ranges from 0.2 to 1.1. The TDS value ranges from 142ppm to 847ppm. The standard desirable limit of alkalinity in portable water is 120 ppm and the maximum permissible level is 600 ppm. The values of alkalinity in the water samples of locations of District Kurukshetra are in between 45 ppm to 210 ppm. The value of alkalinity of water provides an idea of natural salts present in water.

Table 1: Sampling Locations of Kurukshetra

S. No.	Sampling Locations	Sample Name	Sources
1.	Bus Stand (Pipli)	S1	Water Tap
2.	New Bus Stand	S2	Water Tap
3.	Railway Station (Thanesar)	S3	Hand pump
4.	Dept. of Physics (KU.K.)	S4	Water Tap
5.	Bhramsarovar	S5	Pond
6.	Petrol Pump Sector-17	S6	Water Tap
7.	Lok Nayak Jai Parkash Hospital	S7	Water Tap
8.	NIT (K.U.K.)	S8	Water Tap
9.	Sri Durga Mandir	S9	Water Tap
10.	Lohar Majra	S10	Hand pump
11.	Jyotisar (Kund)	S11	Pond
12.	Jyotisar Tap Water	S12	Water Tap
13.	Jyotisar Nahar	S13	Water Tap
14.	Mohan Nagar	S14	Water Tap
15.	Arya Girls College	S15	Hand pump
16.	Arunaya Dham (Shiv Temple)	S16	Hand pump
17.	Geeta Colony	S17	Water Tap
18.	Sainsha Village	S18	Hand pump
19.	Village Murtzapur	S19	Hand pump

Table 2: Physiochemical parameters of groundwater from nineteen different locations in Kurukshetra, Haryana

Sample No.	Sample Name Location	pH value	Total Alkalinity (ppm)	Electrical Conductivity	Total Hardness (ppm)	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Dissolved Oxygen (ppm)	TDS (ppm)	Cl (ppm)
1.	S1	8.36	155	0.4	189.19	32.44	156.75	5.0	292	35
2.	S2	8.36	160	0.5	275.67	140.54	135.13	5.0	375	40
3.	S3	7.75	210	1.1	464.86	205.41	259.45	3.2	847	195
4.	S4	7.96	165	0.7	286.49	145.95	140.54	4.5	497	150
5.	S5	7.45	50	0.2	113.51	27.03	86.48	4.1	142	23
6.	S6	8.24	160	0.6	297.29	162.16	135.13	4.0	444	98.4
7.	S7	8.09	185	0.6	297.29	151.35	145.94	4.8	444	155.1
8.	S8	7.94	160	0.5	248.64	108.1	140.54	4.2	375	145.2
9.	S9	7.90	165	0.7	302.7	140.54	162.16	6.3	497	79.8
10.	S10	7.59	140	0.5	286.48	151.35	135.13	3.3	375	171
11.	S11	8.53	120	0.3	172.97	48.64	124.32	4.3	219	80
12.	S12	7.86	115	0.4	205.4	44.24	162.16	4.1	292	78.3
13.	S13	8.37	45	0.2	118.91	16.21	102.7	2.2	142	20
14.	S14	8.43	135	0.4	156.75	54.05	102.7	4.5	292	75.2
15.	S15	8.17	180	0.5	189.18	81.08	108.1	4.6	375	180
16.	S16	7.65	140	0.5	156.75	16.21	140.54	4.3	375	78.8
17.	S17	7.92	190	0.6	156.75	59.46	97.29	3.3	444	202.4
18.	S18	9.96	190	0.5	243.24	80.62	162.16	2.9	375	195
19.	S19	7.96	150	0.5	297.29	108.1	189.19	3.5	375	180.2

