

## Original Research Article

# **HYDROCHEMICAL ASSESSMENT OF GROUNDWATER AROUND AMAENYI AND STATE SECRETARIAT DUMPSITES IN AWKA, SOUTHEASTERN NIGERIA.**

### **ABSTRACT**

The effects of two dumpsites located at Amaenyi and State Secretariat Awka on groundwater resources was investigated using hydrochemical parameters. A total of eighteen (18) groundwater samples were collected from areas in the vicinity of the dumpsites and analysed for various hydrochemical and biological parameters using standard methods. The results of the analysis were subjected to interpretations using various methods such as spatial distribution maps, water quality indices (WQI, HPI, Cd and MEI), comparing with international and local standards and statistical analysis. The results indicate that parameters such as Ec, TDS, Na, K, Ca, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were in compliance with the acceptable limits of World Health Organization and Nigerian Drinking Water Standard. However, HCO<sub>3</sub><sup>-</sup>, total hardness, COD, BOD, DO1, DO5, Pb, Fe, Cd and Hg exceeded the permissible guidelines in some samples. WQI rated 20% of the samples excellent, 20% unfit in Amaenyi area while 37.5% very poor and 62.5% unfit for consumption in State Secretariat area. HPI rated groundwater as highly contaminated while Cd classified most of the water samples as indicating low contamination and sample A1 as highly contaminated. Also, MEI indicated groundwater has low heavy metal pollution. The correlation analysis indicates strong positive relationship between BOD, COD, DO1 and DO5, between total hardness, bicarbonate, calcium and sulphate, and between lead, magnesium and chloride. It was concluded that groundwater in the study area is mostly contaminated and the contaminants is attributed to be from the waste dumpsites and other anthropogenic activities.

**Keywords: Water quality, dumpsites, water quality indices, hydrochemical analysis.**

### **INTRODUCTION**

Waste disposal and management remains one of the major challenges in the developing countries today (Renou *et al.*, 2008). Waste, if not properly disposed could lead to contamination of surface and groundwater in its immediate environment. The various anthropogenic activities such as manufacturing and consumption, leads to waste generation. Recently, so much solid waste is being generated that disposal has become a major problem in many urban cities especially in Nigeria. Most developing countries use dumpsites as the primary method for disposing of innocuous solid waste because of their considerable advantages, such as low technological

barriers and economic efficiency (Gonzalez-Valencia *et al.*, 2021). However, several dumpsites in developing countries are operated below acceptable standards (Oyeku and Eludoyin, 2010) and the wastes are not sorted; hence, leachates and toxic gases are accidentally released into the environment (Alimba *et al.*, 2012; Schropp and Al-Mutairi, 2010). Thus, it is common to find unhygienic dumpsites in public places (i.e., close to residential buildings) (Alimba *et al.*, 2006).

The areas close to dumpsites have a greater chance of water pollution due to the possible contamination by leachate originating from the dump sites (Adamcová *et al.*, 2017; Oyeku and Eludoyin, 2010; Samadder *et al.*, 2017). The effect of leachate on groundwater has been reported (Abu-Qdais 2010; Guan *et al.*, 2014). Leachate is of serious concern since it is a complex mixture, composed of several pollutants, such as heavy metals, soluble inorganic and organic compounds, suspended particles, and nutrients (Mavakala *et al.*, 2016; Naveen *et al.*, 2017). In recent times, the impact of leachates on groundwater and other water resources has attracted a lot of attention (Baun and Christensen 2004, Ojo, *et al.*, 2014; Okolo, *et al.*, 2022) because of its overwhelming environmental importance. Leachates migration from wastes sites and the release of pollutants from wastes (under certain conditions) pose a high risk to groundwater resource if not adequately managed. The wastes contaminate the water sources making them unfit for intended purposes. This research was carried out with a view of assessing groundwater quality around two major waste dumpsites in Awka town. The essence is to ascertain their influence on water quality especially as regards heavy metal enrichment. In the end the suitability of the water for drinking purposes and the level of contamination will be determined. The results will be achieved through, hydrochemical analysis and interpretation using different approaches.

### **Location/ accessibility of the study area**

The study area lies between latitudes  $06^{\circ} 13' 00''\text{N}$  and  $06^{\circ} 14' 30''\text{N}$ , and longitudes  $07^{\circ} 4' 30''\text{E}$  and  $07^{\circ} 6' 30''\text{E}$  (Fig. 1). The major routes that facilitate mobility within the study area are the old Enugu - Onitsha road (through Zik's Avenue) and the Enugu - Onitsha Express way and other minor roads. Awka is bounded by towns such as Nibo in the south west, Mgbakwu and Okpuno in the north east and Umuawulu, Isiagu, and Ezinato, in the south east.

