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Case Study

Hydrogeochemical Analysis and Groundwater Suitability for Drinking and Irrigation of Kalyani Industrial Belt, West Bengal, India

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Abstract

This study presents a comprehensive evaluation of groundwater quality for the year 2021 -2024 of the Kalyani industrial area using various statistical tools. The different had rochemical parameters like pH, Temperature (T), Total Hardness (TH), Total Alkalinity (TA), Total Dissolved Solid (TDS), concentrations of sodium ion (Na^+), potassium ion (K^+), calcium ion (Ca^{2+}),magnesium ion (Mg^{2+}), fluoride ion (F^-), chloride ion (Cl^-), sulphate ion (SO_4^{2-}), nitrate ion (NO_3^-), bicarbonate (HCO_3^-) ion concentration etc have been analysed. After analysis, the quantitative results were equated with the drinking water quality standards set by WHO (World Health Organisation). Box and whisker plots have been used to understand the distribution of data of each parameter in different time scale. A correlation - regression study has been executed to assess the interrelationships amongst the various parameters of water quality. Hydro-geochemistry of this industrial belt has been explained by using Gibbs and Chadda diagram and analysis demands that the nature of the study zone is Ca-Mg-HCO_3type. Ion exchange mechanism has been established trough bivariate relationship, ion exchange plot followed by Chloro-Alkaline Indices (CAI) analysis by using different ion concentration. Based on investigated parameters, the overall water quality was judged by calculating WQI (Water Quality Index) and the calculations demand that average WQI of the study area is 44.589, which is comparatively good for the usage of irrigation, domestic, industrialisation purpose. Furthermore, the irrigation suitability water for irrigation was also analysed, using some selected indices which revealed that water quality was fit for irrigation Overall, the water is appropriate for most uses with minimal treatment, though it must be treated before drinking. Irrigation suitability indices confirm that the groundwater of the Kalyani industrial belt is generally suitable for irrigation.

Keywords: Groundwater, WHO, Box plot, Gibbs diagram, Hydro-geochemistry, Irrigation suitability and WQI.

Introduction

In the 21st century, one of the most global issues is to ensure safe, drinkable water for all. Near about 785 million individuals still don't have reliable admittance to clean drinkable water[1]. Underground water is a remarkable freshwater resource. Almost one-third to half of the global inhabitants depends on groundwater for drinking purposes[2]. Incidentally, Pollution of ground-water is a major critical issue which affecting many communities of the developing countries[3]. Increasing urbanization, industrialization and agricultural intensification have resulted in the degradation of water quality in many areas. Several studies have reported high levels of hardness, salinity, and ionic concentrations exceeding permissible limits, thereby affecting water suitability[4,5]. Drinking polluted water endangers human health and leads to a range of illnesses in many areas of the world[6]. In the case of eastern India, predominantly in the West Bengal, under-groundwater quality issues are becoming increasingly severe due to both geogenic and anthropogenic factors. Experiments have highlighted the existence of arsenic contamination in water, posing serious health risks to populations[7]. Additionally, regional assessments have shown that the chemistry of under-groundwater is mostly controlled by activities of human and geological formations, which significantly affect its suitability for various uses[8]. The chemical of underground water is governed by some hydro-geochemical processes through interactions among water, aquifer materials, and environmental conditions. These processes are influenced by lithology, climate, and human activities, which collectively determine the concentration and mobility of dissolved ions[9,10].

Gibb's diagram is one of the most widely used approaches to understand these mechanisms that explains relationship between chemistry of water along with the controlling factors like rock–water interactions, evaporation, precipitation[11]. Recently, the amalgamation of statistical techniques and water quality indices has enhanced the interpretation of complex hydro-chemical datasets and provided a wide-ranging understanding of groundwater systems[12,13]. Internationally, Water quality Index (WQI) calculation has gained significant importance as it simply the various complex water quality data into a single value to facilitate the decision makers for the groundwater quality assessment[14]. Additionally, multivariate statistical techniques, including correlation and regression analysis, are widely applicable to identify various relationships amongst the different water quality parameters and to determine the sources of

contamination[13]. Furthermore, the evaluation of groundwater suitability through different indices for irrigation is crucial for sustainable agricultural practices[5]. In spite of extensive studies in various parts of India and abroad, there remains a lack of recent, comprehensive assessments focusing on rapidly industrializing zones such as the Kalyani industrial belt. The present study aims to evaluate the several hydro-geochemistry and water suitability for drinking purpose and irrigation purpose in study region during 2021–2024 using some statistical tools, hydro-geochemical models, and different water indices for water quality. Findings of this study are expected to contribute for the sustainable water management strategies for both the provincial and universal levels.

Methodology

Area of analysis and data collection: The Kalyani industrial belt, a major industrial hub, is situated on the eastern part of the Hooghly River bank within the upper Delta of Ganga, under Nadia district of West Bengal. Soil and water of this area are fertile and predominantly alluvial in nature. At present, it is an urbanized zone and near about 9.75 meters high forms the mean sea level. The geographical coordinates of this belt lie approximately between 22°58′30″ N and 88°26′04″ E. For the study of hydro-geochemistry as well as the irrigation and drinking suitability of the under - ground water groundwater of this area, different parameters for the quality measurement of water were received from open-source data available from WBPCB (west Bengal Pollution Control Board). The WBPCB evaluates water quality at several strategic locations in accordance with the guidelines of CPCB (Central Pollution Control Board) under the NWMP (National water Monitoring Programmed) and experimented results are maintained in its publicly accessible database. Kalyani industrial belt is one of the strategic locations for monitoring of ground water quality. The dataset used in this study were collected over a period from 2021 to 2024, in where monitoring conducted on a regular semi-annual basis during the months of April and October each year. The received data, utilized for the present analysis are presented in Table-1. The experimented value of total alkalinity and Phenolphthalein alkalinity have been used for the derivation of data of bicarbonate (HCO_3^-) and carbonate (CO_3^-) ions.

Table-1: Water quality data of Kalyani industrial area.

