

Effect of Sugar Mill Effluents on Ground Water Quality

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ABSTRACT

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Groundwater, the main source of irrigation, drinking or domestic purposes, is affected due to discharge of industrial effluents. The sugar industry contain remnants of chemical used for processing like caustic soda, sodium chloride, lime, sulphur and softening agents etc. and have potential to cause groundwater quality deterioration. In order to assess the quality parameters, ground water samples of various sources were collected from around the sugar mills placed at Gopalganj and Samastipur, Bihar. Altogether 30 groundwater samples were processed to detailed analysis of various parameters following the standard guideline of APHA, WHO study under investigation alarming pH ranges (6.8-8.6), 400-1350 mg/l of $\text{Ca}^{2+}+\text{Mg}^{2+}$, $\text{CO}_3^{2-}+\text{HCO}_3^-$ (95-520 ppm in terms of CaCO_3) and (234.3-468.4) ppm chloride concentrations were obtained might be certainly problematic for drinking purpose. Amongst the parameters concentration of chloride, $\text{CO}_3^{2-}+\text{HCO}_3^-$ and $\text{Ca}^{2+}+\text{Mg}^{2+}$ were found beyond the permissible limit (with increasing trend of $\text{Ca}^{2+}+\text{Mg}^{2+}$ almost up to 8-10 km from both the sugar mills) for irrigation. Based on categorization of irrigation classes under the study indicated that the sources fall under either medium or high salinity hazards required special attention for irrigation purpose.

Introduction

Groundwater has emerged as the dominant place in agriculture and food security in India. It is estimated that over 60% of irrigated agriculture, which itself is 70% of the total in India, is covered by groundwater (<http://www.iimahd.ernet.in/publications/data/2009-03-08Gandhi.pdf>). However, 71% of our earth is covered with water, but salt free water is only 3% of the total. In fact, very small part of the salt free water (0.007% of the total) is having such a quality to satisfy human needs (<http://environment.nationalgeographic.co.in/environment/freshwater/freshwater-crisis/>).

Of the world, India is having 2.6% of land and 17% of the population with only 4% of the water resources Draft National Water Policy (2012) as recommended by National Water Board in its 14th Meeting held on 7th June, 2012.

The main factors responsible for increasing water pollution are exponential growth of population, urbanization, industrialization and agricultural revolution. Groundwater quality is affected due to discharge of poor quality water from various industries and urban waste water to the natural water courses. The sugar

industry contain remnants of chemical used for processing like caustic soda, sodium chloride, lime, sulphur and softening agents etc. which degrade the quality of groundwater.

During the last few decades, disposal of sewage-sludge without proper treatment from urban areas and effluents from industries have caused the deterioration in the quality of groundwater. The need has arisen to review and recognise environmental problems associated with sugar mills. The effluents discharged from the sugar factories, distilleries etc. introduced in to the groundwater might be causing undesirable qualities. Therefore, the present study has been carried out to assess the various quality parameters of ground water sample of different water bodies situated in the vicinity of sugar mills.

Materials and Methods

The research activities were carried out at the College of Agricultural Engineering, Rajendra Agricultural University, Pusa. Altogether 30 groundwater samples of various sources were collected from surrounding areas of the sugar mills located at Gopalganj and Hassanpur (Table 1) according as water quality standard guideline APHA, WHO. All the samples (1 litre each) were treated with 2-3 drops of toluene before analysing in the laboratory to assess the various quality parameters to check the microbial growth.

Methodology

Measurement of pH

The pH was determined by immersing the electrodes of pH meter in a 100ml clean beaker containing about 50ml of the water sample. The pH meter measured the electromotive force across the electrodes in

water samples. The meter was graduated to read directly in pH units along with the electromotive force (mV) scale. A standard buffer solution (of known pH) was used to calibrate the instrument before determining the pH of test solutions.

Measurement of Electrical Conductivity (EC)

The electrical conductivity was measured by dipping the cell of the EC meter in 40ml water sample and expressed as $\mu\text{mhos/cm}$ at 25°C .

Sodium

The determinations of Na and K were carried out directly with the help of flame photometer using appropriate filters and standard curves prepared.

The curve was drawn by plotting flame photometer readings at 589nm (when excited in a gas flame) against the known concentrations (5, 10, 20, 40 and 50me/l). The concentrations of Na in the unknown samples were read from the curve.

