Physico-Chemical Quality of Some Spring Water Samples through Correlation Studies in Four Mandals of Tribal Area of Visakhapatnam District, Andhra Pradesh, India

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Abstract: ***Water is very crucial with the allusion of public health conditions. Water quality assessment was performed by collecting spring samples from four Mandals of tribal areas of Visakhapatnam District, Andhra Pradesh.The study was conducted to evaluate the physico-chemical quality of some spring water sources based on the consumption of tribal community. Ten samples were collected and analysed for physical-chemical quality for pH, Electrical conductivity(EC), total dissolved solids (TDS), total hardness(TH), calcium hardness(CaH),magnesium hardness(MgH), Total alkalinity(TA), chlorides (Cl), fluoride(F), nitrates(NO_3), sulphate(SO_4^2), phosphates(PO_4), Dissolved oxygen(DO), biological oxygen demand(BOD),and Turbidity in pre and post monsoon seasons, the correlation studies indicate thathigh strong correlation of calcium with total hardness(0.70) and nitrates with phosphates (0.74) in pre monsoon season, a strong correlation was observedwith DO and BOD(0.82) turbidity with phosphate (0.76) in post monsoon season. The result indicate that the some of the parameters like EC,turbidity, TDS, total hardness, total hardness, calcium, magnesiumand DO are above the limits of WHO and BIS (ISO:100500) limits in pre and post monsoon season, mostly in post monsoon period and some parameters are found to be normally high. Hence the spring water is not favoured for drinking mostly in post monsoon period and required treatment or to look for other sources (bore wells) than springs in this area.***

Keywords: Spring samples, evaluate, analysed, physico-chemical, correlation and monsoon

1. Introduction

Water is a necessity for all living beings, without it; there would be no life. Life originated in water and the ultimate basis of it, the protoplasm, is a colloidal solution of complex organic molecules in a watery medium (70 to 90%). Moreover, wherever water exists in nature it always holds life. So the study of a water body is the study of life as well. Ground water constitutes 97% of global fresh water and is the major preferred source of drinking water in rural as well as urban areas, particularly in the developing countries like India because treatment of the same, including disinfection is often not required (WHO and UNICEF, 2004).Water is essential at all levels of life, cellular to ecosystem. It is essential to circulation of body fluids in plants and animals, and it stands as the key substance for the existence and continuity of life through reproduction and different cyclic process in nature; it plays the central role in mediating global scale ecosystem processes, linking atmosphere, lithosphere, and biosphere, by moving substances among them, and enabling chemical reactions to occur.

Spring water has been very important to man's existence. Early human civilization centred depended on spring and streams. When ground water appears at the surface, springs are formed. Springs are a good source of water supply for small towns, especially near hills or bases of hills. Spring water is also likely to contain minerals which are dissolved from sub soil layers. Spring water from shallow strata is more likely to be affected by surface pollution. With the ever-increasing demand for water, the population is forced to tap all available sources, while the quality of water, irrespective of the source, has deteriorated due to pollution. Even though the general levels of public health have improved during the last few decades, impure water is being identified now as a primary causative agent for certain disease. It is therefore very important to monitor the purity of available water, identify the pollutants, their source and device methods to make the water safe for consumption.

Nature has an innate mechanism to maintain its purity after every natural use. But it is unable to do this at the rate at which modern humans add dirt to it. Nature does not know how to deal with several toxins and pollutants that are flowing from industrial and other wastes. Therefore, humans are bound to monitor the impact of this activity on natural freshwaters continuously.

Due to various ecological factors either natural or anthropogenic, the ground water is getting polluted 20 (Kass et al., 2005, Amina et al., 2004, Oren et al., 2004 and Anwar 2003). Unlike many materials, there is no substitute for water in many of its uses (Sylverster, 2003). In many regions, water scarcity and water pollution became an issue (Falkenmark, 1990; Arnell, 1999; Bouwer, 2000). Nearly half of the Earth's population does not have enough water to drink; and demand is doubling every 21 years (Vidal, 1995). Even though the general levels of public health have improved during the last few decades, impure water is being identified now as a primary causative agent for certain diseases. It is therefore very important to monitor the purity of available water, identify the pollutants, their source and device methods to make the water safe for consumption.

The quality of drinking-water is a powerful environmental determinant of health. Drinking-water quality management has been a key pillar of primary prevention for over one-and-a-half centuries and it continues to be the foundation for the prevention and control of waterborne disease. The rural population of India comprises more than 700 million people residing in about 1.42 million habitations spread over 15 diverse ecological regions. It is true that providing drinking water to such a large population is an enormous challenge.

The drinking water analyses for physical-chemical properties are essential for public health studies. The bacteriological analysis determines the portability of water. The provision of potable drinking water for rural and urban areas is necessary to prevent the dangers of water diseases and public health prevention. Potable water has to comply with certain physical, chemical and microbiological standards (Okonko et al., 2008), which should not contain microorganisms and chemicals at harmful levels (Arunabh and Bhatt, 2008).