Parameter	Unit	Oct' 24	April' 24	Oct' 23	April' 23	Oct' 22	April' 22	Oct' 21	April' 21
pH	-	7.62	7.40	6.93	8.64	7.10	7.38	7.85	7.43
T	º C	29.00	28.50	28.00	30.00	28.00	29.00	27.00	28.00
TH	(mg/L)	262.63	336.00	290.91	220.00	190.91	414.00	607.84	489.58
TA	(mg/L)	300.00	388.00	317.46	297.13	320.25	317.31	364.96	315.04
TDS	(mg/L)	346.00	388.00	372.00	318.00	384.00	524.00	982.00	466.00
PA	(mg/L)	Nil	Nil	Nil	4.98	Nil	Nil	Nil	Nil
Na^+	(mg/L)	16.50	10.60	12.80	11.00	9.70	14.60	18.70	15.00
K^+	(mg/L)	4.30	2.80	3.40	3.00	3.40	2.80	3.20	3.20
Ca^{2+}	(mg/L)	72.87	128.84	80.16	46.49	36.44	93.04	117.88	37.78
Mg^{2+}	(mg/L)	19.64	7.78	22.09	25.27	24.30	44.26	76.24	35.44
F^-	(mg/L)	0.30	0.15	0.32	0.22	0.40	0.17	0.30	0.33
Cl^-	(mg/L)	10.00	9.00	7.50	6.20	9.99	83.97	179.94	84.97
SO_4^{2-}	(mg/L)	12.08	9.70	-	12.44	5.65	13.51	20.74	9.51
NO_3^-	(mg/L)	0.74	0.10	0.03	0.09	0.09	0.07	0.16	0.12
HCO_3^-	(mg/L)	366.00	473.36	387.3	312.50	390.71	387.12	445.15	384.35
CO_3^{2-}	(mg/L)	0.00	0.00	0.00	98.35	0.00	0.00	0.00	0.00

EC	*µs/cm*	622.00	805.00	714.00	595.00	625.00	954.00	1400.00	979.00

Box plotting: Box-and-whisker plots, originally proposed by Tukey [15], were used for this study to show the data spreading of hydro geochemical parameters. These plots are effective for summarizing large datasets and identifying variability and outliers in water quality parameters[16,17]. Every plot represents a summary of five - numbers viz. minimum, maximum, 1st quartile (Q_1, 25th percentile), median (Q_2, 50th percentile) and 3rd quartile (Q_3, 75th percentile). Plot also represents the middle 50% of the data through the inter quartile range (IQR = $Q_3 - Q_1$), while the median is shown as a central line within the box. The plot also extends to the minimum and maximum values, and any data points beyond these limits are treated as outliers.

The position of the median within the box also express the distribution pattern and skewness and the relative lengths of the whiskers. A centered median indicates a symmetrical distribution, whereas an off-centre median suggests either positive or negative skewness. The skewness can be estimated from the three quartiles by using Bowley's[18] formula in Equation-1.

$$\text{Bowley's skewness} = \frac{(Q3+Q1-2Q2)}{(Q3-Q1)} \quad (1)$$

Where zero value signify the plot is symmetry, value greater than zero signify positively (right) skewed and median is nearer to Q_1 and value less than zero signify negatively (left) skewed and median is nearer to Q_3.

Analysis accuracy through Ion Balance Assessment method: Water samples were evaluated for electrical neutrality based on the principle that the total major cationic milliequivalents and total anionic milliequivalents in natural waters are approximately equal. So, for evaluating ionic charge balance for cations and anions errors (ICBE), ionbalance calculations were performed using measured water quality data. Concentrations of dissolved ions, initially determined in mg/L through standard analytical procedures, were converted to meq/L (milliequivalents per litre) following Equation-2.

$$\text{Meq/L} = \frac{\text{Concentration in mg/L} \times \text{valence}}{\text{molecular or atomic weight}} \quad (2)$$

For every sample, the sum of total cation concentrations and the sum of total anion concentrations in meq/L unit were computed. Charge balance accuracy was assessed by calculating the percentage difference (% difference)[19] between total cations and anions using Equation-3 in where acceptable ion balance error is typically within 5% for high-quality data and 10% for less precise analyses, approved for further examination and values outside this range may indicate analytical errors or missing ions.

$$\%\text{Difference} = \frac{\sum\text{Cations} - \sum\text{Anions}}{\sum\text{Cations} + \sum\text{Anions}} \times 100 \quad (3)$$

Pearson's correlation: Pearson's coefficient[20] of correlation (*r*), developed by Karl Pearson. It is widely used for the measurement of the strength and direction for a linear relationship between the two or more variables and mathematically expressed as

$$r = \frac{n\sum XY - \sum X \sum Y}{\sqrt{[n\sum X^2 - (\sum X)^2][n\sum Y^2 - (\sum Y)^2]}} \quad (4)$$

In where "r" represents correlation coefficient, "n" represents total number of records for each parameter, X and Y represent different variables. The range of *r* is from −1 to +1. The plus value designates a positive linear relationship, while a minus value designates a negative linear relationship; zero value implies no linear correlation. Closer value of ±1 indicates the stronger relationship. According to James D. Evans[21], on the basis of "r" values correlation ship are classified as very weak for "0.00–0.19", weak for "0.20–0.39", moderate for "0.40–0.59", strong for "0.60–0.79)" and very strong for "0.80–1.00".

Gibbs Ratio Calculation: To elucidate the mechanisms governing water chemistry, the Gibbs ratio was calculated for both cations and anions following the approach proposed by R. J. Gibbs[11]. The Gibbs diagram is widely recognized as an effective tool for identifying comparative effect of rock-water interaction, precipitation, and evaporation–crystallization methods monitoring the hydro chemical features of natural waters[22].

In the present study, potassium (K^+) was excluded due to its relatively minor contribution and possible analytical uncertainty. Accordingly, the Gibbs ratios were computed using the following modified expressions:

$$\text{Gibbs ratio (cation)} = \frac{Na^+ + K^+}{Na^+ + K^+ + Ca^{2+}} \quad (5)$$

$$\text{Gibbs ratio (anion)} = \frac{Cl^-}{Cl^- + HCO_3^-} \quad (6)$$

In where concentrations of all ions are expressed in meq/L unit (milliequivalents per litre).

Plot have been drawn based on the calculated Gibbs ratios against total dissolved solids (TDS) to identify the dominant processes influencing water chemistry and to know the insight into the hydro geochemical evolution of water systems[23,24].

Chadda Diagram: Chadda diagram or plot is a hydro-chemical scatter plot was developed by D. K Chadda[25] in 1999 to understand the hydro-chemical process of water. This plot is developed by using the differences between alkaline earth metal ions (total Ca and Mg ion concentration) and alkali metal ions (total Na and K ion concentration) in the X axis and the differences between weak acidic ions (total concentration CO_3 and HCO_3 ions) and strong acidic ions (total concentration of Cl

and SO_4 ions) in Y axis where the concentration of all the ions is being calculated in percentage milliequivalent per Liter (meq/l) as per following equations.

$$\mathrm{X-axis\ (cation\ difference)} = (Ca^{2+} + Mg^{2+}) - (Na^{+} + K^{+}) \quad (7)$$

$$\mathrm{Y-axis\ (anion\ difference)} = \left(CO_3{}^{2-} + HCO_3{}^{-}\right) - \left(Cl^{-} + SO_4{}^{2-}\right) \quad (8)$$

Both the axis is plotted in % milliequivalents (meq/l)

Chloro-Alkaline Indices (CAI): Schoeller[26] proposed the chloro-alkaline indices CAI-I and CAI-II which is widely used in hydro geochemical studies to examine the ion exchange processes which are occurring in-between groundwater and aquifer materials.