Calcium and magnesium (EDTA titration method)

5 ml of the water sample in a porcelain dish was diluted to about 25ml distilled water. One ml of ammonium chloride-ammonium hydroxide buffer and 3 to 4 drops of Erichrome Black T indicator were added and titrated with the standard Versanate solution. The colour change was wine red to blue or bluish green. From the volume of 0.01N EDTA (standardized against 0.01N CaCl_2) solution required for titration, the concentration of $\text{Ca}^{2+} + \text{Mg}^{2+}$ was obtained directly in me/l as below:

$$\text{Ca}^{2+} + \text{Mg}^{2+} * 1000;$$

V_v = ml of Versanate solution used, N = Normality of Versanate solution and

V_s = Volume of aliquot taken (ml)

Carbonates and bicarbonates (Richards, 1954)

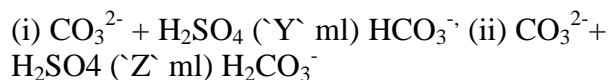
The estimation was based on simple acidimetric titration using different indicators working in alkaline pH range (above 8.2) or in acidic pH (below 6.0). The reagents used were:

Phenolphthalein indicator: 0.25% solution in 60% ethyl alcohol

Methyl orange indicator: 0.5% solution in 95% alcohol

Standard sulphuric acid (0.01N)

5 ml of the water sample was titrated against 0.01N sulphuric acid until the disappearance of pink colour (Phenolphthalein end point) while conversion of Carbonate in to Bicarbonate and burette reading was noted as `Y` ml. Further, it was titrated using methyl orange indicator (yellow) and the burette reading was noted as `Z` ml. Consequently, the reaction was followed as:



Carbonate and bicarbonate were calculated as

$$\text{CO}_3^{2-} = 2Y * N * (1000/V_s) = 2Y * 2 = 4Y \quad \& \quad \text{HCO}_3^- = (Z - 2Y) * 2 * N * (1000/V_s) = (Z - 2Y) * 2$$

Residual Sodium Carbonate (RSC)

It was calculated from the analysis data for carbonates plus bicarbonates (me/l) and Calcium plus Magnesium (me/l) in the following manner:

$$\text{RSC} = (\text{CO}_3^{2-} + \text{HCO}_3^-) - (\text{Ca}^{2+} + \text{Mg}^{2+})$$

Sodium adsorption ratio

Sodium adsorption ratio was synthesized from known concentration of Na^+ and $\text{Ca}^{2+} + \text{Mg}^{2+}$ as follows:

$$\text{SAR} = \text{Na} / (\text{Ca} + \text{Mg})$$

Total dissolved solid

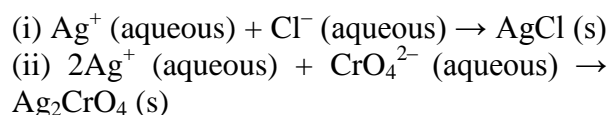
The total dissolved solid was calculated by multiplying the EC value (dS/m) by a factor 640 and expressed in ppm or mg/l.

$$\text{TDS (ppm)} = \text{EC} * 640$$

Chloride

The Chloride concentration was determined by titration with silver nitrate (0.02 N). The silver nitrate solution was slowly added till the end point of titration occurred when all the Chloride ions were precipitated as silver chloride.

Then additional silver ions reacted with the chromate ions of the indicator (potassium chromate) to form a red-brown precipitate of silver chromate. The reactions were followed as:



Firstly, 5ml of the sample (V_s) was brought to pH 7-8 by adding HNO_3 / NaOH after diluting it to about 25ml with water. It was then titrated with `X` ml standard AgNO_3 solution (with stirring) by using 5 to 6 drops of K_2CrO_4 indicator until the first reddish brown precipitate appeared and Cl^- was calculated as

$$\text{Cl}^- = (\text{X} * \text{N}) * (1000/V_s) = \text{X} * () = \text{X} * 4$$

Nitrate-nitrogen

Nitrates are the most oxidised forms of nitrogen and the end product of the aerobic decomposition of organic nitrogenous matter. The evaluation of nitrogen is of paramount importance in understanding the nutritional status of water bodies. Nitrate reacts with phenol di-sulphonic acid (PDA) to produce a nitro derivative, which in alkaline solution develops a yellow colour. The colour produced follows Beer's law and is proportional to the concentration of NO_3^- -N present in the sample. The concentration of NO_3^- -N was determined using a colorimeter or spectrophotometer.