The area is located on the north eastern part of Visakhapatnam district and 112 km away from Visakhapatnam, Andhra Pradesh. The main source of drinking water in Araku valley region is open wells and tank (spring water storage device). Natural springs (Oota) are the only source available for drinking water as well as utility purpose in remote villages. The remote villages have only spring water as a source for drinking and utility. The area is endemic and epidemic prone and its vast geography and scattered and remote habitations pose a great challenge for ensuring good health to tribes. The tribal population consume water without treatment in unhygienicconditions; the impact of the developmental activities on drinking water has not been studied.

Aims and objectives

- To analyse the Physico-chemical quality of spring water, during pre and post monsoons.
- To find the correlation of physico-chemical parameters in pre and post monsoon season in spring samples.

2. Material and Methods

Study Area Geographical Location

The study area lies between 17°-34' 11" and 18°-32' 57" northern latitude and 18°-51' 49" and 83°-16' 9" in eastern longitude. It is bounded on the north partly by Orissa state and partly by Vizianagaram district, on south by East Godavari district, on west by Orissa state and east by Bay of Bengal. Araku Valley is 112 KM away from Visakhapatnam. It is famous for the scenic beauty and is a major touristic destination. The area of the valley is roughly 36 km², and the altitude is between 600 to 900 meters above sea level. The average minimum temperature ranges from 30° to 40°C in November/December while average maximum temperature ranges from 35°C to 40°C in May/June. Regarding rainfall and seasonal conditions usually the southwest monsoon starts from 3rd week of April every year and northeast monsoon starts from October.

Table 1: Sample Location and Samples Collected

S.no	Sampling location name	Sample code	latitude	Longitude
1	Karsaliguda	S_1	18°18'44.9"N	82°54'35.6"E
2	Old post office coloney	S_2	18°19'33.7"N	82°53'9.8"E
3	Madagada	S_3	18°19'25.6"N	82°52'53.7"E
4	Kinangguda	S_4	18°16'40.6'N	82°55'57.7"E
5	Janamguda	S_5	18°16'00.6"N	82°56'42.6"E
6	Kumbaraveedi	S_6	18°16'10.3"N	82°54'51.6"E
7	Kurdi	S_7	18°19'5.3"N	82°49'44.3E
8	Kondhuguda	S_8	18°13'21.25''N	83°00'47.09'E
9	Peddagaruvu	S_9	18°14'27.3"N	82°42'44.0''E
10	Sukuru	S_{10}	18°13'21.25''N	82°62 ' 38.2" E

Sampling

Spring water samples were collected by simple random sampling methodfrom variousvillages depending on the consumption of the local people. The water samples collected in sterilized bottles label with sample code and transported to the laboratory in an icebox and stored at 4°C, by following the standard procedure laid by APHA 2005. The sample were processed and analysed for their physical, chemical and bacteriological parameters.The solvents were distilled before use. Triple distilled water was generally used for the preparation of solutions and for carrying out the experiments.

The physical, chemical analyses were carried out at the Department Environmental Sciences laboratory, in Andhra University Visakhapatnam. The physical and chemical parameters pH, Electrical conductivity (EC),Dissolved Oxygen (DO),Biological oxygen demand (BOD) Total Dissolved Solids (TDS), Total Hardness (TH),Turbidity, Total alkalinity(TA), Calcium, Magnesium, Fluoride, and Chloride, Nitrates, Phosphate were determined.

Analysis

Samples were collected from Oct 2014- Dec2015 respectively in Table1. The temperature was determined using a mercury thermometer (TensonDelux make) on the spot, and the pH was measured by pH meter (Elico make), Electrical conductivity was measured by using a digital conduct meter (systronic make). Nephlo/Turbido meter was used for turbidity determination. The samples are also analyzed for TDS, Total hardness, nitrate (NO3), calcium, Mg, chloride by using Titration methods. DO was determined by WINEUR'S Iodometric method. The Flouride was determined by SPADAN'S UV-Spectrophotometric method. (Systronic make). Turbidimetric method was employed for the estimation of sulphate (SO4), nitrate amount was derived by using the phenol disulphonic acid method. All the results were compared with the BIS (ISO-100500, 1994) and WHO standards for drinking water quality.