These parameters indicate the direction of exchange of sodium ion and potassium ion in groundwater and calcium ion, or magnesium ion in host rocks. For the calculations, ion concentrations are expressed in milliequivalents per litre (meq/L) unit.

CAI-I is computed using chloride as the reference ion as follows:

$$\text{CAI-I} = \frac{Cl^{-} - (Na^{+} + K^{+})}{Cl^{-}} \quad (9)$$

CAI-II is calculated by incorporating additional major anions like bicarbonate ion, sulfate ion, carbonate ion, and nitrate ion to account for broader hydro geochemical influences:

$$\text{CAI-II} = \frac{Cl^{-} - (Na^{+} + K^{+})}{SO_4^{2-} + HCO_3^{-} + CO_3^{2-} + NO_3^{-}} \quad (10)$$

Both the indices were interpreted based on their sign and magnitude. Positive CAI values indicate reverse ion exchange, where Na^+ ion and K^+ ion in groundwater replace Ca^{2+} ion and Mg^{2+}ion from aquifer materials. Negative values indicate direct ion exchange, in where Ca^{2+} ion and Mg^{2+} ion in groundwater are exchanged by Na^+ ion and K^+ ion released from the aquifer.

Water Quality Index: Weighted Arithmetic WQI (Water Quality Index) is a robust, widely applied method to aggregate multiple quality parameters into a single composite value, thereby providing a all-inclusive assessment of total water quality[27].

This WQI enables the assessment of water suitability for human consumption by incorporating the collective effects of different physicochemical parameters.

In the present investigation, WQI was determined using the weighted arithmetic method, first introduced by Robert M. Horton[28] and later refined by R. M. Brown et al.[29]. The mathematical formulation employed for calculation WQI is represented in Equation-11

$$\mathrm{WQI} = \frac{\sum Q_n W_n}{\sum W_n} \quad (11)$$

Where: Qn = the quality rating of nth water quality parameter, Wn = the corresponding unit weight of that parameter.
Furthermore, as per the suggestion of *Brown et al.*[29] Q_n for any discrete parameter, the expression is as given in Equation-12.

$$Q_n = \frac{V_n - V_i}{S_n - V_i} \text{ X } 100 \quad (12)$$

where V_n denotes the experimental value, S_n denotes the prescribed standard permissible value, and V_i refers to the corresponding ideal value. For most water quality parameters, the ideal value is taken as zero, except for pH and dissolved oxygen[30], for which the ideal values are considered to be 7.0 and 14.6 mg/L, respectively.

Again, the unit weight (W_n) for each parameter is determined based on its standard permissible value, as given in Equation (13)

$$W_n = \frac{K}{S_n} \quad (13)$$

where Sn represents the recommended standard value of the nth water quality parameter and K denotes the proportionality constant. The value of K is determined from the standard values of various water quality parameters which are under consideration of the study and is computed by using the following expression as given in the Equation-14:

$$K = \frac{1}{\sum \frac{1}{S_n}}, n = 1,2,3,4 \quad (14)$$

This calculating procedure certifies that parameters with lower permissible limits exercise a greater effect on the overall WQI, thereby enhancing the understanding and steadfastness of water quality assessment. The overall water quality status based on observed results is directed by the WQI as per Table-2[28,31-33].

Irrigation suitability: The suitability of water for irrigation purposes is commonly evaluated using six important hydrochemical indices namely Soluble Sodium Percentage (SSP), Sodium Adsorption Ratio (SAR), Magnesium Adsorption Ratio (MAR), Residual Sodium Carbonate (RSC), Kally's Ratio (KR) and Permeability Index (PR). Among these indices the Soluble Sodium Percentage (SSP) was calculated by using following equation as described by Raghunath[34] & Todd[35].

$$SSP(\%) = \frac{Na^{+}}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}} \times 100 \quad (15)$$

where, all the ions are being calculated in milliequivalent per Liter (meq/L) unit.

Sodium Adsorption Ratio (SAR) and Magnesium Adsorption Ratio (MAR) also have been computed by using the equations nos. 16 and 17as proposed by Michale[36] and Raghunath[34] respectively.

Table-2: WQI and corresponding water quality status.

WQI range	Status	Grade	Possible usages
25≤	Excellent quality	A	Safe for drinking, irrigation and industry
26 to 50	Good quality	B	Safe for domestic, Irrigation and Industry
51to 75	Fair quality	C	Safe for irrigation and industrialisation
76 to 100	Poor quality	D	Only for Irrigation
101to 150	Very Poor quality	E	Restricted Irrigation
≥150	Unfit for drinking	F	Proper treatment is needed before any use

$$SAR = \frac{Na^+}{\sqrt[2]{\frac{Ca^{2+}+Mg^{2+}}{2}}} \quad (16)$$

and

$$MAR = \frac{Mg^{2+}}{Ca^{2+}+Mg^{2+}} \times 100 \quad (17)$$

Where, all the ions are calculated in milliequivalent per Liter (meq/L) unit.

For the measurement of hazardous effect of carbonate and bicarbonate ions on water for irrigation suitability purpose, Raghunath also proposed an equation to measure the Residual Sodium Carbonate (RSC), following an equation as given in equation no 18 –

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \quad (18)$$

where, all concentrations are in milliequivalents per Litre (meq/L) unit.

For the identification of the amount of sodium ion over magnesium and calcium ions, an equation had been formulated by Kally[37] which is given in equation no 19.

$$KR = \frac{Na+}{(Ca2+ + Mg2+)} \quad (19)$$

where, the concentration terms are calculated in milliequivalent per Liter (meq/L) unit.

For proper usefulness of water in agricultural, Permeability of water samples had been formulated as Permeability Index (PI) as proposed by Doneen[38] through the formula following equation no 20.

$$PI = \frac{Na+ + \sqrt{HCO_3^-}}{Ca^{2+}+Mg^{2+}+Na^+} \times 100 \quad (20)$$

where, the concentration terms are calculated in milliequivalent per Liter (meq/L) unit.

Results and Discussion

Hydro-chemical attributes of Groundwater: Seventeen different water quality parameters have been used to evaluate the hydrochemistry of ground water quality under Kalyani industrial belt. The acceptability and suitability of all these parameters have been compared by using WHO[2] acceptable and permissible limit as drinking water standard benchmarks. The Statistical overview of the parameters has been recorded in Table-3 with mentioning of minimum value, maximum value, mean value, standard deviation (SD) and coefficient of variance (CV).