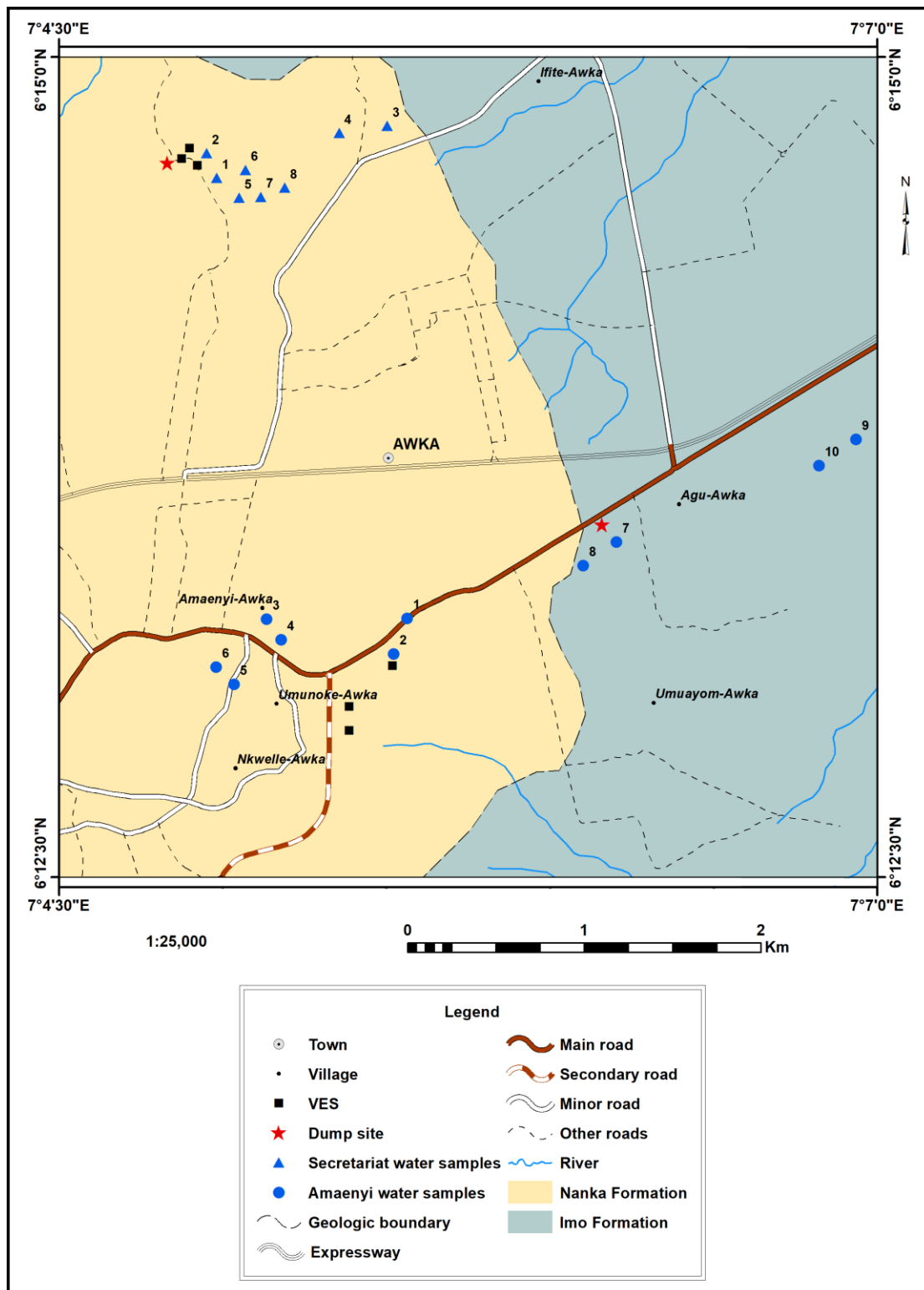


Fig. 1: Location and geologic map of the study area

## Geology of the study area

The study area, which is found within the Niger Delta basin, is underlain by the Imo Formation and the Eocene Ameki Group (Fig.1). The Imo Formation is considered to be the basal unit of the Tertiary Niger Delta Basin which overlies the Nsukka Formation of the Anambra Basin. A major marine transgression was induced by the subsidence in the early Paleocene which led to the deposition of the Imo Formation and its subsurface equivalent, the Akata Formation. This was followed upwards by the Eocene to Oligocene regressive events during which the Ameki Group (Ameki Formation, Nanka Formation and the Nsugbe Formation), Ogwashi-Asaba and their subsurface equivalent, the Agbada Formation were deposited. Deposition in the basin was capped by the continental (Fluviatile) Benin Formation (Murat, 1972). Short and Stauble, (1967) and Ekwenyeet *al.* (2014) stated that the Imo Formation is extensively distributed across southeastern Nigeria and dated Paleocene to Lower Eocene. Reyment, (1965) estimated the unit to be about 1000m thick and contains three sand bodies- Ebenebe Sandstone, Umuna Sandstone, and Igbaku Sandstone. Nwajide, (2013) identified that large-scale cross-beds and well-sorted sandstone primarily characterize the Ebenebe Sandstone member of the Imo Formation, which serves as the aquifer for most of Awka metropolis. The shales of the Imo Formation are fissile and are occasionally interbedded with sandstone intercalations, giving rise to prominent aquifer-aquitard systems (Ezeigbo, 1987).

The facies of the Ameki Group conformably overlies the Imo Formation and contains three stratigraphic components: the Ameki Formation, the Nanka Formation and the Nsugbe Formation, which pinch out both westwards and eastwards (Nwajide, 1980, 2013). The Ameki Formation is estimated to be 1200 – 1500m thick, and comprises mainly sands, minor silt with thin shelly limestone and calcareous clay intercalations (Reyment, 1965; Nwajide, 2013). The Nanka Formation is estimated at 305m thickness. It is mainly sand and minor calcareous clay/mud with heterolith (Nwajide, 1980, 2013; Ekwenyeet. *al.*, 2014). The Nsugbe Formation is predominantly sands with some conglomerate bands, estimated to be about 100m thick (Nwajide, 2013).

