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Ground Water Quality Assessment in Paper Mill Effluent Irrigated Area - Using Multivariate Statistical Analysis

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Abstract: Paper mill effluent while flowing, percolates through soil and slowly mixes with ground water bodies (Open well), water samples were collected from three stations (S1, S2 and S3) in and around paper mill. This paper represents the characteristics of ground water quality and the effect of paper mill effluent, which is using recycled water for irrigation and domestic purpose. Cluster analysis (CA), principal component analysis (PCA) and multidimensional scale plot (MDS) appear were employed to evaluate the tropic status of water quality for three monitoring stations. High pollution load was observed in the ground water bodies due to continuous flow of effluent near the ground water sources. Effluent water consists of 3400 mg/l suspended solids. However, pH varied from 5.5-7.6. The biochemical oxygen demand and chemical oxygen demand ranged from 2-780 and 60 - 1520 mg/l respectively. SAR, RSC and SSP level was high from S2 and S3, both were unsuitable for both domestic and irrigation purposes. An elevated coliform bacterial count indicates that these water samples S2 and S3 were not suitable for domestic purpose. The dendrogram of the effluent water quality parameters evidently indicate that Maruthi Paper mill does not meet nominal National standard set by central pollution control board to discharge in agricultural field.

Key words: Ground water % Paper mill effluent % Physico chemical parameters % Pollution

INTRODUCTION

The utilization of waste water for irrigation has increasingly gained importance in various countries of the arid and semi arid regions as water is becoming a scarce commodity [1]. Even though the quantity and quality of water available for irrigation is variable from place to place in India, many groundwater exploitation schemes in developing countries like India are designed without due attention to quality issues. A number of studies on groundwater quality with respect to drinking and irrigation purposes have been carried out in the different parts of India [2, 3].

The paper mill effluent contains huge amount of solids, Biological Oxygen Demand, Chemical Oxygen Demand, color and lignin besides creating tremendous foaming nuisance [4]. Effluent treatment plant (ETP) was an important safety measure, but small paper mill will not afford for ETP construction. Due to the strict enforcement of effluent discharge, industries are opting reuse of effluent for irrigation. Successful utilization of paper and pulp mill waste water in various crops like paddy, wheat, onion, sugar cane, vegetables and fodder grass [1] and stated the paper mill effluent not only contains nutrients that enhance growth of the plants but toxic materials that interfere with ground water, soil nature and soil organisms [5]. Degradation of ground water quality can be reported from deep percolation from intensively cultivated fields [6]. The present study has therefore been undertaken to assess the current status of ground water quality and to determine the effect of paper mill effluent on ground water bodies of effluent irrigated area, Kabilar malai union of Namakkal district, Tamil Nadu, India.

MATERIALS AND METHODS

Study Area: The study area located between 11.6° N Lat and 78.1° E Long Kabilar malai Union of Namakkal district of Tamil Nadu, India (Figure 1). Paper mill pumped waste

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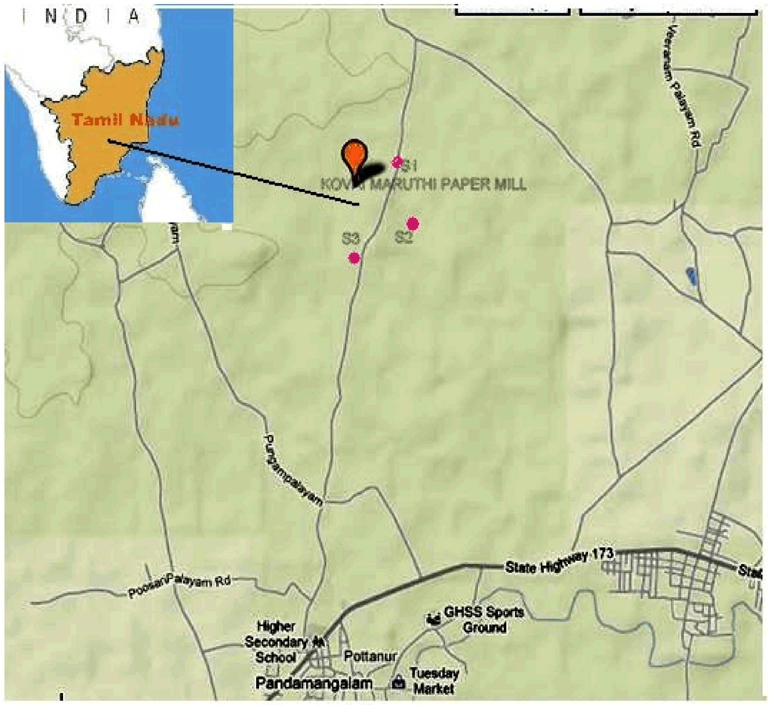