Table 2: Analytical methods and equipment used in the study

S.No.	Parameter	Method	Instruments/ Equipment
A.	Physico-chemical		
1.	pH	Electrometric	pH Meter
2.	TDS	Electrometric	Conductivity/TDS Meter
3.	Hardness	Titration by EDTA	-
4.	Chloride	Titration by $AgNO_3$	-
5.	Nitrate	Phenol disulphonic Method	UV-VIS Spectrophotometer
6.	Fluoride	SPADNS	UV-VIS Spectrophotometer
7.	Turbidity	Nephlometric method	Turbidity Nephlometer
8.	Sulphates	(TurbidometricMethod)	colorimeter
9.	Calcium	Titration by EDTA	-
10.	Magnesium	Titration by EDTA	-
11.	DO	Titration by Sodium thiosulphate solution	-
12.	BOD	5 days incubation at 20°C followed by titration	BOD Incubator

3. Result and Discussion

pH:pH is one of the most important parameters in studies of water pollution, being easy to monitor on a continuous basis. The present study represent the pH in the range between 6.09 to 7.84 in pre monsoon and 7.61 to 8.75 in post monsoon with mean of 7.24 and 8.26 in pre and post monsoon respectively. This resembles that the pH value is neutral to slightly basic in nature in post monsoon period and in the pre monsoon period it complies with the standard of WHO and BIS i.e. 6.5 to 8.5.According to Kunte and collaborators (1998) pH value ranged from 3 to 10.5 could favour both indicator and pathogenic micro-organism growth. Generally the pH values of water source vary due to changes in temperature and biological activities. pH alters the taste of water but has no direct adverse effect on health. All biochemical reactions are sensitive to the variation of pH. For effective disinfection with chlorine, pH should preferably be less than 8.5higher pH reduces the germicidal potentiality of chlorine and induces the formation of toxic trihalomethanes (Trivedy&Goel, 1986).Negative correlation of pH was observed with, EC, TDS, phosphate, calcium, chlorine, nitrates and DO in pre monsoon period this has been reversed to positive correlations in post monsoonperiod, figures is seen from the tabulated results. The other physico-chemicalcontaminants had marginal correlation with the pH values, the highest correlation with nitrates, phosphates and sulphates, (0.57,0.52,0.56) respectively in post monsoon period.

Electrical Conductivity (EC):

The Electrical Conductivity of the samples ranged from 35 to 730µS/cm and 222 to 1106µS/cm in pre and post monsoon respectively. EC of groundwater in all the sources was found to exceed the maximum permissible limitof 400 µS/cm for drinking water (BIS, 2003).The Electric conductivity of the springs found higher than the permissible limits in post monsoon when compared to pre-monsoon. Kuchekar et al., (2008) observed that the Electrical conductivity of water samples was high in monsoon than in the post monsoon the reason may be during monsoon, the silt carried through runoff got mixed with the water and resulted in high Electrical conductivity. EC of the water increases with increased concentrations of Na+, K+, Cl-, alkalinity and total dissolved solids and a marked increase in conductivity of the water is an indication of the addition of pollutants to the water (Trivedy&Goel, 1986 and Prakash&Somasekhar, 2006).EC found to be negatively correlated with nitrates, phosphates and sulphates and fluoride in pre monsoon and with chlorine, TDS, and total Hardness in post monsoon season. A strong correlation was observed with Total alkalinity (0.70) in pre-season and with nitrates and phosphates (0.64;0.74) in post monsoon period. Similar relationship was observed by Bishnoi& Malik (2008) for TH at Panipat ,Patil&Patil (2010) at Amalner. Kumar &Sinha (2010) report that at Moradabad in northern India, conductivity showed significant correlation with ten parameters.

Table 10: Physico- Chemical Parameters of springsin pre-monsoon

S.Nos.	*Village*	*Source*	*pH*	*EC*	*TDS*	*TSS*	*Cl*	*TH*	*CaH*	*MgH*	*TA*	*F*	*Nitra*	*Phosp*	*Sulp*	*DO*	*BOD*	*Turbidi*
1	Karsakiguda	Spring	7.6	96	140	0.9	13.69	124	72	66.3	13.3	0.67	2.21	5.1	14	1.62	0.9	8.8
2	Old post office	Spring	7.3	112	184	3.1	22.3	185	113	72	85	0.28	1.10	4.5	11	3.3	1.1	5.6
3	Madagada	Spring	6.52	106	250	1.8	42.3	86	31	55	36	0.28	22.45	9.2	24	5.6	2.8	18.5
4	Kinangguda	Spring	6.9	633	1560	1.3	10.9	144	20	124	82	0.8	7	0.5	0.54	6.2	1.3	9.3
5	Janamguda	Spring	7.4	222	129	0.9	14.6	92	24	68	35	0.74	BDL	1.2	1.9	5.4	0.6	7.5
6	Kumbaraveedi	Spring	7.85	99	1223	0.3	11.9	124	104.	18.5	9.8	0.67	11	7.2	22.1	3.2	1.5	47.2
7	Kurdi	Spring	7.4	35	745	0.4	9.78	71.2	35.2	36	18.3	0.63	2.21	2.2	84	5.6	2.6	17.5
8	Kondhuguda	spring	6.09	633	1470	1.3	56	128	78	50	60	0.23	2.3	1.8	13.6	4.7	1.4	18.9
9	Peddagaruvu	spring	7.76	196	1291	2.6	68	88	49	39	45	0.3	4.4	0.3	8.75	6.6	3.2	10.2
10	Sukuru	spring	7.65	730	1280	3.2	65	160	110	50	85	0.2	BDL	0.5	0.6	3.9	1.4	12.9