The range of pH values were from 6.93 -8.65 with the four years average value of 7.54(± 0.53) with low coefficient of variance (6.9%) i.e. low variability with time duration. Water quality was slightly alkaline in nature and most of the values were within the permissible range of 6.5-8.5) as prescribed by WHO[2]. Electrical conductivity (EC) represents the saltiness of water. Groundwater EC of 400 µS/cm at 25^0C is safe for human consumption as per WHO[2] and highest permissible limit is 1500 µS/cm as WHO[2].

In study area, it has been found that range of EC is 595-1400 with the average of 836±271.69 with high coefficient of variance (32.5%). TDS concentration in the study point varied from 318 – 982 with the average value of 472.5±216.22 and coefficient variance of 45.8% in where 75% of the data are below the desirable level as per WHO[2]. The temperature ranges have been found from 27^0C to 30^0C with the average value of 28.44^0C±0.90 with highly low variability (3.2%). Though there is no limiting boundary of drinking water temperature but it is better to drink water at temperature 15^0C as per WHO[2].

In the case of Calcium and Magnesium ions, the desirable to permissible limits is 75-200 and 30-150 respectively in mg/l as per WHO[2]. Our study point show Ca^{2+} varied 36.44-137.70 with average of 89.19 ±37.28 and CV is 41.8% and Mg^{2+} varied with 7.78-76.24 with average 31.88±20.92 and CV is 65%.
The Total hardness recorded over the study period from 190.91 to 607.81 with average reading 351.48±143.21 with highly coefficient of variance of 40.8% showing several instances exceeding recommended. WHO[2] prescribed the normal range TH for drinking water as 100-500 and classified water as soft water (TH less than 75 mg/L), moderately hard (TH 75 to 150 mg/L), hard (TH 150 to 300 mg/L) and very hard in where TH if greater than 300 mg/L. Following this classification no samples of our study area are under soft and moderate hard category rather majority for the samples belong to hard to very hard region, this temporal variation may be due reason of the possible influence of some kind of groundwater interaction, anthropogenic inputs or seasonal variations.

Following the guideline of WHO[2], the recommended range of Na^+ and K^+ ion concentration are 200 mg/l and 300 to 600 mg/L respectively but study zone revealed that the Na^+ ion concentration very with the range of 9.70 mg/L to 18.70 mg/l with the average value of 13.61±3.14 with moderate coefficient of variance 23% and K^+ ion concentration vary from 2.8 mg/L to 4.3 mg/l with the average value of 3.26±0.48 with moderated coefficient of variance 14.7%. Data also revealed that there is a noticeable temporal variation of concentration for both the ions. Na+ ion values remained relatively low and within the permissible limits and K^+ ion concentrations were also consistently low showing minimal fluctuation compared to Na^+. Based on the average values, the order concentration of different captions is like $Ca^{2+} > Mg^{2+} > Na^+ > K^+$.

Chloride ion, Cl^- concentration range were found from 6.20 mg/L - 179.94 mg/L with the average value of 61.23±63.09 with very high CV of 103% though all the values are very less than the recommended value of WHO[2]. Sulphate ion (SO_4^{2-}) concentration in the studied is 5.65mg/L - 20.74mg/L with mean value of 10.45±4.47 with 43% CV. This ion concentration is very low compared to the recommended value of WHO[2]. Nitrate ion (NO_3^-) concentration in this study ranged from 0.03 to 0.74 with the mean value of 0.175±0.231 with very high CV of 132%. In is clear that all the results of nitrate ion concentration are less than the recommended value of WHO[2]. The one of the important ions, fluoride ion concentration in drinking water is 1.0 -1.5 mg/L as per the guidelines of WHO[2]. The study point demand that the F^- ion concentration is ranged from 0.15 to 0.4 with the average value of 0.27± 0.09 and 31.3% coefficient of variance. Study show that the carbonate ion (CO_3^{2-}) concentration is nil in most case except the sample of april'2023 in where the concentration of CO_3^{2-} is 98.35 mg/L while bicarbonate ion (HCO_3^-) concentration are ranged from 312.50mg/L to 473.36mg/L with a average value of 393.24±48.60 with medium coefficient of variance 12.35% in where the recommended value of the concentration of CO_3^{2-} ion concentration is 300 mg/L as per WHO[2]. Anions are present in the mean abundance order of $HCO_3^- > Cl^- > SO_4^{2-} > F^-$. So, the results suggested that relatively high bicarbonates concentration with exhibiting moderate temporal variation in all the samples indicate the water is alkaline in nature which was also supported by the pH values. The high concentration of bicarbonate is associated with hard water that was also supported by the elevated total water hardness values of the study point. By showing the results of anions concentration, it may conclude the studied anions F^-, Cl^-, SO_4^{2-}, and NO_3^- exhibited varying degrees of temporal variation, with most parameters remaining within safe limits.

Table-3: Statistical summary of some Water quality parameters and WHO[2] standards.

Parameters	Minimum	Maximum	Mean	(SD)	(CV)	WHO[3]
pH	6.93	8.64	7.54375	0.525817	0.069702	6.5-8.5
T	27	30	28.4375	0.903861	0.031784	-
TH	190.91	607.84	351.4838	143.2147	0.407457	100-500
TA	297.13	388	327.5188	31.96994	0.097613	-
TDS	318	982	472.5	216.219	0.45760	500-1500
Na+	9.70	18.7	13.6125	3.139353	0.230623	200
K+	2.8	4.3	3.2625	0.480885	0.147398	300-600
Ca^{2+}	36.44	137.78	89.1875	37.27271	0.417914	75-200
Mg^{2+}	7.78	76.24	31.8775	20.91263	0.656031	30-150
F^-	0.15	0.4	0.27375	0.085847	0.313596	1.0-1.5
Cl^-	6.20	179.94	61.32	63.08596	1.028799	250-1000
$SO4^{2-}$	5.65	20.74	10.83	4.666561	0.430892	200-600
NO_3^-	0.03	0.74	0.175	0.231332	1.321897	50

HCO_3^-	312.50	473.36	393.2437	48.60338	0.123596	300 (2011)
EC(µS/cm)	595.00	1400.00	836.75	271.6898	0.324697	1500(2011)

The ion balance calculation yielded a percentage difference of 4.08%, which falls within the acceptable limit of ±5%. This indicates good agreement between the total cation and anion concentrations, confirming the reliability and internal consistency of the analytical data. Therefore, the dataset is considered to be of high quality and suitable for subsequent hydro-chemical calculations and statistical analyses.