Fig. 1: Study area
S1= Station1; S2 = Station 2; S3 = Station 3

water into irrigated fields 2 km away from the mill, this waste water irrigation field was surrounded by many fertile agricultural fields and open wells. Three sampling stations were selected S1- Control water (input water of paper mill), S2- Effluent water used for irrigation, S3 - Open well adjacent to effluent water irrigated field.

Collection of Sample and Analysis of Water: Paper mill effluent was collected from the source at the point of discharge. Sampling was done during 2000 for six months (March - August), in order to assess the impact of effluent irrigation on the ground water quality. The water quality parameters pH, electrical conductivity (EC), total dissolved solids (TDS), total solids (TS), total alkanity (TA), total hardness (TH) and important cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}) as well as anions such as chlorides (Cl^{-}), nitrates (NO_3^{-}), Phosphate (PO_4^{-}) and sulphates (SO_4^{-}) were assessed using the standard procedure [7]. Dissolved oxygen by Winkler's method, BOD and COD, Sodium Absorption Ratio (SAR), Residual Sodium Carbonate (RSC) and Soluble Sodium Percentage (SSP) were analyzed by the procedure adapted by [8]. Enumeration of Coli form bacteria (MPN technique) was followed by the procedure of [9].

Statistical Analysis: Co-efficient of correlation (r) was worked out to understand the relationship between the various parameters and to test the significance of the models. It was considered to be not significant when the value of the probability of significance (p) was greater than 0.05. Means and standard deviations were calculated for each parameter. All these statistical analyses were performed using SPSS statistical (Version 7.5 for Windows XP, SPSS and Chicago, IL, USA). Various multivariate statistical methods including Principal Component Analysis (PCA), Non-Multidimensional Scale Plot (MDS) and Cluster analysis (CA) was analyzed using PAST (statistical Version 1.93 for Windows XP).

RESULTS AND DISCUSSION

Physico-Chemical Parameters of Water: Indian standard values of various physicochemical parameters and the results of the ground water samples and microbial levels are presented in Table 1. pH varied from 5.5-7.6 and S3 registered high pH values 7.6. The pH of S2 was acidic (5.5), where as S1 and S3 were slight alkaline; [10] stated that naturally occurring water were slightly alkaline. The acidic nature of S2 was due to the disposal of industrial effluent. Physico-chemical parameters of water and microbial level revealed significant correlation with a

Table 1: Physico-chemical parameters of water samples from Stations 1-3

Parameters	Indian standard	Samples		
		Station1	Station2	Station3
pH	6.5 - 8.5	7.10	5.50	7.60
EC (mmhos/cm)	2250	700.00	4800.00	5200.00
TDS (mg/l)	500-2000	500.00	2650.00	2900.00
Total Solids (mg/l)	-	650.00	3400.00	3250.00
Alkalinity (mg/l)	200-600	120.00	1200.00	1250.00
Total Hardness (mg/l)	300-600	275.00	1850.00	2350.00
Calcium (mg/l)	75	60.00	521.00	588.00
Magnesium (mg/l)	30	30.00	134.00	220.00
Sodium (ppm)	50	70.00	165.00	512.00
Potassium (ppm)	10	2.50	12.50	31.00
Sulphate	<192	0.00	747.00	900.00
Nitrate	45	12.00	40.00	15.00
Choloride (mg/l)	250-1000	60.00	460.00	570.00
Dissolved oxygen (ml/l)	5.0-6.0	6.10	Nil.00	3.50
BOD	-	2.00	780.00	25.00
COD	150-255	60.0	1520.00	112.00
Soluble sodium percentage (SSP)	60-75	43.71	23.10	37.12
Residual sodium carbonate (RSC)	-	1.70	6.64	1.28
Total coliform		43.00	1100.00	1100.00
E.coli /100 ml		28.00	740.00	900.00