## METHODOLOGY

Desk study, reconnaissance, and laboratory analysis were adopted for this study and the essence was to carry out the hydrochemical analysis of the various water samples from nearby wells and boreholes in the study area. Random sampling method was employed for collecting groundwater samples. A total of eighteen (18) water samples from nearby wells and boreholes and a control sample outside of the immediate environment of the dumpsite (Fig. 2) were collected. The samples were collected in one-liter plastic sample bottles. In the site, the boreholes/wells were pumped for 5 mins to allow the water standing in the pipe to be removed. After which, the bottles were rinsed with the well/borehole water before collection to ensure that only water from the aquifer remains in the bottle. After collection, the water samples for cation analysis were filtered and acidified with 2 drops of nitric acid for stabilization, to reduce the chemisorption of trace metal ions onto the surfaces and to prevent hydrolysis and precipitation of cations. The sample plastic bottles for cations were labelled A. Then, another set of samples were collected for anion analysis which were not filtered or acidified and were labelled B. The sample bottles were then covered with the caps and stored in a box containing ice cubes and transported to the laboratory for hydrochemical analysis using standard method according to APHA (2005).

Water quality indices such as Water Quality Index (WQI), Heavy Metal Pollution Index (HPI), Contamination Index (Cd) and Metal Enrichment Index (MEI) were also computer to provide information on the contamination/pollution level of the samples.

### Water quality Index (WQI)

The values of water quality parameters such as pH, turbidity, electrical conductivity, nitrate, sulphate, chloride, calcium, magnesium, sodium, TDS and carbonate were used to compute water quality index (WQI) using the standard for drinking water quality approved by the World Health Organization (2008). The weighted arithmetic index method used by Akoteyon *et al.*, (2011) in a similar study, in line with Brown *et al.*, (1972) was applied for the calculation of the WQI of the water samples. Further quality rating or sub-index ( $Q_n$ ) was calculated using the following formula:

$$Q_n = \frac{V_n - V_o}{S_n - V_n} \times 100 \quad (1)$$

Where:  $Q_n$  = quality rating for the  $n^{\text{th}}$  water quality parameter  $V_n$  = estimated value of the  $n^{\text{th}}$  parameter at a given sampling point,  $S_n$  = standard permissible value of the  $n^{\text{th}}$  parameter  $V_o$  = ideal value of  $n^{\text{th}}$  parameter in pure water (generally,  $V_o = 0$  for most parameters except pH). Thus,

$$Q_{pH} = \frac{V_{pH} - 7}{8.5 - 7} \times 100 \quad (2)$$

The unit weight was calculated by a value inversely proportional to the recommended standard value  $S_n$  of the corresponding parameter.  $W_n = K/S_n$  (3)

Where:  $W_n$  = unit weight for the  $n^{\text{th}}$  parameter  $S_n$  = standard value for the  $n^{\text{th}}$  parameter  $K$  = constant for proportionality.

The overall WQI was calculated by aggregating the quality rating with the unit weight linearly. Thus,

$$WQI = \frac{\sum Q_n W_n}{\sum W_n} \quad (4)$$

Where: WQI = water quality index,  $\sum$  = summation,  $Q_n$  = quality rating for the  $n^{\text{th}}$  water quality parameter,  $W_n$  = unit weight for the  $n^{\text{th}}$  parameter.

### Heavy Metal Pollution Index (HPI)

The index indicates the total quality of water with respect to heavy and is based on weighted arithmetic quality mean method and developed in two steps (Mohan *et al.*, 1996). The first step is establishing a rating scale for each selected parameter giving weightage. The second step is by selecting the pollution parameter on which the index is to be based. The rating system is an arbitrarily value between zero and one and it selection depends on the importance of individual quality considerations in a comparative way or it can be assessed by making values inversely proportional to the recommended standard ( $S_i$ ) for the corresponding parameter as proposed

(Prasad and Bose, 2001, Abd El- Hamid and Hegazy, 2017). HPI is calculated from the equations 5.

$$HPI = \frac{\sum_{i=1}^n WiQi}{\sum_{i=1}^n Wi} \quad (5)$$

Where  $Q_i$  = the sub-index of the parameter,  $W_i$  = the unit weightage of the parameter,  $n$  = the number of parameters considered, the sub-index ( $q_i$ ) of the parameter is calculated from equation 6.

$$Q_i = \sum_{i=1}^n \left( Mi - \frac{I_i}{S_i} - I_i \right) \times 100 \quad (6)$$

Where  $M_i$  = the monitored value of the heavy metal,  $I_i$  = the ideal value of the parameter,  $S_i$  = the standard value of the parameter. HPI of 100 indicates high heavy metal pollution (critical pollution index) while values greater than 100 indicate water that is not potable. The weightage was taken as the inverse of the permissible limit,  $S_i$  is the WHO (2010) standard for drinking water and  $I_i$  the guide value for the selected element.

### 3.3.3 Contamination Index ( $C_d$ )

$C_d$  is the assessment of water quality by the calculation of the degree of contamination. The value is computed separately for each sample of water analyzed. The sum of the contamination factors of individual components exceeding the permissible value was taken as the maximum admissible concentration (MAC) (Nasrabadi, 2015). The  $C_d$  summarizes the combined effects of several quality parameters considered harmful to domestic supply. The  $C_d$  is calculated from equation 7 and 8.

$$C_d = \sum_{i=1}^n Cfi \quad (7)$$

$$Cfi = \frac{Ca}{Cn} - 1 \quad (8)$$

Where  $Cfi$  = contamination factor for the component,  $Ca$  is analytical value for component and  $Cn$  is the permissible concentration of the component. The resultant  $Cd$  values are grouped into three categories as follows:  $Cd < 1$  (low),  $Cd = 1 - 3$  (medium) and  $Cd > 3$  (high) according to Nasrabadi (2015).