Data distribution: The results of a Box and whisker plots also have been used for proper presentation of data that has been placed in Table-4. Box–Whisker analysis reveals temporal variability in physicochemical characteristics. The pH remained slightly alkaline with low variability (IQR = 0.495) and a right-skewed distribution, indicating occasional higher values. Temperature showed minimal variation (IQR = 1) with near-uniform conditions over time. Parameters such as TH and TDS exhibited comparatively higher variability (IQR = 210.48 and 136, respectively), with right-skewed distributions. A notable outlier in TDS (982 mg/L) suggests episodic increases, possibly due to seasonal or external influences. Major ions like Na^+, K^+, Ca^{2+}, Mg^{2+} and F^-, Cl^-, SO_4^{2-}, NO_3^-, HCO_3^- generally showed slight to moderate right-skewness, indicating that most observations clustered at lower concentrations with occasional peaks. Outliers in K^+ and Mg^{2+} further reflect short-term fluctuations. The high right-skewness of NO_3^- possibly linked to temporal anthropogenic inputs. Similarly, electrical conductivity (EC) displayed moderate variability (IQR = 300), reflecting changes in ionic concentration over time. So, it is evident for Box-Whisker plots, most parameters remain relatively stable, certain variables show temporal fluctuations and occasional spikes, highlighting the influence of seasonal and external factors at the study zone.

Correlation matrix shows (Table-5) significant relationships among water quality parameters. Strong positive correlations between Calcium ion and TH (r = 0.8345), Magnesium ion and TH (r = 0.7792) indicate that water hardness is mainly controlled by Ca^{2+} and Mg^{2+} ions. Sodium (Na^+) exhibits strong positive correlationship with SO_4^{2-} (r = 0.8133), NO_3^- (r = 0.7917), and K^+ (r = 0.7571), suggesting possible anthropogenic influences. Very high correlation in-between K^+ and NO_3^- (r = 0.9721) shows a common source, likely agricultural inputs. Moderate correlations of TDS with Mg^{2+} and Na^+ reflect their contribution to dissolved solids. Negative correlations between F^- and pH (r = -0.7309), indicate inverse relationships among certain parameters.

Table-4: Outlook of data distribution based on Box and Whisker plot.

Parameters	Q1	Median (Q2)	Q3	IQR	Outliner/s	Skewness
pH	7.24	7.415	7.735	0.495	No	right skewed
T	28	28.5	29	1	No	Slight left skewed
TH	241.32	313.46	451.79	210.475	No	right skewed
TA	307.52	317.39	342.61	35.085	No	slightly right skewed
TDS	359	386	495	136	Yes (982)	right skewed
Na+	10.8	13.7	15.75	4.95	No	Slight right skewed
K+	2.9	3.2	3.4	0.5	Yes (4.3)	Slight right skewed
Ca^{2+}	59.68	86.6	123.36	63.68	No	Slight right skewed
Mg^{2+}	20.87	24.78	38.28	17.41	Yes (76.24)	right skewed
F^-	0.225	0.31	0.33	0.105	No	slight right skewed
Cl^-	8.25	9.99	84.47	76.32	No	right skewed
SO_4	6.58	10.39	13.01	6.43	No	right skewed
NO_3	0.085	0.105	0.14	0.055	No	highly right skewed

HCO_3	370.5875	387.21	431.405	60.8125	No	Slight right skewed
EC	622.75	759.5	972.75	300	No	Slight right skewed

Hydrogeochemical Evolution: The Chadah diagram (Figure-1) helps to classify the natural water into different hydro-chemical facies and the reaction mechanism which control the water chemistry. To identify the characteristic of water, the entire diagram is divided into eight sub-field (Figure-2) and every sub-field signify different type of characteristic water based on its nature and strength of its chemical components like recharging type water (Ca-Mg-HCO_3 type), base ion-exchange type water (Na-HCO_3 type), Saline type water (Na-Cl type). etc. Hydrogeochemical assessment of groundwater in the study belt indicates that the system is mainly controlled by rock–water interaction along with secondary influences of ion exchange and localized anthropogenic inputs. Chadha diagram classifies most samples as Ca–Mg–HCO_3 type water, reflecting supremacy of alkaline earth metals over alkali metals. For instance, in October 2024, $Ca^{2+} + Mg^{2+}$ (≈ 5.26 meq/L) significantly exceeds $Na^+ + K^+$ (≈ 0.83 meq/L), while in April 2024 $Ca^{2+} + Mg^{2+}$ reaches ≈ 7.08 meq/L against $Na^+ + K^+$ ≈ 0.53 meq/L, confirming fresh recharge conditions.

Table-5: Correlation coefficient based on Pearson's correlation calculations.

	pH	T	TH	TA	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	SO_4^{2-}	NO_3^-
pH	1												
T	0.34022	1											
TH	0.22984	-.07543	1										
TA	0.05223	-.44456	0.34721	1									
TDS	-0.19128	-.23825	0.46378	0.020044	1								
Na^+	-0.3989	-.16842	-0.24269	-0.58048	0.460919	1							
K^+	-0.15542	0.20420	0.02233	-0.43093	0.405341	0.757092	1						
Ca^{2+}	0.01956	-.02686	0.83449	0.162329	0.237056	-0.50369	0.172148	1					
Mg^{2+}	0.386721	-.10291	0.77916	0.443284	0.526613	-0.37902	-0.17116	0.306016	1				
F^-	-0.73095	-.47297	-0.23122	-0.1162	0.280271	0.500137	0.22217	-0.08132	-0.32904	1			
Cl^-	0.54929	0.24694	0.331577	-0.62218	0.418905	0.369704	0.196916	0.323002	0.182829	-0.021	1		
$SO4^{2-}$	-0.31646	0.00908	-0.32095	-0.54869	0.411015	0.813316	0.308018	-0.21032	-0.33301	0.44236	0.521432	1	
$NO3^-$	-.20734	-.10584	0-.02581	-0.52789	0.408666	0.79173	0.972073	0.146876	-0.22888	0.285479	0.259725	0.480657	1

