International Research Journal on Advanced Engineering Hub (IRJAEH)
e ISSN: 2584-2137
Vol. 03 Issue: 10 October 2025
Page No: 3996-4000
https://irjaeh.com
https://doi.org/10.47392/IRJAEH.2025.0584

Chemical Footprints: Tracing Fertilizer and Pesticide Contamination in Wells near Kole wetlands

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Abstract
Fertilizers and pesticides are the most prevalent pollutants in agricultural runoff, posing a serious threat to groundwater quality. This study investigates their influence on groundwater in Division 45 of the Thrissur Corporation. Water samples were collected from wells located at varying distances from the Kole wetland during December 2023 and analysed for key chemical parameters. The results indicate that concentrations of ammonium, fluoride, sulphate, chloride and nitrate are all within permissible limits. The Dissolved Oxygen lies within the acceptable range.
Keywords: *Brucine method; Groundwater quality; Kole wetlands; Nessler's method.*

1. Introduction
Water is typically considered a renewable resource, but its availability in hard rock formations is naturally limited. Across the globe, areas with a sustainable groundwater balance are steadily decreasing. Three key issues influence water usage: depletion caused by excessive extraction; waterlogging due to inadequate drainage and poor integrated use; and pollution stemming from agriculture, industry, and other human activities. Moreover, the quality of freshwater sources is facing serious threats. The natural quality of water is largely determined by its physical surroundings and origin. A major challenge in water management is to minimize environmental harm while maximizing economic benefits from its use. Both natural processes and human actions contribute to changes in water quality, either directly or indirectly. The application of fertilizers and pesticides in farming significantly endangers the quality of water resources. [1] The paddy fields of Kerala have been gradually polluted by the use of pesticides and fertilizers used in the agriculture. [2] The literature describes that pollutant from the paddy fields will enter into the nearby wells and will lead to serious health hazards. [3] Both short-term and long-term health hazards have been reported from exposure to high levels of pesticides, particularly in individuals who work directly with pesticides, such as farmers and in people who live nearby the fields. [4] The levels of pesticides and fertilizers normally found in drinking water is usually quite low and would not be likely to cause immediate health problems. However, exposure to small amounts of pollutants in drinking water over a long period of time cause severe health effects. [5] Our study is an approach to understand the impact of fertilizers and pesticides on quality of groundwater in areas of division 45 of Thrissur co-operation. Agriculture is one of the major occupations in Division 45 of Thrissur Municipal Corporation with paddy as major cultivable crop. The town geographically lies between 76.1953670E Latitude and 10.5135782oN longitude. The commonly used chemical fertilizers in the study area are Urea, Potash, Factamphose, NPK mixture, in addition to this, farmyard manures are also used. The pesticides used are Benzene Hexa Chloride, Malathion, Quinalphose and Monocrotophose. The soil type, which is predominant in the study area are clay soil. The concentrations of fluoride, sulphate, chloride, nitrate and ammonium in the wells located

at varying distances from the Kole wetland were determined. The DO values were also analysed.

2. Method

2.1. Collection of water samples

Water samples were collected in pre-sterilized plastic containers. The Kole wetland located within Division 45 of the Thrissur Corporation was selected as the study site to assess the impact of application of pesticides and fertilizers on water quality. Water samples from wells situated at different distances from the Kole wetland were collected in the month of December 2023. The details of 10 samples used for the investigation is provided in Table 1.

2.2. Chemical Analysis

2.2.1. Estimation of ammonium

The spectrophotometric Nessler's method is used for ammonia estimation. 1 mL of 10% NaOH was added to 100 mL of water sample. The resulting solution was stirred and filtered. The colourless middle fraction was collected and 1drop of 50% EDTA was added then mixed well. 2 mL of Nessler's reagent was added to the above solution and shaken thoroughly to get a brown-coloured complex. The absorbance was measured using a spectrophotometer at 420 nm [6]

2.2.2. Estimation of fluoride

1 drop of $NaAsO_2$ solution was added to 100 mL of sample to remove residual chlorine. 5 mL of acid-zirconyl alizarin reagent was added to the above solution and mixed thoroughly. After 1 hour, the absorbance was measured using a spectrophotometer at 530 nm. [7]

Table 1 Description of samples collected

Sl. No.	Distance from field(m)	Name of sample
1	10	W1
2	50	W2
3	100	W3
4	300	W4
5	500	W5
6	700	W6
7	900	W7
8	1100	W8
9	1300	W9
10	1500	W10