### 3.3.4 Metal Evaluation Index (HEI)

Heavy metal evaluation index focuses on the concentration of heavy metals in water and is used to estimate the water quality (Singh *et al.*, 2017, Okolo *et al.*, 2017). The index classifies water into  $HEI < 800$  (moderate pollution),  $HEI > 800$  (high pollution). The HEI is calculated following Mohan *et al.* (1996) as shown in equation 9.

$$HEI = \sum_{i=1}^n Hc/Hmax \quad (9)$$

Where  $H_c$  = the permissible concentration

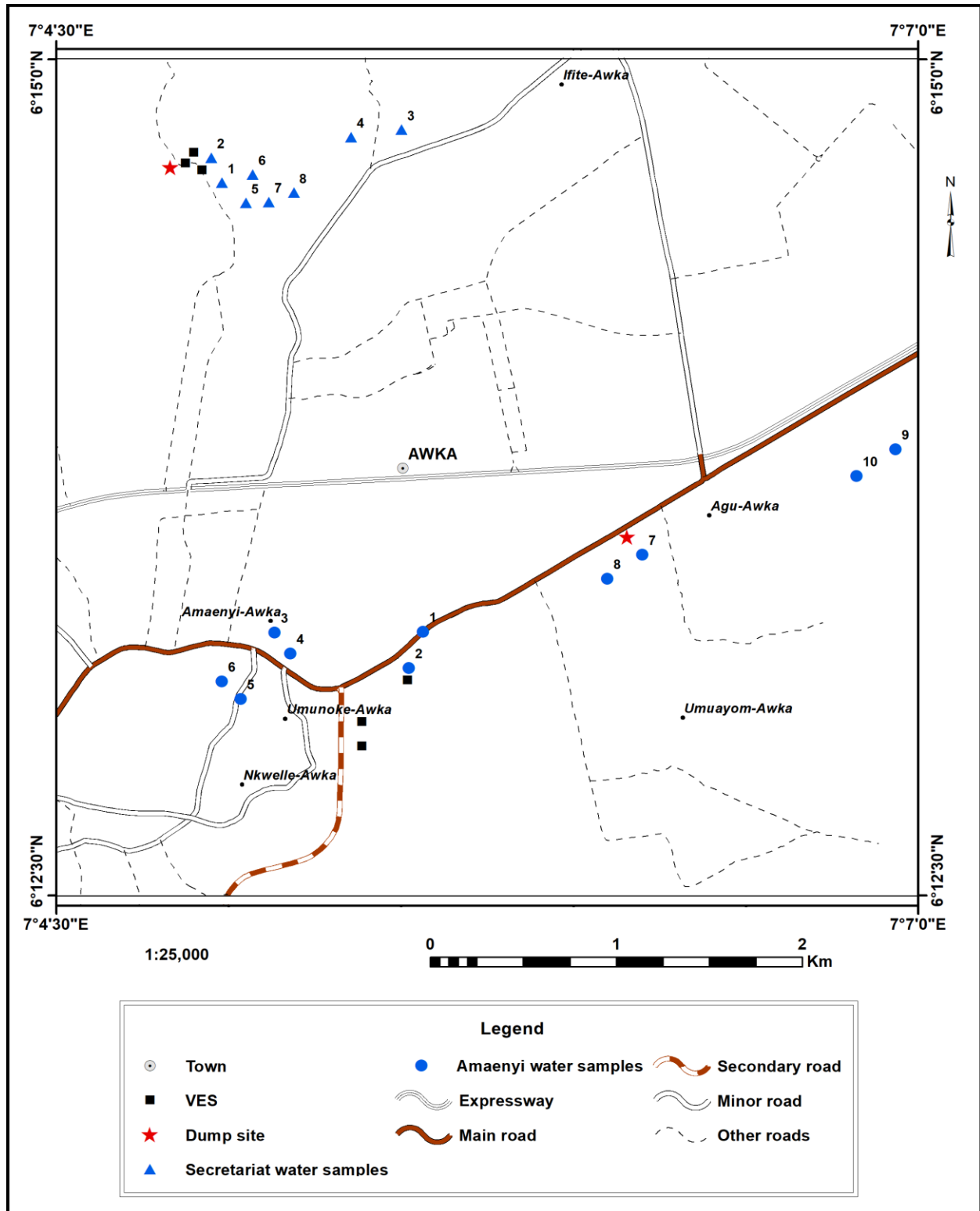


Fig. 2: The samples location points

## 4.0 RESULTS AND DISCUSSION

The result of water analysis for groundwater around the dumpsites at Amaenyi and State Secretariat are presentment in Tables 1 and 2. The physical, chemical and biological parameters will be discussed under different subheads.

### 4.1 The Physical Parameters

The physical parameters analyzed include electrical conductivity (Ec) and total dissolved solids (TDS). TDS is a measure of the dissolved substances in water including the organic matter. TDS was categorized into < 1,500mg/L (Fresh water), 1,500 – 5,000mg/L (brackish water) and > 5,000mg/L (Saline water) by WHO (2010). The concentrations of the parameter range from 14mg/L to 474mg/L and 22mg/L to 96 mg/L in Amaenyi and State Secretariat areas respectively. The values classify the water samples from study area as fresh water. Low concentrations of TDS as depicted by samples A2, A5, S1, S2 and S5 results in flat and insipid taste as reported by Kumar *et al.* (2007). Conversely, electrical conductivity measures the ability of water to conduct electric currents. The ability is enhanced by the presence of dissolved salts, which according to Madu *et al.* (2022), is a useful indicator of salinity. The conductivity values in the study area are within the guidelines. The observed mean values are 130.6 us/cm and 91.85 us/cm for Amaenyi and State Secretariat areas respectively. The result of the present study is in manner similar to that reported by Ige, *et al.*, (2022). Thus, the EC values point toward low to moderate mineralization of the water. The samples whose EC and TDS values appeared as outliers have been influenced by the dumpsites in the study area.