Table 10: Physico- Chemical Parameters of springs in post-monsoon

S.No.	Villag	Sour	pH	EC	TDS	TSS	Cl	TH	CaH	MgH	TA	F	Nitra	Phos	Sulp	DO	BOD	tuty
1	Karsakiguda	Spring	7.67	373	2199	0.8	36	110	80	30	50	0.3	5.5	3.9	16.21	10.2	3.4	18.5
2	Old post office	Spring	8.59	375	1091	3.4	114	125	70	55	36	0.3	9.2	4.8	17	6.3	2.1	15.2
3	Madagada	Spring	8.75	1106	661	9.9	36	90	80	10	40	0.2	9.7	6.9	18	9.5	3.3	48.2
4	Kinangguda	Spring	8.57	812	405	1.1	85	265	170	95	90	0.3	8.2	4.5	18	6.3	1.2	13.2
5	Janamguda	Spring	8.22	222	418	0.5	71	105	75	30	38	0.1	5.1	3.8	19	1.4	0.2	18.2
6	Kumbaraveedi	Spring	7.91	981	250	2.2	78	50	105	55	60	0.3	9.1	4.9	13	5.3	0.8	11.1
7	Kurdi	Spring	8.48	888	100	0.9	28	100	55	45	56	0.1	6.5	4.3	24	8.1	2.1	10.2
8	Kondhuguda	spring	8.45	502	256	1.9	39	203	59	144	71	0.3	8	3.4	23	6.2	0.7	14.1
9	Peddagaruvu	spring	8.12	435	226	1.3	109	135	113	22	45	0.1	2	4.1	11	8.2	1.1	13.2
10	Sukuru	spring	7.89	236	122	0.7	83	307	142	165	69	0.2	0.5	3.4	12	4.8	1.3	16.5

Turbidity: The turbidity values ranged between 5.6 to 47.2 NTU and 10.2 to 48.2 NTU respectively in pre and post monsoons with mean of 15.6and 17.8 NTU in both the season respectively. In all the water samples the turbidity values were above the WHO and BIS standards. The presence of in organic nutrients such as nitrogen and phosphorus which may stimulate the growth of algae, also contribute to turbidity (Sawyer et al., 2000). In the study turbidity values may be high due to the suspended particles, which are mixing with the surface runoffs from hilly slopes in the water sources which aremostly located in low lying areas near the agricultural fields in tribal areas during the rainy season.Turbidity can protect microorganisms from the effects of disinfection (Manivasakam, 2000) and stimulate the growth of bacteria in the water and thereby exert a significant chlorine demand during water treatment. It is therefore important to keep the turbidity low, preferably below 1 NTU (Brock, 1966; Stotzky, 1966) while producing safe drinking water by using chlorine as disinfectant. Turbidity showed negative correlation with chlorides, total alkalinity, and totalHardness and in pre and post monsoonperiod. A significant strong Correlation was found with phosphates (0.76) in pre period the other parameters are moderately correlated in both the seasons.

Chlorides: Chlorides occur naturally in all types of water but the concentration is very low in natural water. Higher value of chloride indicates pollution of water and gives an undesirable taste. The Chloride concentration ranges from 28 to 114 mg/L and 9.78 to 68 mg/L in post and pre monsoon respectively. 250mg/L (WHO) is recommended for chloride; comparatively lower concentrations of chlorides were found along allthe spring sources. Chloride that dissolves easily in water is toxic to most aquatic organisms because it reacts quickly with other substances in water (Padmanabha and Belagali, 2001).The correlation of chloride with Calcium, total alkalinity DO and BOD found positively and negatively correlated with other parameters in pre monsoon period, in post season it is moderately correlated with total hardness. Yamakanamardi et al (2011) found a positive correlation of chloride with calcium, magnesium and sodium, indicating noncarbonate hardness, and with TDS and EC, indicating salinity at Belgaum city in northern Karnataka.