Table 2: Correlation between the physic chemical parameters of ground water

	pH	EC	TDS	TS	AL	TH	Ca	Mg	Na	K	S	No2	Cl	DO	BOD	COD	SAR	SSP	RSC	T. Co	E.Co
pH	1.000																				
EC	-0.210	1.00																			
TDS	-0.190	1.00	1.00																		
TS	-0.330	0.99	0.99	1.00																	
AL	-0.250	0.99	0.99	0.99	1.00																
TH	-0.060	0.98	0.99	0.96	0.98	1.00															
Ca	-0.170	0.99	0.99	0.98	0.99	0.99	1.00														
Mg	0.174	0.92	0.93	0.87	0.91	0.97	0.93	1.00													
Na	0.521	0.72	0.73	0.63	0.69	0.82	0.74	0.93	1.00												
K	0.390	0.81	0.82	0.73	0.79	0.89	0.83	0.97	0.98	1.00											
S	-0.130	0.99	0.99	0.97	0.99	0.99	0.99	0.95	0.77	0.86	1.00										
No2	-0.940	0.51	0.50	0.61	0.55	0.37	0.48	0.15	-0.21	-0.07	0.44	1.00									
Cl	-0.080	0.99	0.99	0.96	0.99	0.99	0.99	0.96	0.80	0.88	0.99	0.40	1.00								
DO	0.785	-0.70	-0.70	-0.85	-0.80	-0.67	-0.74	-0.47	-0.12	-0.26	-0.71	-0.90	-0.68	1.00							
BOD	-0.960	0.45	0.43	0.56	0.49	0.31	0.41	0.08	-0.28	-0.14	0.38	0.99	0.33	-0.91	1.00						
COD	-0.960	0.45	0.44	0.56	0.49	0.31	0.42	0.08	-0.28	-0.13	0.38	0.99	0.34	-0.91	0.99	1.00					
SAR	0.734	0.50	0.52	0.39	0.47	0.63	0.53	0.79	0.96	0.91	0.57	-0.47	0.61	0.15	-0.53	-0.53	1.00				
SSP	0.853	-0.69	-0.60	-0.78	-0.70	-0.57	-0.66	-0.36	-0.03	-0.14	-0.63	-0.97	-0.59	0.99	-0.95	-0.95	0.27	1.0			
RSC	-0.980	0.36	0.35	0.47	0.40	0.21	0.33	-0.02	-0.37	-0.23	0.28	0.98	0.24	-0.87	0.99	0.99	-0.60	-0.9	1.000		
T. Co	-0.280	0.99	0.99	0.99	0.99	0.97	0.99	0.89	0.66	0.76	0.98	0.58	0.97	-0.82	0.52	0.52	0.43	-0.7	0.430	1.00	
E.Co	-0.120	0.99	0.99	0.97	0.99	0.99	0.99	0.95	0.78	0.86	0.99	0.43	0.99	-0.71	0.36	0.37	0.58	-0.6	0.276	0.98	1

strong affinity for each other (Table 2). EC varied from 700-5200 (mmhos/cm) with maximum 5200 (mmhos/cm) recorded from S3 and showed strong positive correlation with TDS ($r = 1.000$; $P<0.01$); EC and Ca ($r = 0.999$; $P<0.05$); EC and TA ($r = 0.999$; $P<0.05$). EC was an important parameter to determining the water quality for domestic and agricultural purpose. EC of water samples more than 1000 mmhos/cm was not suitable for agricultural purpose [11]. EC and Na^+ play a vital role in suitability of water for irrigation; Higher EC in water creates a saline soil, whereas higher salt content in irrigation water causes an increase in soil solution osmotic pressure [10]. The salts, besides affecting the growth of plants directly, also affect the soil structure, permeability and aeration, which indirectly affect plant growth [12]. The total concentrations of soluble salts in irrigation water can be classified into low (C1), medium (C2), high (C3) and very high (C4) salinity zones. The zones (C1-C4) have the value of EC less than 250, 250-750, 750-2,250 lS cmG^{1} and more than 2,250 lS cmG^{1} respectively. Based on the classification water samples S1 comes under medium (C2) and S2 and S3 falls under very high (C4).