### 4.2 Chemical Parameters

pH range in samples were 6.06 to 7.92 and 4.14 to 6.58 for Amaenyi and State Secretariat areas respectively. pH is the hydrogen ion concentration and a measure of acidity or alkalinity of an environment or substance. The values in the present study indicate acidic to alkaline water. In the Amaenyi area the water can be classified as slightly acidic (6.06-6.28) and slightly alkaline to alkaline (6.59-7.92). However, the water in State Secretariat were acidic (4.1 -5.89) 87.5% and slightly acidic (6.58) 12.5%. More importantly the pH values in State Secretariat contravene the permissible standards. High acidity in water environment has been variously attributed as signatures of anthropogenic pollution especially in the vicinity of dumpsites (Okolo *et al.* (2020), and Emecheta *et al.*, (2023). Decaying organic matter produces hydrogen ions which are responsible for acidity (Freeze and Cherry, 1979) though referred to as small may become significant in an area with an active dumpsite.

The major ions in the order of decreasing concentration, for the anions is  $\text{HCO}_3 + \text{CO}_3 > \text{SO}_4 > \text{Cl} > \text{NO}_3$  while for cations is  $\text{Na} + \text{K} > \text{Ca} > \text{Mg}$  in Amaenyi and State Secretariat areas respectively. Bicarbonate for Amaenyi area range from 50 – 262mg/L were within the guideline values although the concentration in sample A5 exceeded the guideline values. Bicarbonate acts as a buffer in solution thus helping to moderate acidity. The high bicarbonate values in Amaenyi area may be one of the reasons why the water in that area is mostly alkaline. The range of total hardness in samples is 50 – 210mg/L and 75 – 166mg/L in Amaenyi and State Secretariat areas respectively. The values were within the permissible guidelines for drinking water except samples A5 and S3 which exceeded the permissible limits. Total hardness has been implicated in the use of more soap for washing and formation of scum.

Table 1: Result of physicochemical parameters of groundwater samples from around the Amaenyi dumpsite

Parameters	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	Mean $\pm$ SD	WHO	NSD WQ (2015)
pH	6.23	7.12	6.89	7.42	6.06	6.28	7.58	6.59	7.92	6.86	6.90	6.5-8.5	6.5-8.5
Conductivity (us/cm)	126.70	145.30	146.40	121.80	45.00	156.00	134.50	146.40	138.90	145.00	130.60	500.00	100.00
Total Hardness (mg/l)	60.00	80.00	120.00	70.00	210.00	80.00	60.00	100.00	90.00	50.00	92.00	200.00	150.00
Chloride (mg/l)	25.00	15.00	12.00	5.00	10.00	12.00	8.00	14.00	10.00	13.00	12.40	250.00	250.00
Bicarbonate (mg/l)	75.00	50.00	150.00	87.50	262.50	125.00	100.00	75.00	50.00	62.00	103.70	250.00	100.00
Sulphate (mg/l)	59.27	70.42	68.15	90.00	129.03	48.89	52.01	65.00	71.00	40.77	69.45	250.00	100.00
Nitrate (mg/l)	4.60	4.81	5.36	6.11	7.87	3.76	5.88	4.76	3.90	3.87	5.09	50.00	50.00
Calcium (mg/l)	4.89	4.60	4.94	5.19	5.38	5.01	4.80	4.81	5.01	4.82	4.95	75.00	75.00
Magnesium (mg/l)	3.89	3.20	2.94	3.10	2.98	3.01	3.10	2.99	3.10	3.20	3.15	150.00	150.00
Sodium (mg/l)	5.42	5.02	6.24	4.90	5.08	5.10	5.00	5.20	5.01	5.13	5.21	200.00	200.00
Potassium (mg/l)	5.87	5.64	6.98	4.99	4.90	4.78	4.92	4.88	4.94	4.89	5.28	50.00	50.00
TDS mg/l	156.00	44.00	474.00	71.00	14.00	126.00	82.00	100.00	61.00	64.00	119.20	500	500.00
DO1 mg/l	56.60	72.00	82.50	62.90	64.70	65.00	78.00	88.90	80.00	64.80	71.54	5.00	5.00
DO 5 mg/l	47.30	53.90	65.30	50.40	55.70	48.80	65.20	65.80	58.80	52.40	56.36	5.00	5.00
BOD mg/l	93.00	181.00	172.00	125.00	90.00	88.00	164.00	152.00	145.00	96.00	130.60	5.00	5.00
Carbonate mg/l	54.00	58.00	116.00	36.00	36.00	72.00	68.00	80.00	56.00	88.00	66.40	200.00	150.00
COD mg/l	188.00	252.00	188.00	220.00	28.00	186.00	282.00	180.00	160.00	68.00	175.20	20.00	20.00
Cadmium (ppm)	0.056	0.040	0.082	0.050	0.034	0.046	0.040	0.082	0.050	0.034	0.05	0.05	0.003
Mercury (ppm)	0.014	0.019	0.012	0.017	0.007	0.002	0.012	0.016	0.014	0.003	0.012	0.01	0.001
Iron (ppm)	0.489	0.378	0.389	0.422	0.284	0.231	0.228	0.202	0.321	0.314	0.33	0.3	0.3
Coliform (cfu/ml)	10.00	20.00	22.00	7.00	8.00	5.00	13.00	21.00	4.00	2.00	11.00	0.00	10
Lead (ppm)	0.032	0.00	0.00	0.00	0.00	0.01	0.003	0.01	0.00	0.00	0.006	0.01	0.01