2.2.3. Estimation of sulphate

50 mL of the sample was acidified with HCl, 10 mL of $BaCl_2$ solution was added and boiled. The white precipitate of $BaSO_4$ formed was filtered using Whatman No. 40 filter paper. The filter paper was dried and ignited using the muffle furnace at about 800 oC. The residue was cooled and weighed. [8] The concentration of sulphate ion is calculated using the following equation,

$$\text{Sulphate (mg/L)} = \frac{\text{Mass of BaSO4 in mg x 1000 x}\frac{96}{233}}{\text{Volume of sample in mL}}$$

2.2.4. Estimation of chloride

Titrimetric method was used to estimate chloride ion. 10 mL of sample was transferred to a 100 mL conical flask. 2 drops of potassium chromate indicator were added to the solution and titrated against 0.01 N $AgNO_3$ solution. At the end point, colour changes from yellow to brick red [9&10]. The concentration of chloride ion is calculated using the following equation,

$$\text{Chloride ion (mg / L)} = \frac{\text{N x V x 1000 x 35.5}}{\text{Volume of sample in mL}}$$

where, N is the normality of $AgNO_3$, V is the volume of $AgNO_3$ used for titration.

2.2.5. Estimation of nitrate

10 mL of sample was taken in a 50 mL Erlenmeyer flask, 2 mL of NaCl solution was added, shaken well and placed in a cool water bath.10 mL of H_2SO_4 solution and 0.5 mL of brucine – sulphanilic acid solution was added slowly, mixed thoroughly and kept in a boiling water bath for 20 minutes. The contents were cooled and the absorbance was recorded in a spectrophotometer at 410 nm. A standard curve between absorbance and concentration of various standard nitrate solutions was plotted and the concentration of nitrate in the sample was estimated from the graph. [11]

2.2.6. Estimation of Dissolved Oxygen

Water samples were collected in BOD bottles without air bubbles. To the sample, 1 mL of Winkler A solution (4.8 gm of manganese sulphate dissolved in 100mL distilled water) and Winkler B solution (1.5 gm KI solution dissolved in 100 mL 70% KOH solution) was added. The yellow-coloured cloudy precipitate formed was dissolved by adding 1 mL of

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con. H2SO4. 20 mL of the above solution was pipetted out into a conical flask and was titrated against 0.01 N sodium thiosulphate using starch as indicator. The end point is the disappearance of blue colour [12]. The DO was calculated using the following equation,

$$\mathbf{DO\ (mg\ /L) = \frac{A\ x\ 0.01\ x\ 1000\ x\ 8}{Volume\ of\ sample\ in\ mL}}$$

where, A is the titre value, 0.01 is the normality of sodium thiosulphate solution,8 is the Eq. wt. of oxygen.

3. Results and Discussion

3.1. Results

Water samples from wells located at varying distances from the Kole wetland were collected and fluoride, sulphate, nitrate, chloride, and ammonium ions were analysed. The dissolved oxygen levels were also monitored in the collected samples.

Table 2 Fluoride and Ammonium ions

Sample name	Fluoride (ppm)	Ammonium (ppm)
W1	0	0
W2	0	0
W3	0	0
W4	0	0
W5	0	0
W6	0	0
W7	0	0
W8	0	0
W9	0	0
W10	0	0