Water hardness is a measure of capacity of water to react with soap. Hardness is very important property of ground water from utility point of view for different purposes. Standard permissible limit for total hardness specified by ICMR and BIS is 300 ppm of $CaCO_3$. A fluctuating trend i.e., from 113.51 ppm to 464.86 ppm is observed in the measured total hardness values in the nineteen locations of District Kurukshetra. The permissible limit of chloride in drinking water is 250 ppm. The chloride concentration in water samples from all the locations ranged from 20 ppm to 205 ppm. The concentration of chloride in the samples is within the permissible limit. For domestic use, the maximum desirable limit for calcium is 75 ppm whereas in case of non availability of water calcium upto 200 ppm could be accepted. Calcium concentration in water samples from all the locations was found to vary from 16.21 ppm to 205.41 ppm. Magnesium concentration in water samples from all the locations ranged from 86.48 ppm to 259.45 ppm. The highest permissible limit of Magnesium concentration is 150 ppm. Magnesium concentration in most of the samples is above the highest permissible limit. Dissolved oxygen (DO) in water is the vital gas for many animal organisms. It is consumed in water from decomposition of organic matters. It is a highly fluctuating factor in water. In this study dissolved oxygen content varied in a limited range of 2.9 ppm to 6.3 ppm.

4.2 Correlation Studies

Study of correlation reduces the range of uncertainty associated with decision making. The correlation coefficient 'r' was calculated using the equation.

$$r = \frac{\sum xy}{\sqrt{\sum x^2 \times \sum y^2}}$$

The correlation matrix for the water quality parameters are given in Table 3.

Table 3: Correlation matrix for the water quality parameters

Parameters	pH	EC	TDS	TA	TH	Cl⁻	Ca²⁺	Mg²⁺	DO
pH	1	-0.25329	-0.2572958	0.0032212	-0.182283	-0.297284767	-0.13136328	-0.208094	0.1441
EC		1	0.9977	0.7957	0.8631	0.5987	0.7932	0.7292	0.1086
TDS			1	0.7966	0.8669	0.6101	0.7885	0.74453	0.0720
TA				1	0.6527	0.7293	0.6228	0.5166	0.2143
TH					1	0.4997	0.9272	0.8331	0.0774
Cl⁻							0.4916	0.3734	-0.302784
Ca²⁺							1	0.5654	0.1421
Mg²⁺								1	-0.03816
DO									1

4.3 EDXRF Studies

Samples from seventeen different locations of Kurukshetra were analyzed using EDXRF technique without any chemical pre-treatment. Elements such as Ca, Fe, Mn, Br, Sr and Zn are measured. The final concentration of the elements present in the different samples is given in Table 4. Typical X-ray spectra of the water sample from Brahma Sarovar is presented in Figure 1. The peaks of Cu and Zn are from the absorbers used in the geometrical setup. The Mo Kα and Mo Kβ peaks are of the x-ray tube anode used. It can be seen from the peak heights that there is no variation between the fractions for the calcium. The mean concentration of the elements for this study were found to follow the order Ca>Sr>Zn>Mn>Fe>Br.

From the quantification of the samples, it is observed that the concentration of calcium is high. Calcium is responsible for hardness of the water. Hardness of water leads to encrustation of water supply structure. It can be explained that dilution, precipitation, adsorption to sediments and local anthropogenic input probably affect metal concentrations in the ground water of Kurukshetra region. In regard to the concentration change of the heavy metals along the different locations, water samples showed the varied variation of the elements. A close look at the elemental concentration in table for water samples of different locations shows variation in concentrations but all elements are within the safe limit.

The best thing in the water samples of Kurukshetra is that it is free from the toxic elements, e.g., sulphur, arsenic, selenium, cadmium, lead etc, which may pose hazards to the health. Presence of these elements affects the biotic and abiotic systems. These may interact with antibodies and the auto-immune response system. Also the uptake of these elements onto surfaces during DNA replication and transcription may result in the genetic damage like excess of Fe in the human body is dangerous and can cause cancer.