Total Hardness: It can be seen in the Table, Totalhardness at all the sources were less than the WHO guideline values are of 500 mg/L as $CaCO3$. As a matter of fact, this guideline value is not proposed on the basis of health. Consumers can tolerate water hardness in excess of 500 mg/L. Water hardness above 500 mg/L needs excess use of soap to achieve cleaning.In the spring water total hardness ranges from 71.2 to 185 mg/L, 50 to 307mg/L, and with mean of 55.02 mg /L during pre and post monsoon.The total hardness values for all the samples are below the 600 mg/L permissible limit of BIS-2003, in both the seasons in all stations.Calcium and magnesium may be added to the natural water system as it passes through soil rock containing large amounts of these elements in the way of mineral deposits (Renn, 1970)..Depending on pH and alkalinity, water with hardness more than 200mg/l, which is found in most of the samples analysed, results in scale formation of the distribution system (Singanan et al 1996). Researchers have indicated that there are negative relationships between cardiovascular diseases and hardness in drinking water (Schroeder, 1960; Lacey and Shaper, 1984).High correlation of TH is seen with magnesium (0.37), chlorides (0.37), alkalinity (0.7), EC (0.44), calcium(0.70) and TDS (0.13), Negative correlation is seen in all other parameters in pre monsoon period. In the post monsoon period significant strong correlation was observed with chlorine (0.21), Total alkalinity (0.70) calcium (0.64) and magnesium (0.81) and others are negatively correlated.The calcium and magnesium are highly correlation with the total hardness this area.

Calcium and Magnesium (Ca+,Mg+)

Calcium Hardness were found in the range of 20 to 113mg/L and 55 to 170 mg/L with the mean of 63.62and 94.9mg/L in pre and post monsoon respectively. The magnesium Hardness was between the range of 18.5 to 124mg/L and 10 to 165mg/L with mean of 57.8and 55.1mg/L in pre and post monsoon respectively. The values of calcium and magnesium hardness were above the permissible limit in both the monsoon period compared to the WHO standard value of 75 mg/L. The desirable limits for calcium and magnesium for drinking water are 75 and 30 mg/L, respectively (BIS 1991). In the study (Madhusudhana Reddy &SubbaRao, 1995) reported high calcium content in the water. The increase of magnesium is quite proportionate with calcium in both the seasons. About 85% of the samples of the study area fall within the desirable limits of 75 and 30 mg/L for calcium and magnesium in both pre- and post-monsoon seasons and the remaining 15% of the samples exceed the desirable limit but are well within the permissible limits which are prescribed for drinking water. The contributing factor for this high value could be sulphates of magnesium that can pollute the groundwater on account of sea water incursion (Somasundaram et al, 1993). Calcium content in the groundwater samples exhibits very high correlation with total hardness (0.70), phosphate (0.22) total alkalinity (0.16) and turbidity (0.29). Negative correlation is seen with pH, TDS, EC, BOD and D.O in pre monsoon period, where as in post monsoon season strong correlation was exhibited with total hardness (0.64), totalalkalinity (0.65) and magnesium Hardness (0.62) and negatively correlated with remaining all other parameters. The magnesium concentration in the spring water samples exhibit strong correlation with total hardness (0.37), total alkalinity (0.55) and Fluoride (0.32) the other parameters are negatively correlated in pre-season. In the post monsoon season similar strong correlation of magnesium observed with magnesium hardness (0.65) total alkalinity (0.61), and fluoride (0.19).

Total Dissolved Solids (TDS): The TDS concentration was found to be in the range of 129 to 1560mg/L and 100 to 2190mg/L with mean of 827.2 and 572.8mg/L in pre and post monsoon respectively. Since TDS higher than 1000 mg/L impart taste to the water, therefore, a desirable value of 1000 mg/L is proposed by WHO. Furthermore, a value higher than 1000 mg/L results in excessive scales in water pipes, heaters, boilers and household appliances (WHO), Geneva, (2004). However 20% of samples are within the permissible limit and 80% of samples are having high total dissolved solids TDS, this may be due to the weathering of rocks and soil. The TDS values indicate ingression / intrusion of saline water into the groundwater aquifer as well as anthropogenic causes (Kurian, 2001; SwarnaLatha, 2008). TDS beyond 500 mg/L decreases palatability and can lead to gastro-intestinal diseases (Maiti, 2001). Literature indicates that concentrations of TDS in water vary considerably over time and location due to differing solubility of the minerals in different geological regions and nutrient-rich surface waters that contaminate water (Indirabai& George, 2002).The relationship of TDS value with other physico-chemical parameters, EC, chlorides, total hardness,total alkalinity,DO,BODand turbidity in pre monsoon season, all other parameters are negativelycorrelated. Invariably, previous investigators across the continents found this relationship (Mehta, 2010). A negative correlation was observe in pH, EC, total hardness, calcium ,magnesium, total alkalinity, sulphates ,nitrates and phosphates high correlation is observed between TDS and DO (0.46), BOD (0.67) and Fluoride (0.43). A high correlation is observed between TDS and concentrations of most of the ions pointing to higher residues in the transient consumer.