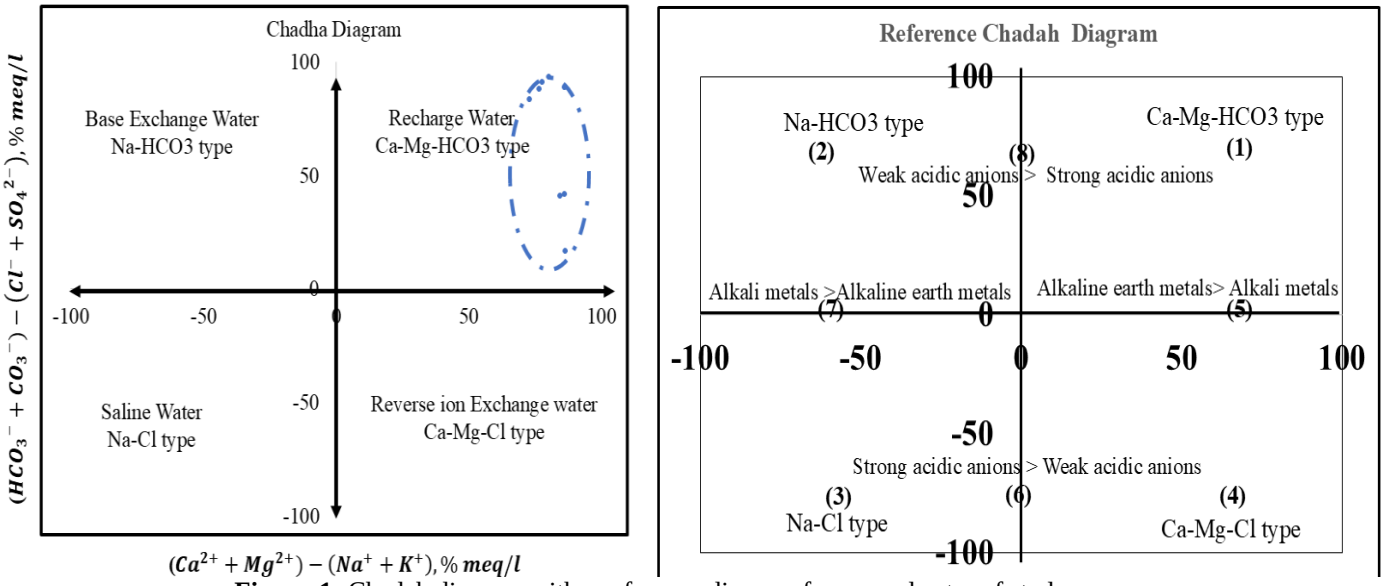


Figure-1: Chadah diagram with a reference diagram for groundwater of study zone.

Mechanisms controlling groundwater chemistry has been determined through Gibbs ratio analysis (Figure-2). The TDS data range is from 318 to 982mg/L, while Gibbs Ratio I (cation) varies between 0.0763 and 0.2183 with the mean value of 0.1464 and Gibbs Ratio II (anion) ranges from 0.0316 to 0.4098 with the mean value of 0.1426. The low cation Gibbs ratios (<0.25) show the supremacy of Ca^{2+}over Na^+, suggesting that water chemistry is mainly controlled by rock–water interaction. The anion Gibbs ratios show some variability, with most samples having low values (<0.1), indicating bicarbonate dominance and confirming carbonate weathering as the primary process. However, a few samples (April'22-K, Oct'21-K, and April'21-K) exhibit higher values (0.2712, 0.4098 and 0.2752), reflecting increased chloride contribution. This may be due to evaporation effects during dry periods or possible anthropogenic inputs.

The relationship between TDS and Gibbs ratios supports these findings, where higher TDS corresponds to increased anion ratios, indicating solute concentration. Seasonal variation is evident, with April samples showing higher ratios due to evaporation, while October samples reflect dilution from recharge. Overall, water chemistry of the study zone is mostly controlled with the rock–water interaction, with minor influences from evaporation and external inputs, indicating a mixed hydrogeochemical regime. Gibbs plots further indicate that groundwater chemistry is primarily governed by weathering processes. Elevated bicarbonate concentrations (≈ 5.94–7.74 meq/L) support carbonate weathering is the predominant geo-chemical progression controlling solute acquisition.

Furthermore, inter-relationship in-between Ca^{2+} + Mg^{2+} and HCO_3^- (Figure-3a) shows, several samples lie near the 1:1 equi-line, confirming carbonate dissolution as a major contributor to groundwater chemistry. For example, October 2023 shows Ca^{2+} + Mg^{2+} (≈ 5.83 meq/L) and HCO_3^- (≈ 6.35 meq/L), indicating near-equilibrium conditions. However, deviations are observed in October 2021 and April 2022 where Ca^{2+} + Mg^{2+} increases up to ≈ 8.29–12.17 meq/L compared to HCO_3^- (≈ 6–7.7 meq/L), suggesting additional processes such as ion exchange or minor mineral contributions.

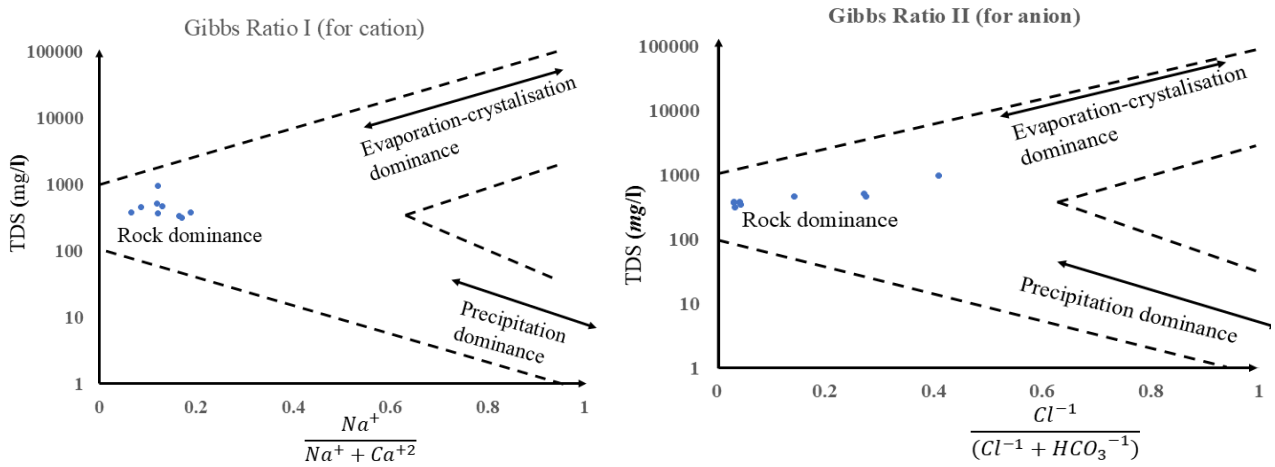


Figure-2: Plot for (a)Gibbs ratio I for cations and (b) Gibbs ratio II for anions.