Table 4: Elemental concentration (μg/cm^2) in water samples from seventeen different locations

Sample Name	Ca	Fe	Br	Sr	Mn	Zn
S1	98.225	0.125	0.172	6.213	-	-
S2	91.358	0.065	0.023	1.515	-	0.176
S3	121.387	0.254	-	4.159	0.058	0.653
S4	71.582	0.036	0.065	2.142	0.062	-
S5	59.630	0.095	0.308	3.305	-	0.846
S6	96.364	0.211	0.045	3.678	0.016	0.022
S7	106.550	0.025	-	2.063	-	0.190
S8	50.086	0.313	0.153	4.215	-	-
S9	52.223	0.200	-	1.508	-	2.514
S10	78.084	0.039	0.056	2.604	-	1.545
S11	41.379	0.040	-	2.381	-	0.741
S12	304.052	0.040	-	3.908	2.621	6.672
S13	92.713	0.033	-	1.446	-	0.531
S14	150.910	0.342	-	7.996	-	0.117
S15	272.842	3.078	-	4.247	-	-
S16	77.927	0.021	0.164	2.262	-	0.482
S17	139.588	1.706	-	2.576	-	1.263
Median	92.713	0.095	0.109	2.604	0.06	0.653
Maximum	304.052	3.078	0.308	7.996	2.621	6.672
Minimum	41.379	0.021	0.023	1.446	0.016	0.022
Mean	112.05	0.39	0.12	3.31	0.69	1.21
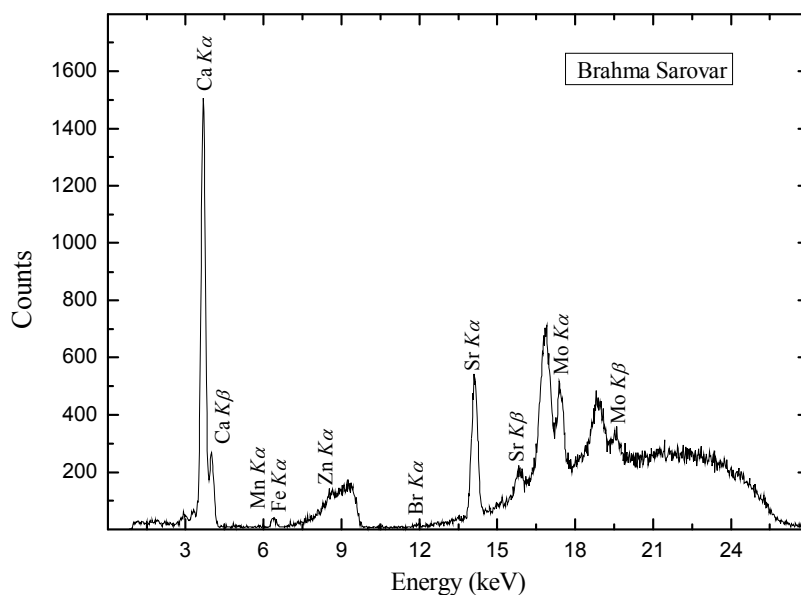
Figure 1. Typical X-ray spectra of water sample from Brahma Sarovar

5. Conclusions

The present studies of physiochemical parameters of groundwater from nineteen locations of District Kurukshetra, Haryana was carried out. The quality of drinking water depends upon the harmful elements present in it. Each parameter was compared with the standard desirable limits prescribed by World Health Organization (WHO), Bureau of Indian standard (BIS) and Indian Council of Medical Research (ICMR) to assess the quality of ground water. The physio-chemical parameters namely pH, electrical conductivity, Total Dissolved Solids, Total Alkalinity, Total Hardness, Chloride, Calcium, Magnesium and dissolved oxygen were determined.

The results showed significant variations in water quality parameter in the study areas. The pH of water samples ranges in the entire area shows alkaline trend. The average of alkalinity has exceeded the desirable. Ground water of District Kurukshetra is suitable for drinking and domestic purposes but in some areas there is need of treatment to minimize the contamination specially alkalinity. It is hard to imagine that one person can make a difference in protecting and conserving water supplies but each individual can really help the environment. However, the hazardous effects of fertilizers, pesticides, animal wastes and sediments have not been detected in the ground water samples. It is advised that the animal waste and domestic waste should not be deposited near the water sources. The use of fertilizers and pesticides in the agriculture should be limited and proper and only the standard quality pesticides should be used. Our study reveals that EDXRF can be used to measure the elemental concentrations in different water samples.

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