Fluoride: Fluoride concentration in the spring samples observed between the range of 0.2 to 0.8 mg/L and 0.1 to 0.3mg/L with mean of 0.48 and 0.22 in before and after monsoon periods. The presence of fluoride in drinking water is essential and WHO (1984) prescribed 1.5 mg/L fluoride as desirable limits in drinking water. In this study fluoride concentration registered ranged from 0.1 to 0.6mg/L, with the mean of 0.27 mg/l. The concentration of fluoride ions in spring water samples in study area is observed to be within the permissible limits of WHO and BIS standards. In most of the surface and groundwaters, theconcentrations of fluoride are usually in the range of 0.5-1.5 mg/L. But in areas that are rich in fluoride containing minerals, well waters may contain up to about 10 mg/L of fluoride. There are reports that the concentrations of fluoride are high in rivers and lakes mostly due to contributions through soil and in some occasions through industrial discharges (WHO, 1970; NRCNAS, 1971). The solubility of $CaF2$ that is present in minerals increases with the increase in total alkalinity in the groundwater (RamamohanaRao et al, 1993; Saxena& Ahmed, 2001). In the study fluoride is moderately correlated with pH (0.28), magnesium (0.32), sulphate (0.15), and turbidity (0.12).and negatively correlated with other parameters, in pre monsoon period. The other parameters correlated with Fluoride in post monsoon are magnesium (0.19), total alkalinity (0.39), nitrates (0.52) and BOD (0.17).and negatively correlated with sulphate (-0.02).

Sulphates: Sulphates are a naturally occurring anion found almost in all types of water. It gets leached into the ground water by many processes. One of those may be the breakdown of organic substance in the soil as mentioned by Alexander (1961). Sulphate concentration was identified in the range of 0.54 to 84 mg/L and 11 to 24 mg/L with mean of 18.04 and 17.12 mg/L in pre and post monsoon respectively. Sulphate ion is one of the major anions occurring in natural waters since they are readily soluble in water. Sulphate occurs naturally in waters as a result of leaching from gypsum and other common minerals (Manivaskam, 2005) No sample from the different sources has exceeded BIS and WHO prescribed standards i.e. (200mg/L)in theoverall study area the ground water appears to be suitable for drinking purposes in respect of SO_4. The concentration of sulphate in surface waters is usually low, in the range of 20-50 mg/L, where as in groundwater; it is usually high, in the range of 50-250 mg /L. The levels of sulphate in these water samples are low. Sulphate concentration is significantly correlate with fluoride (0.15), DO(0.11), BOD (0.46) and turbidity(0.25) in pre monsoon. The fluoride strongly correlate with pH(0.56), EC (0.22), nitrate (0.48), and partially correlated with DO, BOD and turbidity in post monsoon period. Sodium, magnesium and calcium sulphate ion-pair associations are formed in seawater at 25°C (Kester&Pytkowicz, 1969).

Nitrate: Presence of nitrate in water leads to organic pollution. The nitrates concentration of the spring samples were ranged between 0 to 22.4mg/L and 0.5 to 9.5mg/Lwith mean of 5.26 and 6.38mg/L in pre and post monsoon respectively. Some samples found to be below the detectable level(BDL). The nitrates concentrations in all the samples were below the prescribed limit of WHO, the level of nitrate in the water samples is low. The WHO standard for nitrate is 50mg/L and above this limits may cause cyanosis disease or blue baby syndrome in infants less than 3months (WHO, 2006).(Jellison et al., 1993 and Romero et al., 1998). Blum (1956) reported that highest values of NO3 in rainy season may be due to the addition of N in the form of runoff water; Nitrates dissolve readily in water and move freely with water through soil and rock where they are usually consumed by microorganisms. (Lawrence et al., 2001) reported that, metabolically, an estimated 4 kg of nitrogen is released per year per person and under aerobic conditions, a significant percentage of this nitrogen will be oxidized to form nitrate. The concentrations of nitrates in natural waters reported in literature are generally in the range 10-50 mg/L (Jain et al, 2008).The nitrate concentration highly correlate with phosphate (0.74) and moderately correlate with Sulphate (0.08), DO (0.21), BOD (0.43), andturbidity (0.48) and others are negatively correlated in pre monsoon season. In post monsoon season nitrate significantly correlated with pH (0.57), EC (0.64), Fluoride (0.52) and phosphate (0.74) moderately correlate with, sulphate (0.08), DO, BOD and turbidity and parameters remain negatively correlated. Similar report by Young (2010) that high dissolved oxygen in groundwater correlates with high concentrations of nitrates.