Table 2: Physicochemical parameters of water samples in State Secretariat

Parameters	S1	S2	S3	S4	S5	S6	S7	S8	Mean	WHO (2008)	NSDWQ (2015)
pH	6.58	5.89	5.11	4.14	5.88	5.89	5.18	4.50	5.40	6.5-8.5	6.5-8.5
Conductivity us/cm	123.90	164.60	12.60	53.50	153.90	134.20	18.60	73.50	91.85	500	500
Total Hardness (mg/l)	130.00	120.00	166.00	100.00	90.00	80.00	75.00	85.00	105.75	200.00	150.00
Chloride (mg/l)	9.00	12.00	6.00	16.00	8.00	9.00	10.00	8.00	9.75	250.00	250.00
Bicarbonate (mg/l)	162.50	120.00	207.50	125.00	150.00	100.00	90.00	80.00	129.38	250.00	250.00
Sulphate (mg/l)	44.76	88.04	112.10	99.60	100.58	60.87	70.86	80.87	82.21	250.00	250.00
Nitrate (mg/l)	2.49	4.10	7.23	6.84	4.82	5.02	5.13	5.24	5.22	50.00	50.00
Calcium (mg/l)	5.89	5.08	4.18	5.05	4.98	4.81	4.78	4.70	4.93	75.00	75.00
Magnesium (mg/l)	3.18	3.00	3.19	3.29	3.20	3.24	3.21	3.24	3.19	150.00	150.00
Sodium (mg/l)	4.88	4.88	4.78	5.44	4.81	4.90	4.89	4.88	4.93	200.00	200.00
Potassium (mg/l)	5.08	4.90	4.99	4.79	4.89	4.88	4.99	4.81	4.92	50.00	50.00
TDS mg/l	47.00	22.00	62.00	96.00	58.00	28.00	75.00	86.00	59.25	500.00	500.00
DO1 mg/l	56.70	68.90	132.30	83.70	58.70	64.80	20.50	32.30	64.74	5.00	5.00
DO 5 mg/l	41.60	57.30	108.80	67.10	51.60	60.20	92.80	87.20	70.83	5.00	5.00
BOD mg/l	151.00	116.00	235.00	166.00	148.00	122.00	180.00	139.00	157.13	5.00	5.00
Carbonate mg/l	74.00	70.00	102.00	160.00	92.00	82.00	55.00	81.00	89.50	150.00	150.00
COD mg/l	92.00	252.00	188.00	252.00	108.00	292.00	148.00	152.00	185.50	20.00	20.00
Cadmium ppm	0.045	0.022	0.034	0.044	0.045	0.022	0.034	0.044	0.036	0.05	0.003
Mercury ppm	0.003	0.005	0.009	0.003	0.003	0.004	0.001	0.005	0.004	0.01	0.001
Iron ppm	0.39	0.42	0.40	0.35	0.33	0.480	0.41	0.38	0.40	0.3	0.3
Coliform cfu/ml	1.4 x 10 <sup>1</sup>	1.2 x 10 <sup>1</sup>	1.3 x 10 <sup>1</sup>	1.5 x 10 <sup>1</sup>	1.0 x 10 <sup>1</sup>	1.4 x 10 <sup>1</sup>	1.1 x 10 <sup>1</sup>	1.0 x 10 <sup>1</sup>	1.24 x 10 <sup>1</sup>	10 <sup>1</sup>	
Lead ppm	0.0046	0.0359	0.0071	0.00	0.0046	0.0152	0.0021	0.00	0.009	0.01	0.01

Biochemical Oxygen Demand (BOD) is a measure of the quantity of oxygen used by microorganisms (e.g., aerobic bacteria) in the oxidation of organic matter. When the process takes place in water, the dissolved oxygen in the water is consumed. The BOD level in samples ranges from 88 mg/L to 181 mg/L and 116 mg/L to 235 mg/L in Amaenyi and State Secretariat areas respectively. A plot of the BOD values shows the background value to be 150mg/L. Therefore, it was observed that in 40% and 63% of samples in Amaenyi and State Secretariat area the background value was exceeded indicating groundwater pollution. The high BOD values could be attributed to input from decaying organic matter from the dumpsites which resulted in higher amount of dissolved oxygen being consumed. Hence, high levels of BOD can be an indicator of groundwater contamination. The present result is consistent with the findings of Akpan, *et al.* (2002) and Essien-Ibok, *et al.* (2010). It was observed that BOD values exceeding the background values were observed in the areas in the vicinity of the dumpsites. Additionally, the areas are built up indicating the influence from wastes from domestic, industrial and other human activities (Fig.3) may also contribute. Equally, the Chemical Oxygen Demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by strong chemical oxidant. The COD values vary from 8 mg/l to 282 mg/l and 92 mg/l to 292 mg/l in Amaenyi and State Secretariat respectively. The COD values in 63% and 80% exceeded the background value of 150mg/L in Amaenyi and State Secretariat areas respectively. The BOD/COD is considered a valuable indicator of pollution according to Lee and Hamid (2014). Also, according to Ngang and Agbazue (2016), BOD/COD ratios of 0.8 or higher indicate highly polluted water. In the present study the BOD/COD ratio in 50% and 63% of groundwater in Amaenyi and State Secretariat respectively indicate high pollution. The classification agrees with the rating using background value. The result of the present study is in a manner similar to the result of Koda *et al.*, (2017). The observed BOD and COD values in both dumpsites can be attributed to the high rate of organic decomposition resulting from the dumpsites which will negatively impact the water quality (Figs.3 and 4). The map of the distribution of COD in the study area clearly indicates that higher values were observed in the groundwater in areas in close proximity with the dumpsites and decrease away from them. Dissolved oxygen (DO) is a term that refers to the total amount of oxygen contained in water at any given time. The parameter indicates the current oxygen level in water required for aquatic organisms living the ecosystems. The higher the DO value the better the water quality. DO1 values in the water ranges from 56.6 – 88.9 mg/l and 20.5 – 132.3 mg/l; while DO5 values ranges from 47.3 – 65.8mg/l and 41.6 – 106.8mg/l in the Amaenyi and State Secretariat areas respectively. The background value for DO1 and DO5 in the study area is 64mg/L. Most of the samples in the study area are within the background value with a few samples exceeding the value. Hence, the DO in the present study does not pose a problem to the groundwater quality. Therefore, the indicators of organic pollution BOD and COD depict groundwater in the study area as highly polluted.