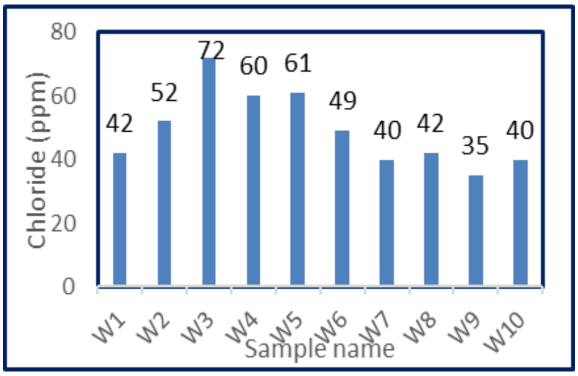

Figure 1 Variation of Chloride

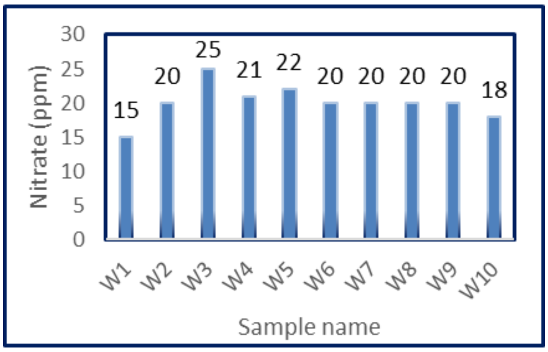

Figure 2 Variation of Nitrate

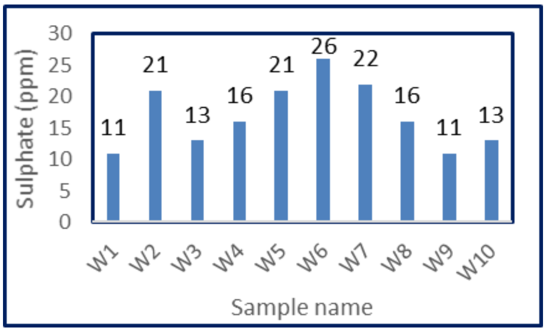

Figure 3 Variation of Sulphate

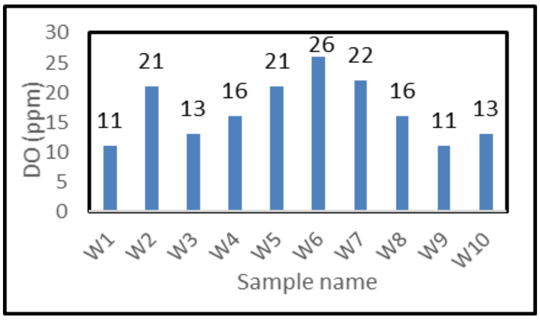

Figure 4 Variation of DO

3.2. Discussions

3.2.1. Fluoride and Ammonium ions

Table 2 shows the results obtained for the analysis of fluoride and ammonium ions in collected samples. The data shows that the fluoride and ammonium ions were not present in any of the analysed samples. This shows that the use of pesticides or fertilizers is not affecting the water present in nearby wells.

3.2.2. Chloride ions

Figure 1 depicts the concentration of chloride ion in different samples. The data reveals that the chloride ion levels range from 35 to 72 ppm. Although most values are moderate, sample W3 shows higher value of 72 ppm. Even though W1 and W2 are more near to the Kole wetland, chloride ion levels are lower than that in W3. This indicates a localized contamination that should be monitored.

3.2.3. Nitrate ions

The concentrations of nitrate ions in the collected samples are plotted in Figure 2. The nitrate concentration in the analyzed water samples ranged from 15 to 25 ppm, with the highest in W3 and the lowest in W1. Most samples showed values around 20 ppm, indicates a common water quality in the region. All results are below the permissible limit of World Health Organization and Bureau of Indian Standards (45 ppm), suggesting that the water is currently safe for consumption with respect to nitrate content. The relatively uniform nitrate distribution implies influences from domestic waste infiltration or agricultural runoff. Although the concentrations are within safe limits, the values suggest a moderate anthropogenic impact on groundwater quality. Continued monitoring is recommended to prevent potential health and environmental risks, as persistent nitrate accumulation can lead to methemoglobinemia and eutrophication over time.

3.2.4. Sulphate ions

Figure 3. shows the variation in sulphate ion concentrations across the collected samples. The sulphate concentration in samples varies from 11 to 26 ppm, with the lowest levels in W1 & W9 and the highest in W6. All samples showed moderate sulphate levels, suggesting relatively uniform distribution across the area of the samples collected. All values are well below the permissible limit of 200 ppm recommended by the WHO and the BIS. This indicates that the water is safe for domestic use concerning sulphate content.

3.2.5. Dissolved oxygen

Figure 4 shows the changes in DO values for the collected samples. DO concentrations of samples range from 7 to 10 ppm. For drinking water, an acceptable DO range is between 4 to 6 ppm. Levels between 8 and 9 ppm are considered excellent. The observed values indicate good water quality and a healthy aquatic environment. This suggest that the wells likely benefited from factors such as adequate aeration and low levels of organic pollution.

Conclusion

The comprehensive analysis of well water samples from varying proximities to the Kole wetland confirms the overall suitability of water for human consumption. The detected anions—sulphate, nitrate, and chloride—are present within permissible limits, ensuring no immediate health risks. The absence of fluoride and ammonium ions further enhances the water's safety profile, particularly by eliminating concerns related to dental fluorosis and nitrogen-based contamination. Moreover, the dissolved oxygen (DO) levels ranging from 7 to 10 ppm indicate a quality water. This suggests minimal organic pollution and effective natural aeration, contributing to the potability of water. The well water in the studied region aligns with safe drinking standards, making it a reliable source for local consumption. The fertilizers and pesticides used in the paddy fields are not affecting the nearby well water during the period of analysis.

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Vol. 03 Issue: 10 October 2025
Page No: 3996-4000
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