Phosphates: Phosphate content in the spring water varies from 0.3 to 9.2mg/L and 3.4 to 6.9 mg/L with mean of 3.25 and 4.4 mg/L in pre and post monsoonrespectively. Phosphates in water bodies, even in small amounts of around 25 mg/L, can cause accelerated growth of algae and aquatic vegetation, thereby leading to eutrophication of the aqueous system (Handa, 1990), also leading to odour and taste problems. Drinking water with phosphates in excess of 100 mg/L is known to cause many health problems as well as interfere with the coagulation process in water treatment plants. No amount of phosphate in water is believed to have effects on human health (EPA, 1995). Desirable limits for phosphates in drinking water have not been specified by WHO as well as BIS. Canadian Department of National Health and Welfare (1969) suggests an upper limit of 0.2 mg/L for PO4 in water, while the European Economic Community (Smeats&Amavis, 1981) specifies 0.54 mg/L.Phosphate exhibit positive correlation with calcium (0.16), sulphate (0.18), BOD (0.11) and turbidity (0.49) in pre monsoon period. In post monsoon phosphate strong positively correlate with pH(0.52), EC (0.74), nitrate (0.61), DO (0.39), BOD (0.52), and turbidity(0.76).

Total Alkalinity: Alkalinity of water is its capacity to neutralize a strong acid and is characterized by presence of all hydroxyl ions capable of combining with hydrogen ions (Koshy and Nayar, 2000). Alkalinity is used as criteria for determining the nutrient status of waters (Sorgensen, 1948; and Moyle, 1949).The total alkalinity of the spring sample range from9.8 to85mg/L and 36 to 90mg/L with mean of 46.9 and 55.5 mg/L in pre and post monsoon respectively. The alkalinity was lower than the WHOprescribed limits of 200 mg/L in spring sources in pre monsoon, and observed to be increased in post moons season, Bhatt et al. (1999) and Trivedy and Goel (1986) who argued that alkalinity is usually higher during the post-monsoon than the monsoon. Venkateswarlu (1969) also observed that alkalinity is affected by rain fall. The value of alkalinity in water provides an idea of natural salts present in water. A strong correlation was observed with EC (0.70), total hardness (0.70) and magnesium hardness (0.55) and partially correlated with TDS (0.32), calcium (0.22) and DO (0.19) other parameters are negatively correlated in pre season of monsoon. The parameters like pH, TDS, chlorides are negatively correlated and total hardness (0.70), calcium (0.62), magnesium (0.61) and fluoride (0.39) are found high positive correlated with total alkalinity in post season of monsoon.

Dissolved Oxygen ;(DO):D.O. is invariably considered as a critical parameter in any investigation of groundwater and its lower content is an indicator of pollution, both from bacteriological causes and chemical interaction of various constituents. The dissolve oxygen content of the spring sample varied from1.6 to 6.6 mg/L and 1.4 to 10.2 mg/L with mean of 4.4 and 6.6 in pre and post monsoon period respectively. Maximum concentration of DO was observedduring post monsoon period, when comparing the sampling sources bore sample found to be high concentration of DO in post monsoon, in all the samples the DO concentration were above the prescribed limit of 05mg/L, which may be attributed to lowering water temperature that increases the solubility of atmospheric oxygen. Dissolved oxygen is a highly fluctuating factor and varies with water temperature and the partial pressure of oxygen in its gas phase (Renn, 1970). DO was negatively correlated with total hardness (0), calcium (0), fluoride (0) and phosphate (0) in pre monsoon season this indicating the biochemical process deplete the water of its dissolved oxygen. In the post monsoon season DO was strongly with EC (0.40), TDS (0.46), BOD (0.82) and turbidity (0.36) it is observed that Do was strongly correlated with BOD. This implies that the dissolved oxygen content has direct relation with biological oxygen demand in post monsoon period in spring water samples.

Biological Oxygen Demand: BOD; Biological or Biochemical Oxygen Demand is the amount of oxygen utilized by microorganisms in consuming the organic matter in waters. BOD is a measure of the actual oxygen demand of wastes under laboratory conditions similar to those found in the receiving waters, and is a good indicator of biodegradability of wastes. The BOD content was found in the range of 0.6 to 3.2mg/L and 0.4 to 3.4mg/L with mean of 1.68 and 1.62mg/L in both the seasons in the spring water samples. The water from the spring is considered as fairly pure in terms of BOD, the values moderately above the limit. BOD above 6 mgL-1 in a water body is considered polluted and high BOD values are attributed to the stagnation of water body leading to the absence of self-purification (Iqbal and Katariya, 1995). Water bodies with BOD 225 to 323 mgL-1 are called septic or anaerobic systems (Chandrasekhar et al., 2003). Usually drinking water has a BOD of less than 1mg/L and water is considered to be fairly pure if BOD is of 3mg/L and doubtful purity is at BOD value of 5mg/L (Rao, 1997.)BOD is strongly correlated with nitrates, Sulphates and DO in pre monsoon season and in post monsoon season it is strongly correlated with TDS, Phosphates, DO and turbidity, this revels that the concentration of the spring samples is directly inter related with the dissolved solid , phosphate content and the measure of turbid in the water samples .