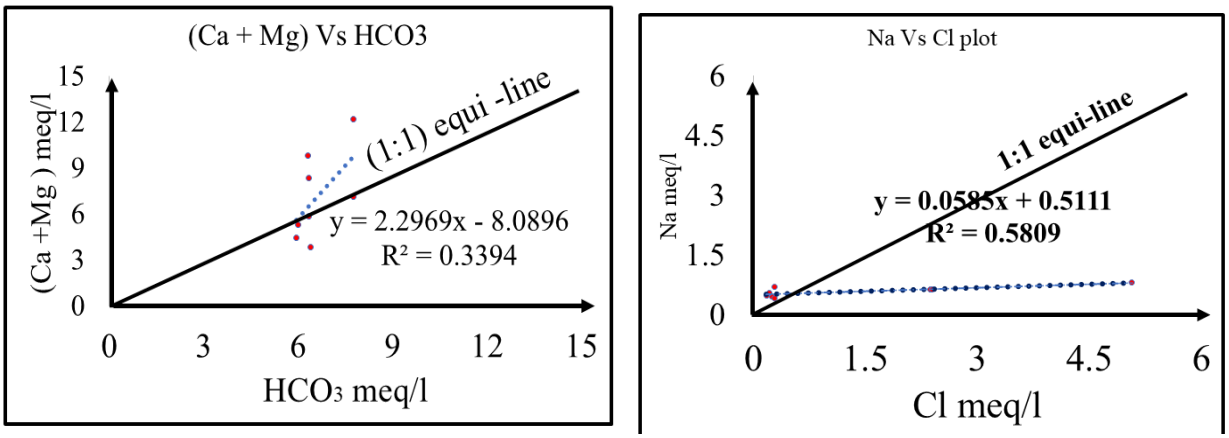


Figure-3: Corelation diagrams (a)(Ca+Mg) vs HCO3 and (b) Na Vs Cl ion.

The relationship between Na^+ and Cl^- (Figure-3b) reveals that the data of samples exhibit Na^+ enrichment over Cl^-, indicating processes beyond simple halite dissolution. For instance, in October 2024 Na^+ (≈ 0.72 meq/L) exceeds Cl^- (≈ 0.28 meq/L), and similar trends are observed in October 2023 (Na^+ ≈ 0.56 meq/L; Cl^- ≈ 0.21 meq/L). However, elevated chloride levels in October 2021 (Cl^- ≈ 5.07 meq/L) and April 2022 (Cl^- ≈ 2.36 meq/L) suggest localized anthropogenic influence within the industrial belt.

Further evidence of ion exchange (Figure-4a) is obtained from the bivariate inter-relationship in-between ($Na^+ + K^+ - Cl^-$) and ($Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}$). Most samples display positive values of ($Na^+ + K^+ - Cl^-$), such as ≈ +0.55 in October 2024 and ≈ +0.43 in October 2023, indicating enrichment of alkali metals relative to chloride. Simultaneously, the corresponding values of ($Ca^{2+} + Mg^{2+} - HCO_3^- - SO_4^{2-}$) tend to be near zero or slightly negative, reflecting a comparative reduction of calcium and magnesium ions. This inverse relationship recommends the existence of cation exchange reactions, where calcium and magnesium ions in underground water are exchanged with Na^+ ion adsorbed on aquifer materials. However, the absence of a well-defined linear trend with the slope of -1 directs that the ion exchange is not only the pre-dominant process but rather a secondary mechanism influencing groundwater chemistry. Evidence of ion exchange is also obtained from CAI analysis (Figure-4b) (Table-6). CAI-I shows both positive and negative values, indicating a dynamic ion exchange system. Positive CAI-I conditions are observed where $Na^+ + K^+$ exceeds Cl^- (e.g., October 2024: 0.83 vs 0.28 meq/L), suggesting reverse ion exchange, whereas higher Cl^- in October 2021 indicates direct ion exchange. CAI-II, incorporating HCO_3^- (5.94–7.74 meq/L), SO_4^{2-} (0–0.43 meq/L), CO_3^{2-} (up to 3.28 meq/L in April 2023), and NO_3^- (0.0004–0.0026 meq/L), shows a more stable geochemical behaviour. The very low nitrate levels indicate negligible agricultural contamination, while carbonate variations reflect localized geochemical heterogeneity.

The integrated interpretation of all hydrochemical plots advocates that groundwater evolution is mostly ruled by carbonate weathering under rock-dominant conditions, producing Ca–Mg–HCO_3 type water. Ion exchange processes are present but act as a secondary mechanism, modifying sodium and calcium–magnesium balance, while localized

chloride enrichment reflects limited anthropogenic influence associated with the industrial setting.

Water quality Index (WQI): The (WQI) computed at six-month intervals for the Kalyani industrial belt ranged from 33.834 to 66.940 (Table-7 and Figure-5), with an average of 45.914 ± 11.369, indicating moderate variation in water quality. According to standard classification, the values fall between "good" (Grade B) and "fair" (Grade C) categories.

Most samples were within the "good" category, while a few instances, such as April 2023 (66.940) and October 2021 (55.741), indicated "fair" quality, suggesting occasional deterioration possibly due to seasonal or anthropogenic influences. The overall yearly average WQI was 44.589, reflecting a generally "good" status.

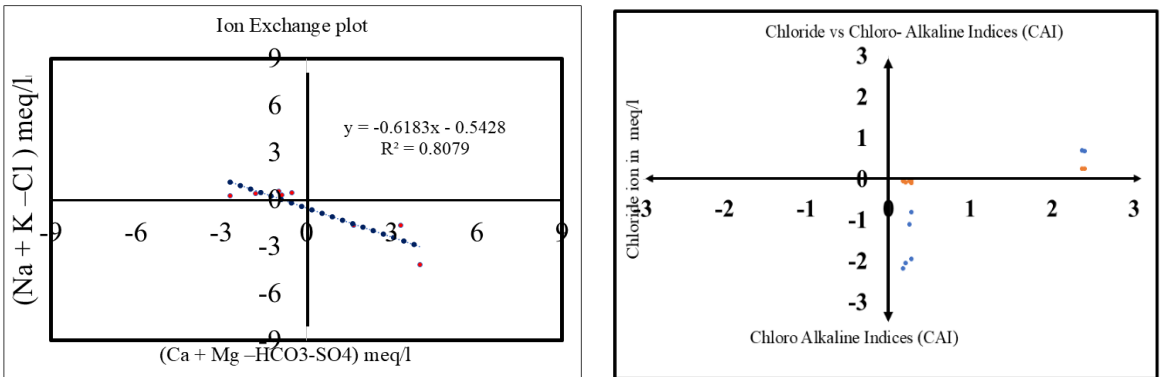


Figure-4: Plot for (a) ion exchange (b) Chloro-alkaline indices for groundwater of study area.

Table-6: Summarised Chloro-Alkaline Indices.