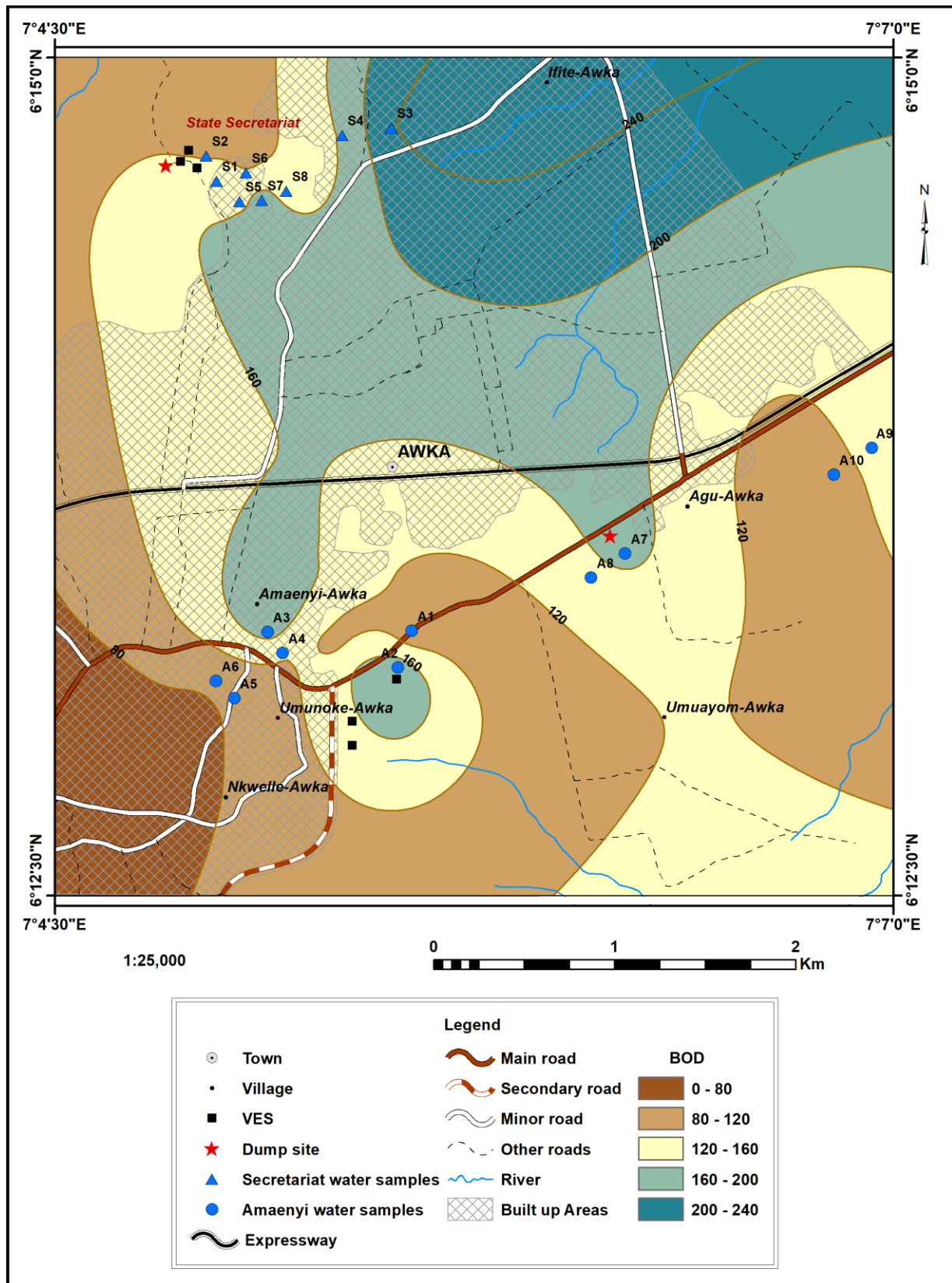


Fig.3: The spatial distribution of BOD in the study area

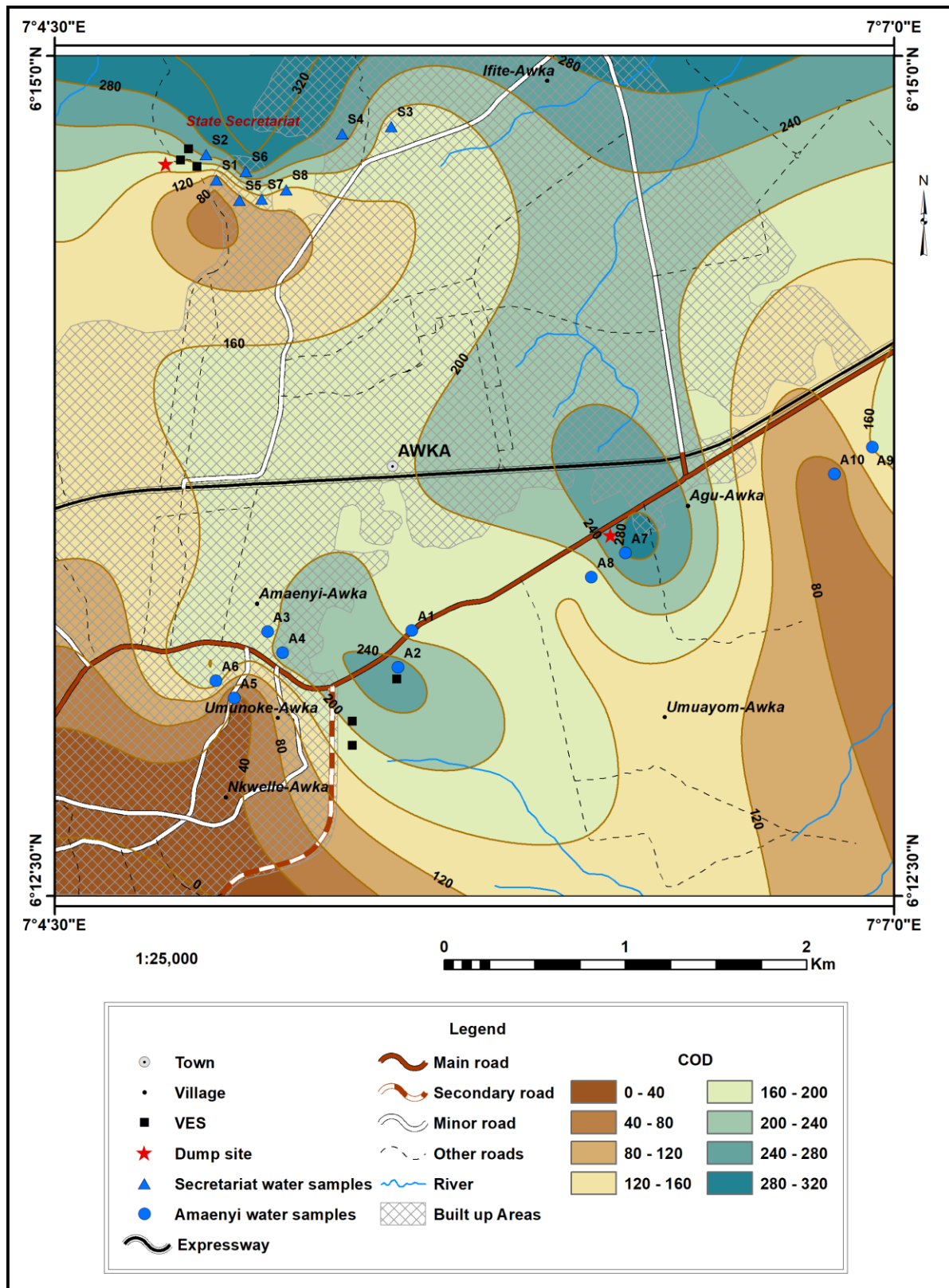


Fig. 4: The spatial distribution of COD in the study area

### 4.3 Heavy Metals

Heavy metals such as Cadmium, Iron, Mercury, and Lead were analysed in water samples from study area. The concentrations of the metals were compared with the WHO (2010) and NSDWQ (2017) permissible limits. Also, some indices (WQI, HPI, CD, and MEI) were further utilized to assess the extent of pollution/contamination.

It was observed that iron ranged in samples from 0.202 – 0.489ppm and 0.33 – 0.42ppm with a mean value of 0.33ppm and 0.4ppm from Amaenyi and State Secretariat areas respectively. The distribution of iron in the study area is shown in Fig.5. In 60% and 100% of samples from Amaenyi and State Secretariat respectively the concentration of iron exceeded the permissible limits of the guidelines. However, the background value of iron in the study area is 0.35ppm. Comparing with the background values indicates that 40% and 75% in Amaenyi and State Secretariat respectively exceeded the background indicating iron pollution in groundwater. The map of the distribution of iron in the study (Fig.5) shows the concentrations were higher in the areas near the State Secretariat dumpsite than the Amaenyi area. Equally, it was observed that areas underlain by the Nanka formation indicated higher iron concentrations. Thus the input sources of iron in the study area can be said to be both anthropogenic and geogenic. Similar observation was reported by Kana (2022). He attributed the increase in iron concentration to input from dumpsites.