4. Conclusion

Chemically contaminated drinking water has been related with majority of health problems. From this study it is evident that, the concentrations of physical, chemical content in spring water found higher than the prescribed limit in all the sources mostly in post monsoon season than the pre monsoon season in four different Mandals of Visakhapatnam District. The particular water from its sources which high in some parameters like turbidity and Total solids, Electrical conductivity, Total dissolved solids, calcium, magnesium ,and DO were found to be above the limits of WHO and BIS, this may be due to the unhygienic practices of tribal people around the spring sources. Hence spring water is not preferred for drinking, unless and until it is treated, if alternate source is not available. Therefore there is a need to aware the people about drinking water sources like deep bore wells and recommend the government to strengthen the efforts for monitoring the drinking water sources with an aim to provide safe and fair water to local tribal community.

Table 5: Correlation matrix of physico-chemical parameters in pre monsoon season

springs	*pH*	*EC*	*TDS*	*Cl*	*TH*	*CaH*	*MgH*	*TA*	*F*	*Nitra*	*Phosp*	*Sulp*	*DO*	*BOD*	*Turbid*
pH	1														
EC	-0.35864	1													
TDS	-0.10199	0.672959	1												
Cl	-0.17318	0.454084	0.391343	1											
TH	0.012606	0.446577	0.133812	0.037432	1										
CaH	0.280569	0.108343	0.095063	0.23003	0.703153	1									
MgH	-0.31707	0.395066	-0.01954	-0.28532	0.376218	-0.38414	1								
TA	-0.28462	0.705378	0.321147	0.390078	0.7059	0.224878	0.555469	1							
F	0.284865	-0.24004	-0.10931	-0.84789	-0.2431	-0.46266	0.325285	-0.44765	1						
Nitra	-0.31765	-0.26574	-0.06315	0.003301	-0.31507	-0.2693	-0.08489	-0.26148	-0.06654	1					
Phosp	-0.10524	-0.58533	-0.47522	-0.26711	-0.08109	0.164215	-0.28931	-0.46541	-0.03645	0.744754	1				
Sulp	0.026458	-0.50348	-0.1247	-0.32324	-0.53335	-0.20002	-0.43351	-0.51272	0.150304	0.087018	0.18715	1			
DO	-0.28936	0.176968	0.34869	0.257642	-0.50685	-0.71185	0.168689	0.1922	-0.02688	0.212634	-0.40715	0.114101	1		
BOD	-0.02904	-0.27102	0.209944	0.427207	-0.58075	-0.29565	-0.40943	-0.19533	-0.36083	0.481655	0.113272	0.465522	0.575645	1	
Turbidi	0.121893	-0.17563	0.325692	-0.13732	-0.14612	0.295371	-0.61419	-0.49297	0.122792	0.436656	0.495622	0.259279	-0.18358	0.139082	1

Table 6: Correlation matrix of physico-chemical parameters in post monsoon season.

Spring	*pH*	*EC*	*TDS*	*Cl*	*TH*	*CaH*	*MgH*	*TA*	*F*	*Nitra*	*Phosp*	*Sulp*	*DO*	*BOD*	*turbidity*
pH	1														
EC	0.438265	1													
TDS	-0.30187	-0.22676	1												
Cl	-0.05479	-0.36995	-0.16716	1											
TH	0.005745	-0.36078	-0.25558	0.217131	1										
CaH	-0.17981	0.005801	-0.22363	0.491362	0.641814	1									
MgH	-0.23554	-0.27077	-0.29658	0.302519	0.810038	0.652942	1								
TA	-0.02566	0.175972	-0.32446	-0.07003	0.701045	0.62544	0.613137	1							
F	-0.05393	0.116547	0.434442	0.031513	0.168556	0.165265	0.192607	0.397874	1						
Nitra	0.579154	0.644774	0.161804	-0.24058	-0.43692	-0.31794	-0.42756	-0.02537	0.525952	1					
Phosp	0.525512	0.742995	0.075846	-0.12108	-0.4644	-0.08106	-0.40832	-0.33615	0.059219	0.61573	1				
Sulp	0.569556	0.227371	-0.05088	-0.65155	-0.10235	-0.58056	-0.29803	0.092506	-0.02906	0.48025	-0.00252	1			
DO	0.056201	0.402493	0.467773	-0.36751	-0.20263	-0.14297	-0.35194	-0.07713	0.158428	0.15702	0.398784	0.019987	1		
BOD	0.076438	0.286803	0.676152	-0.41414	-0.25096	-0.23489	-0.26	-0.30472	0.174333	0.226428	0.528105	0.067309	0.827637	1	
turbidity	0.373346	0.359583	0.192746	-0.33844	-0.19746	-0.14223	-0.32542	-0.37888	-0.05686	0.279097	0.767763	0.026792	0.334464	0.563985	1

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