A calibration curve was prepared by using suitable aliquots of 2, 5, 10, 15, 20 and 25 ml standard nitrate (KNO_3) solution. Each of the aliquots were treated with 2 ml of Phenol di-sulphonic acid before 10 ml of concentrated NH_3 (to develop colour) and then diluted to 100 ml standard volumetric flasks. Contents were mixed well and the solutions from each of the standard flasks were transferred to a cuvette. The absorbance was measured at 410 nm wavelength filter using colorimeter. Simultaneously, a blank solution was prepared. A calibration curve was drawn by plotting absorbance against the concentration of NO_3^- -N. Using the calibration curve, the concentration of NO_3^- -N in the water sample is determined. Concentration (ppm) = $4.8 \times$ Dilution factor* O.D. reading of the sample (4.8 for standard solution)

Water class rating (Wilcox Diagram)

The rating of the water as regards its suitability for irrigation was done by referring to the standard chart available in the soil testing laboratory. The experimentally determined value of $\text{Ca}^{2+} + \text{Mg}^{2+}$ (in me/l) was spotted in the chart and perpendicular was drawn from that point. The EC value of the

water (in the chart) was to be seen and from that point, a slanting line was drawn exactly in a similar manner in which the line from a next higher value was drawn. The point where the EC line intersected the perpendicular drawn from the $\text{Ca}^{2+} + \text{Mg}^{2+}$ spot would lie in a certain zone which gave the water class. A perpendicular from this point of intersection was extended to the SAR line meeting it at some point.

Results and Discussion

This study was taken up with a view to assess the quality of groundwater of different sources in the surrounding areas of Sasamusa sugar mill, Gopalganj (Table 2) and Hassanpur sugar mill, Samastipur (Table 3).

A pH range of 6.5-8.5 is normally acceptable as per guidelines suggested by WHO and BIS. The pH values near Sasamusa sugar mill was in the range of 8.2 to 8.6, while that in the vicinity of Hassanpur sugar mill it varied from 6.8 to 8.0. The Electrical Conductivity near Sasamusa sugar mill varied from 330 to $910 \mu\text{mhos/cm}$ (at 25°C), which was from 410 to $780 \mu\text{mhos/cm}$ (at 25°C) near Hassanpur sugar mill and were found within the safe limit. Also, the concentration of total dissolved solids (TDS) was varying from 211 to 584 ppm for Sasamusa mill and from 262 to 499 ppm for Hassanpur mill. It followed as: excellent, <300 mg/l; good, between 300 and 600 mg/l. Hence, perusal of data indicate that TDS was found within safe limit and could be used safely for drinking as well as irrigation purpose as proposed by (http://www.who.int/water_sanitation_health/dwq/chemicals/t ds.pdf).

The concentration of $\text{CO}_3^{2-} + \text{HCO}_3^-$ (alkalinity) was varying from 95-520 ppm (in terms of CaCO_3). Thus, it was also creating obstruction in using water for drinking purpose.

The concentration of $\text{Ca}^{2+} + \text{Mg}^{2+}$ ranged from 400 to 1200 mg/l near the mill of Sasamusa, while it was 550 to 1350 mg/l around Hassanpur sugar mill. The concentration of $\text{Ca} + \text{Mg}$ was found much higher nearby sugar mills and declined almost upto 8-10 Km away from the both sugar mills in a definite trend. However, high concentration (> 600 ppm) might be developing scales on the water heater, boiler and cooking utensils and also increased soap consumption for washing and was unsuitable for drinking and domestic purpose. It was classified as soft (< 75 mg/l), hard (75-300 mg/l) and very hard (> 300

mg/l) in terms of CaCO_3 (www.dpi.nsw.gov.au, Agfact AC.2, 9th edition, April 2005). The high concentration of $\text{Ca}^{2+} + \text{Mg}^{2+}$ disclosed hardness of water and indicated that such water was not suitable for irrigation purpose. Excessive hardness might also be causing foliar deposits of Calcium or Magnesium Carbonate under overhead irrigation.

NO_3^- -N content in water samples varied from 6.8 to 7.7 ppm and from 6.9 to 7.5 ppm at both sugar mill and was found within safe limit for drinking and irrigation purpose.