TDS ranged between 500-2900 mg/l and S3 registered high TDS values 2900 mg/l; TDS showed strong positive correlation with TA (r= 0.998; P<0.05); TDS and Sulphate (r= 0.998; P<0.05). TDS from S2 (2650 mg/l) and S3 (2900 mg/l) were fell down under the category of brackish water (1000 mg/l) and were not suitable for irrigation [13] and [10] reported that high TDS value of water samples make trouble to cattle's, livestock's and adversely affects the plants by increased soil salinity. High concentration of TDS in ground water may affects persons who suffering from kidney and heart diseases [14]. An increased TS level was recorded in S2 (3400 mg/l) and S3 (3250 mg/l) and TS showed positive correlation with TC (r= 0.999; P<0.05), [15] reports that increases in TS tend to increase the degree of pollution in the water. TA was comparatively higher in the S3 (1250 mg/l), S2 (1200 mg/l) with an average value of S1 (120 mg/l) respectively and showed positive correlation with Ca (r= 0.997; P<0.05). The average values of total alkalinity in the S2 and S3 were exceeded the higher desirable limit given by WHO (1989) and the higher alkalinity indicates pollution [16]. In this present study based on the TA the water quality is poor in the S2 and S3.

TH ranged between 275-2350 mg/l and S3 registered high TH values (2900 mg/l); TH showed strong positive correlation with sulphate (r= 0.997; P<0.05). TH of water samples S1 comes under hard water and S2, S3 were Very hard water and all the water samples were not suitable for domestic purposes. Calcium (Ca) content of S2 and S3 were above the value 200 mg/l [17]. High Ca content in the water makes it unfit for human consumption and damage the industrial machineries where it used for cooling purpose [18]. The Magnesium (Mg^{2+}) content of S2 (134 mg/l) and S3 (220 mg/l) were beyond 50 mg/l rendering the water unpalatable [19]. Generally calcium and magnesium maintain a state of equilibrium in most waters. More Mg^{2+} present in waters will adversely affect the soil quality converting it to alkaline and decreases crop yields; [10] reported that high Mg combines with sulphate act as laxative to human being. Sodium (Na^{+}) an important cation occurs in all natural fresh water sources from 0.1 to 181 ppm [19]. In this present study high Na^{+} content was recorded in S3 (512 mg/l), may be due to the percolation of Na^{+} ions from the S2 irrigated fields. High Na^{+} water breaks the soil aggregates and blocks the soil pores in irrigated fields [20]. An increased level of Potassium (K^{+}) was observed in the polluted water samples S2 (12.5 mg/l) and S3 (31 mg/l), due to the disposal of industrial effluent. The usage of sulphate, sodium sulphate and sodium bisulphate in the paper mill results in the increased concentration of sulphate in S2 (747 mg/l) and S3 (900 mg/l) samples; [21] states that higher concentration of Na_2SO_4 in the water can cause malfunctioning of alimentary canal of human beings. High Nitrate concentration was recorded at S2 (40 mg/l) indicates the pollution level, [22] reported of elevated nitrate concentration in waste water irrigation site at Mexico. Chlorides are highly soluble in water and cannot eliminate by biological and chemical treatments. In this present study high concentration of chloride was recorded in S2 (460 mg/l) and S3 (570 mg/l), due to usage of multistage bleaching of paper mill. The chloride present in the effluent by percolation reaches the ground water and increases the chloride level, [23] states that chloride is the best indicators of water pollution.

DO was relatively high in the S1 (6.1 ml/l), S2 (Nil) and S3 (3.5 ml/l) respectively. The DO values were very low and showed a gradual depletion towards the most critical manifestation of pollution. Absence of DO in the paper mill effluent S2 denotes the pollution level. Similar kinds of results were earlier reported by [24, 25]. These data were consistent with that the decomposition of organic matter resulted in DO depletion [26]. Therefore, regional variations should be considered when using DO as an indicator to evaluate surface water quality. High BOD and COD values were recorded in S2 than S1 and S3; BOD showed highly strong positive correlation with COD (r= 1.000; P<0.01), represented organic pollution such as runoff from solids or waste disposal activities, etc., [27]. The presence of lignin, organic matter and toxic materials in the S2 sample consumes more oxygen and reduces the DO content.