Sample No	CAI-I	CAI-II	Sample No	CAI-I	CAI-II
Oct'24-K	-1.93815	-0.08716	Oct'22-K	-0.80847	-0.03487
April'24-K	-1.10107	-0.03505	April'22-K	0.70128	0.250243
Oct'23-K	-2.04685	-0.06810	Oct'21-K	0.823409	0.510425
April'23-K	-2.17887	-0.04013	April'21-K	0.693245	0.255242

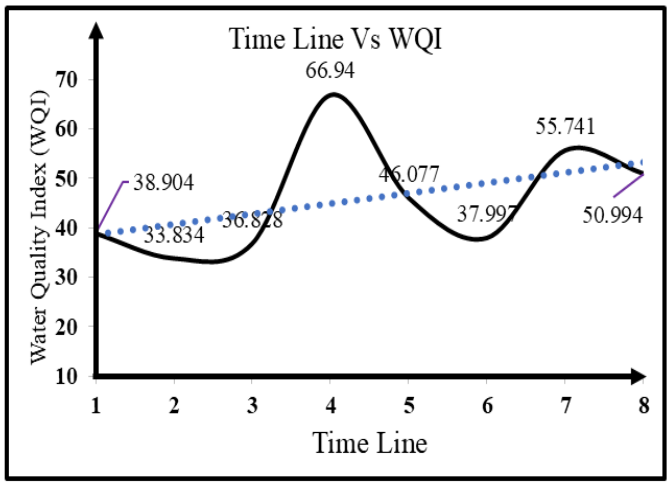


Figure-5: Water quality Index for different time period.

Seasonal variation was evident, with relatively higher WQI values often observed during pre-monsoon periods, may be due to the reason of reduced weakening and augmented pollutant concentration.

The findings indicate that the ground-water of the Kalyani industrial belt is normally appropriate for domestic purpose, irrigation purpose and industrial uses without extensive treatment. However, despite being classified as "good" to "fair," the water is not endorsed for direct as WQI values do not consistently fall within the "excellent" category.

Irrigation suitability: Groundwater constitutes a vital resource in sustaining agricultural productivity, and its suitability for irrigation largely governed by its hydro-chemical characteristics and associated ionic indices. In the present investigation, irrigation potential of groundwater under the Kalyani industrial belt was assessed at six-month intervals (April 2021 to October 2024). The evaluation was carried out using widely accepted irrigation-water quality indices, including Soluble Sodium Percentage (SSP), Sodium Adsorption Ratio (SAR), Magnesium Adsorption Ratio (MAR), Residual Sodium Carbonate (RSC), Kelly's Ratio (KR), and Permeability Index (PI) that collectively provide insight into the potential effects of

groundwater on soil structure, permeability, salinity, and long-term agricultural sustainability. The calculated data of different parameters have been summarised in the Table-8.

Table-7: Water Quality Index (WQI) for all samples

Sample No	WQI	Grade	Quality Status	Yearly (Ave.)	Yearly (Status)	Sample No	WQI	Grade	Quality Status	Yearly (Ave.)	Yearly (Status)
Oct'24	38.904	B	Good	36.369	Good	Oct'22	46.077	B	Good	36.738	Good
April'24	33.834	B	Good			April'22	37.997	B	Good		
Oct'23	36.828	B	Good	51.884	Fair	Oct'21	55.741	C	Fair	53.368	Fair
April'23	66.940	C	Fair			April'21	50.994	B	Good		
					A average	45.914	Yearly Average	44.589	Good		

Table-8: Calculated parameters of water for Irrigation suitability.

Sample No	SSP	SAR	MAR	RSC	KR	PI	Range and Quality[39,40]
Oct'24-K	11.78	0.156	30.73	0.740	0.136	52.98	SSP: Excellent < 20 20-40. Good 40-60. Permissible 60-80. Doubtful 80 < Unsafe SAR: Excellent < 10 10-18. Good 18-26. Permissible 26<. Unsafe MAR: Suitable<50 50> Unsuitable RSC< 1.25 Safe; 1.25-2.50 Marginally; > 2.50 Unsuitable
April'24-K	6.05	0.086	09.04	0.678	0.065	43.04	
Oct'23-K	8.60	0.115	31.21	0.523	0.095	48.20	
April'23-K	9.64	0.114	47.22	3.996	0.109	56.15	
Oct'22-K	9.74	0.108	52.33	2.583	0.110	69.57	
April'22-K	7.05	0.110	43.92	-1.949	0.077	35.32	
Oct'21-K	6.22	0.116	51.57	-4.871	0.069	27.07	
April'21-K	6.19	0.104	29.75	-3.505	0.067	30.23	
Maximum	11.78	0.156	52.33	3.993	0.136	69.57	
Minimum	6.05	0.086	09.04	-4.871	0.065	27.07	
Mean	8.16	0.114	36.97	-0.227	0.091	45.32	

KR: <1 Suitable; 1> Unsuitable; PI: <80 Good; 80-100 Moderate; 100-120 Poor; >120 Very Poor

The Soluble sodium percentage (SSP) values are ranged from 6.05% to 11.78%, with average value of 8.16%, indicating that all the water samples fall under the "excellent" category (<20%), signifying slight sodium risk and suitability for irrigation. Similarly, SAR values varied between 0.086 and 0.156, which are well below the threshold of 10, classifying all samples as excellent, and indicating low sodium adsorption risk to soil structure.

The values of MAR are ranged from 9.04 to 52.33, with the mean of 36.97. Most samples were within the suitable limit (<50), although a few instances (e.g., October 2022 and October 2021) slightly exceeded the threshold, suggesting localized magnesium hazard that may affect soil quality if used continuously without supervision. The majority of RSC values fell within the safe to marginally suitable range (<2.5); though, elevated values during April 2023 (3.996) and October 2022 (2.583) indicate unsuitable to marginal conditions, which may pose alkalinity hazards to soil.KR values are ranged from 0.065 to 0.136 i.e. below 1, confirming that the groundwater is appropriate for irrigation with respect to sodium content. The PI values ranged from 27.07 to 69.57indicating favorable permeability conditions for soil. Overall, the irrigation indices suggest that water quality largely suitable for irrigation purposes. However, occasional elevations in MAR and RSC values highlight the need for periodic monitoring and proper soil supervision practices to prevent long-term soil degradation.

Conclusion

The comprehensive study of the ground water of Kalyani Industrial Belt based of the data from 2021 to 2024 with a six months interval have been revealed that water is mainly controlled by carbonate weathering under rock-dominant conditions, producing Ca–Mg–HCO_3 type. Bivariate relationships indicate that ion exchange processes are present, contributing to sodium enrichment in several samples. Study also revealed that the elevated chloride concentrations in selected samples point toward localized anthropogenic impacts, likely associated with industrial activities. The WQI indicates that water is generally suitable for domestic, irrigation, and industrial uses with minimal treatment; however, it requires proper treatment before using as drinking purposes. The irrigation indices based on different parameters indicate that

groundwater in the Kalyani industrial belt is predominantly fit for use in irrigation.

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