Table.1 Sampling of Groundwater of various sources

S. No.	Source	Depth (ft)	Distance (km)	Sugar mill
1	D.T.W.	200	0.0	Gopalgang
2	H.P.	50	0.1	
3	H.P.	50	1.0	
4	H.P.	45	2.0	
5	H.P.	55	3.0	
6	H.P.	45	4.0	
7	H.P.	55	5.0	
8	H.P.	50	6.0	
9	D.T.W.	250	7.5	
10	H.P.	45	8.5	
11	H.P.	40	10.0	
12	H.P.	50	11.0	
13	D.T.W.	250	13.0	
14	H.P.	55	13.5	
				Hassanpur(Samastipur)
15	D.T.W.	400	0.0	
16	H.P.	40	0.0	
17	H.P.	45	1.0	
18	H.P.	45	1.0	
19	H.P.	70	2.0	
20	H.P.	50	2.5	
21	H.P.	45	3.0	
22	H.P.	50	4.0	
23	H.P.	55	4.5	
24	H.P.	70	5.0	
25	H.P.	100	7.5	
26	H.P.	50	9.0	
27	H.P.	45	10.0	
28	H.P.	40	11.0	
29	H.P.	55	12.0	
30	H.P.	55	13.0	

Table.2 Characteristics of pre-monsoon groundwater samples around Sasamusa sugar mill, Gopalganj

S. No.	Distance	pH	EC	Na	Ca ²⁺ +Mg ²⁺	CO ₃ ²⁻ +HCO ₃ ⁻	RSC	SAR	TDS	Cl ⁻	NO ₃ ⁻ N	Irrigation class
	Km		µmhos/cm	mg/l	mg CaCO ₃ /l	mg CaCO ₃ /l	me/l		ppm	mg/l	Ppm	
1	00.0	8.4	390	3.67	1200	170	(-) ve	1.06	250	8.80	6.8	C ₂ S ₁
2	00.1	8.3	410	3.73	1160	150		1.10	262	10.4	6.9	C ₂ S ₁
3	01.0	8.5	820	6.22	1000	180		1.97	525	9.60	6.9	C ₃ S ₁
4	02.0	8.5	370	0.73	0770	120		0.26	237	8.00	6.9	C ₂ S ₁
5	03.0	8.4	400	2.53	0760	135		0.33	256	9.20	7.3	C ₂ S ₁
6	04.0	8.4	560	1.82	0700	120		0.69	358	8.40	7.0	C ₂ S ₁
7	05.0	8.6	490	2.01	0680	135		0.77	314	8.80	6.9	C ₂ S ₁
8	06.0	8.4	360	1.24	0525	110		0.54	230	8.80	7.0	C ₂ S ₁
9	07.5	8.5	330	0.64	0490	110		0.29	211	11.2	6.8	C ₂ S ₁
10	08.5	8.2	910	6.14	0475	095		2.82	582	11.6	7.7	C ₃ S ₁
11	10.0	8.3	850	6.88	0490	110		3.11	544	11.6	8.9	C ₃ S ₁
12	11.0	8.6	430	6.67	0450	130		3.14	275	11.8	6.9	C ₂ S ₁
13	13.0	8.6	880	7.30	0460	180		3.40	563	11.8	6.9	C ₂ S ₁
14	13.5	8.5	410	9.46	0400	160		4.73	262	13.2	7.1	C ₂ S ₁

Table.3 Characteristics of pre-monsoon groundwater samples around Hassanpur sugar mill, Samastipur