Sodium Adsorption Ratio: Irrigation waters are classified based on sodium adsorption ratio [28] an important chemical parameter for judging the degree of suitability of water for irrigation as sodium content or alkali hazard, which is expressed in sodium adsorption ratio (SAR). The SAR is computed, where the ion concentrations are expressed in meq l-1as shown below:

$$SAR = \frac{Na+}{(Ca^{2+} + Mg^{2+}) / 2} 0.5$$

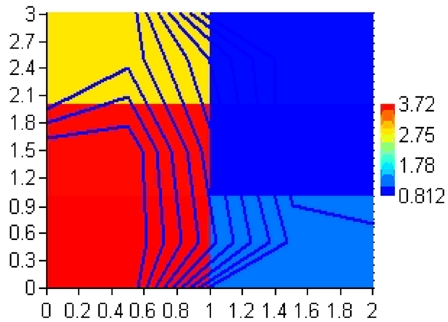

Fig. 2: Matrix plot similarity between the EC and SAR

Table 3: Sodium Absorption Ratio in three different stations

Samples	SAR	Water classification
S1	7.19	Low
S2	6.48	Low
S3	18.02	High

SAR<10= Low; SAR 10-18=Medium; SAR 18-26= High; SAR>26 =Very High

SAR in three different stations was presented in Table 3. There is a close relationship between SAR values in irrigation water and the extent to which Na^+ is absorbed by soils. If water used for irrigation is high in Na^+ and low in Ca^{2+}, the ion-exchange complex may become saturated with Na+, which destroys soil structure, because of dispersion of clay particles. As a result, the soils can be very difficult to cultivate [12]. The sodium hazard is expressed in terms of classification of irrigation water as low (<10), medium (10-18), high (18-26) and very high (>26). SAR value, in the study area is in the range of 6.48-18.02. Matrix plot analysis shows similarity between the EC and SAR (Figure 2); based on the plot analysis the effluent water comes under the poor category also not suitable for domestic and irrigation purposes. High sodium water leads to the development of alkaline soil, which has unfavorable structure and restricts soil aeration. Based on the ionic interaction between Ca, Mg and bicarbonate, Soluble Sodium Percentage (SSP) and Residual Sodium Carbonate (RSC) values were determined. SSP of all water samples were fall within the permissible limit (60 - 75 mg/l). RSC of S2 sample was higher than the permissible limit (2.25 mg/l).

Multivariate Analysis: Cluster analysis (CA) was calculated physicochemical parameters of water and microbial level for all the 3 stations and the result is depicted (Figure 3), based on which 2 distinct groupings could be distinguished that apparently reflected differences in water quality within the study area.

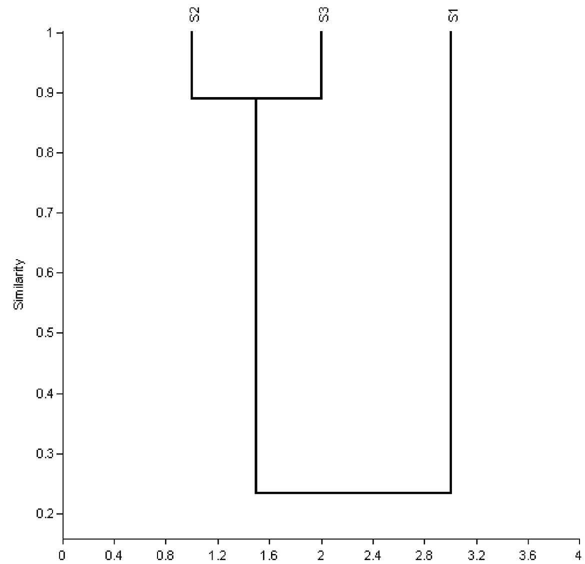

Fig. 3: Bray - Curtis similarities of Physico-chemical parameters of samples
S1= Station1; S2 = Station 2; S3 = Station 3

Group I S1 (Control water); Group II included S2 and S3 (Effluent water used for irrigation and Open well adjacent to effluent water irrigated field) correspond to a relatively Normal water, very high pollution and moderate pollution regions, respectively. In Figure 4 two Group could be distinguished that apparently reflected differences in water quality within the study area. However, from the PCA results, it may convincingly be presumed that in station 2 and 3, pollution is mainly from paper mill effluent solid waste disposal sites. In MDS plot showed that separation of station 1 from the remaining station in Figure 5. In the multivariate analysis (Figure 3-5) it was found that all the samples station 2 (effluent water) and station 3 (irrigated area ground water) were ordinate separately from all other samples which conform to the dendrogram. From the above discussion, we can say that CA, MDS and PCA are a useful tool to analyze the pollution source and monitoring sites. It can offer information to identify polluted sites and help in the decision making on controlling of water pollution.