S. No.	Distance	pH	EC	Na	Ca ²⁺ +Mg ²⁺	CO ₃ ²⁻ +HCO ₃ ⁻	RSC	SAR	TDS	Cl ⁻	NO ₃ ⁻ N	Irrigation class
	km		µmhos/cm	mg/l	mg/l	mg/l	mg/l		ppm	mg/l	ppm	
1	00.0	8.0	780	9.13	1325	260	(-)ve	2.48	499	12.0	6.9	C ₃ S ₁
2	00.0	7.3	750	8.86	1350	520		2.41	461	12.6	7.4	C ₃ S ₁
3	01.0	7.7	750	8.12	1210	235		2.19	474	12.0	7.4	C ₂ S ₁
4	01.0	7.4	750	6.88	1200	235		2.29	474	10.8	6.9	C ₂ S ₁
5	02.0	7.7	480	8.26	0900	130		2.15	307	09.2	6.9	C ₃ S ₁
6	02.5	6.8	650	7.86	0800	260		1.71	416	08.4	6.9	C ₃ S ₁
7	03.0	7.3	540	7.24	0650	175		2.84	346	07.9	7.0	C ₃ S ₁
8	04.0	7.7	530	4.89	0630	170		1.95	339	07.6	6.9	C ₃ S ₁
9	04.5	7.9	560	4.36	0620	230		1.52	358	07.2	7.5	C ₃ S ₁
10	05.0	7.0	750	6.04	0590	245		2.03	474	08.8	7.0	C ₃ S ₁
11	07.5	7.8	410	2.70	0550	120		1.15	262	06.6	6.9	C ₃ S ₁
12	09.0	7.4	420	5.25	0800	260		2.39	269	06.6	7.3	C ₃ S ₁
13	10.0	7.6	520	4.14	0700	200		1.28	333	06.6	7.1	C ₃ S ₁
14	11.0	8.0	640	5.61	0825	260		1.95	410	06.8	7.0	C ₃ S ₁
15	12.0	7.5	590	6.03	0625	245		2.41	378	07.2	7.2	C ₃ S ₁
16	13.0	7.4	420	6.57	1035	355		3.21	269	08.4	7.0	C ₃ S ₁

Table.4 Classification for salinity

Salinity Category	EC ($\mu\text{mhos/cm}$ at 25°C)	No. of sources in category	Percentage of sources
Low	<250	0	0
Medium	250-750	21	70.0
High	750-2250	9	30.0
Very High	>2250	0	0

Table.5 Chloride classification of irrigation water

Chloride (ppm)	Effect on crops	No. of samples	Percentage
< 70	Generally safe for all plants	0	00.00
70-140	Sensitive plants show injury	0	00.00
140-350	Moderately tolerant plants show injury	19	63.33
> 350	Can cause severe problems	11	36.67

The chloride content in water samples were in the range of 284 to 468.6 ppm for Sasamusa mill, while nearby Hassanpur mill, it was varying from 234.3 to 447.3ppm. It was certainly unsafe (> 250ppm) for drinking and irrigation which causing toxicity to sensitive crops purpose (Indian Standard Specifications for drinking water Is: 10500).

In present investigation all the water samples were categorized based on the salinity hazard (Table 4). It is well known that the most influential water quality parameter for crop productivity was measured by electrical conductivity (EC_w). Its high value might be causing inability of the plant to compete with ions in the soil solution for water (physiological drought).

Thus, table 4 revealed that the EC values ranging from 330 to 910 $\mu\text{mhos/cm}$ were either in medium (70.0%) or high (30.0) saline category. Thus, salt tolerant crops (Alfalfa, Barley, Bermuda grass, Corn, Cotton, Sorghum, Soybean and Wheat etc.) could be suggested for saline areas (Rhoades *et al.*, 1992 and Fipps, 2003) according as the other factors suitability.

SAR values indicated that ground water samples of various waterbodies were low in sodium content and were found within

acceptable range for drinking and irrigation purpose (Garg *et al.*, 2008).

It was evident from the data that chloride contents were unsafe for irrigation as discussed earlier. All samples were also classified for irrigation purposed by considering chloride content in present study (Table 5) as proposed by Bauder *et al.*, 2012.

The categorization of irrigation classes was carried out following the water quality chart (Richards, 1954). Based on the categorization of irrigation classes, all the sources came under either medium (C_2S_1) or high salinity hazard (C_3S_1). Hence, special management for salinity control with salt tolerant crops were required.

Groundwater quality parameters viz. $\text{Ca}^{2+} + \text{Mg}^{2+}$, $\text{CO}_3^{2-} + \text{HCO}_3^-$ and Cl^- with alarming pH were certainly problematic for drinking as well as irrigation purpose in the locality of sugar mills. But, TDS was thought to be problem in future. However, $\text{NO}_3^- - \text{N}$, SAR and RSC were certifying the water for drinking and irrigation purposes as well.

Also the sources came under either medium (C_3S_1) or high (C_2S_1) salinity hazards. Hence, salinity control with salt tolerant crops could be recommended for the sugar mill locality.

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