Microbial Level in the Water Samples: Total Coli form count in the present study shows maximum number (1100) in S2 and S3 and TC abun showed strong positive correlation with TA (r= 0.999; P<0.05). According to [29] the coli form count above 500 - 1000 /100ml of water was not suitable for domestic purpose. Coli form group of bacteria was considered as "Indicator Organism" and their

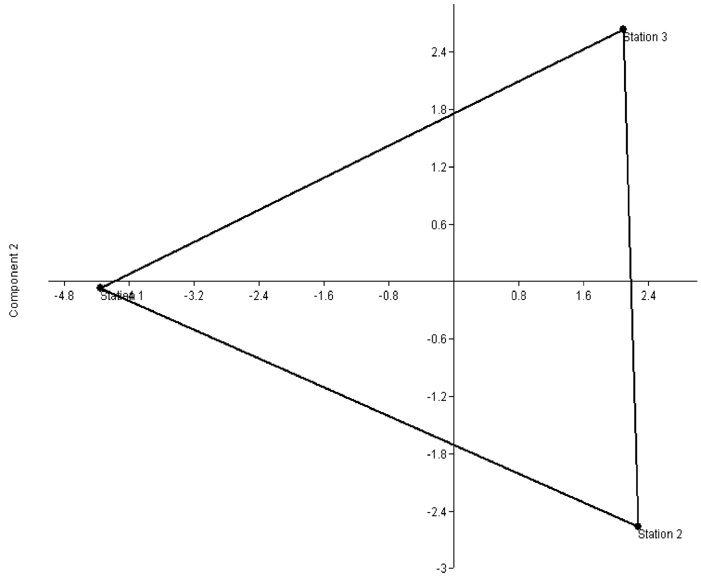

Fig. 4: Principal component analyses of Physico-chemical parameters of samples

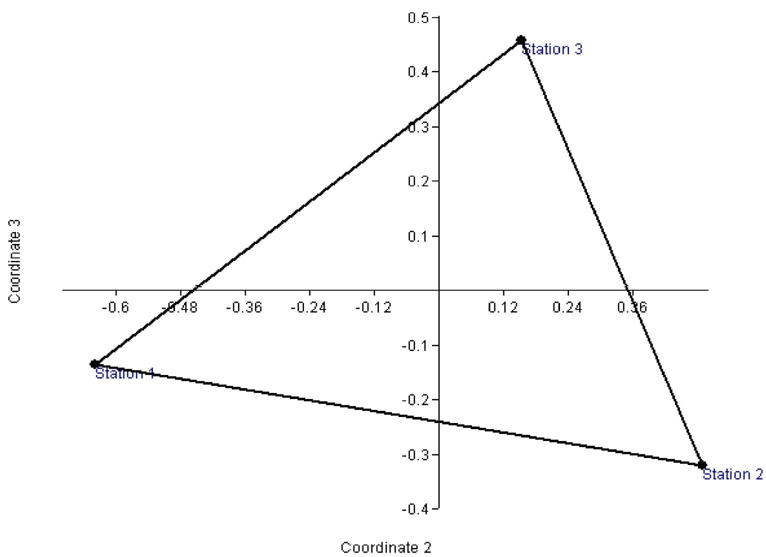

Fig. 5: Multivariate ordination plot analysis of Physico-chemical parameters of samples

presence in water strongly suggested the presence of other pathogenic organisms. Large number of *E. coli* in S2 (740) and S3 (900) indicates the pollution level of water samples. The presence of *E. coli* in water samples under unacceptable conditions may associate with pathogens responsible for the outbreak of certain water borne diseases.

CONCLUSIONS

It can be concluded from the present study than the period effluent irrigation has highly influenced the nitrate accumulation in ground water. More over the levels alkalinity, Ca, BOD, COD, SAR in ground waters of effluent irrigated field were found to be higher and this effluent water is not suitable for irrigation. Hydrological parameters exhibited distinct variations in three categorized study zones. In this case study, different multivariate statistical techniques were used to evaluate variations in the ground water quality assessment in Paper mill effluent irrigated area. CA and PCA helped in identifying the factors/sources responsible for Paper mill effluent irrigated area water quality variations in three different regions. Based on the results we concluded that the water samples S2 and S3 were unsuitable for domestic and irrigation purposes. Immediate need is to maintain existing Effluent Treatment Plant (ETP) of paper mill leads to ground water pollution has a minimum of suspended solids. An effective ETP operation has been recommended to reduce pollution effect and maintain the quality of ground water.

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