The range of cadmium concentration in samples is from 0.034 – 0.082ppm and 0.22 – 0.045ppm with mean values of 0.05ppm and 0.036ppm for Amaenyi and State Secretariat areas respectively. The values for cadmium concentration in State Secretariat area are within the permissible limit although samples A1, A3 and A8 from Amaenyi area exceeded the permissible limit. The background value for cadmium was placed at 0.04ppm which indicated that 50% of samples from both areas respectively exceeded the value. The map of the distribution of cadmium in the study (Fig.6) indicate that high concentrations were observed in areas very close to the Amaenyi dumpsite with concentration decreasing away from the dumpsite. However, the areas around the State Secretariat dumpsite indicate low concentration of cadmium which can be interpreted to mean that this dumpsite is not a major input source of the metal. The present result is similar to various researches that reported elevated concentration of cadmium in soil and groundwater and attributed the same to anthropogenic activities (Emecheta *et al.*, 2023, Gvabaahet *et al.*, 2023 and Okolo *et al.*, 2018).

The range of mercury concentration in samples is from 0.002 – 0.019ppm and 0.001 – 0.009ppm in Amaenyi and State Secretariat areas respectively. The values in the State Secretariat are within the WHO permissible limit but exceed the NSDWQ permissible limit in all of the samples except sample S7. However, in Amaenyi area the mercury concentration in 70% of samples exceeded the WHO permissible limit while the NSDWQ permissible limit was exceeded in all the samples in that area. Also it was observed that the background value of mercury in the study area is 0.005ppm. The background value was exceeded by sample S3 in the State Secretariat area while 80% of samples in Amaenyi area exceeded the background value.

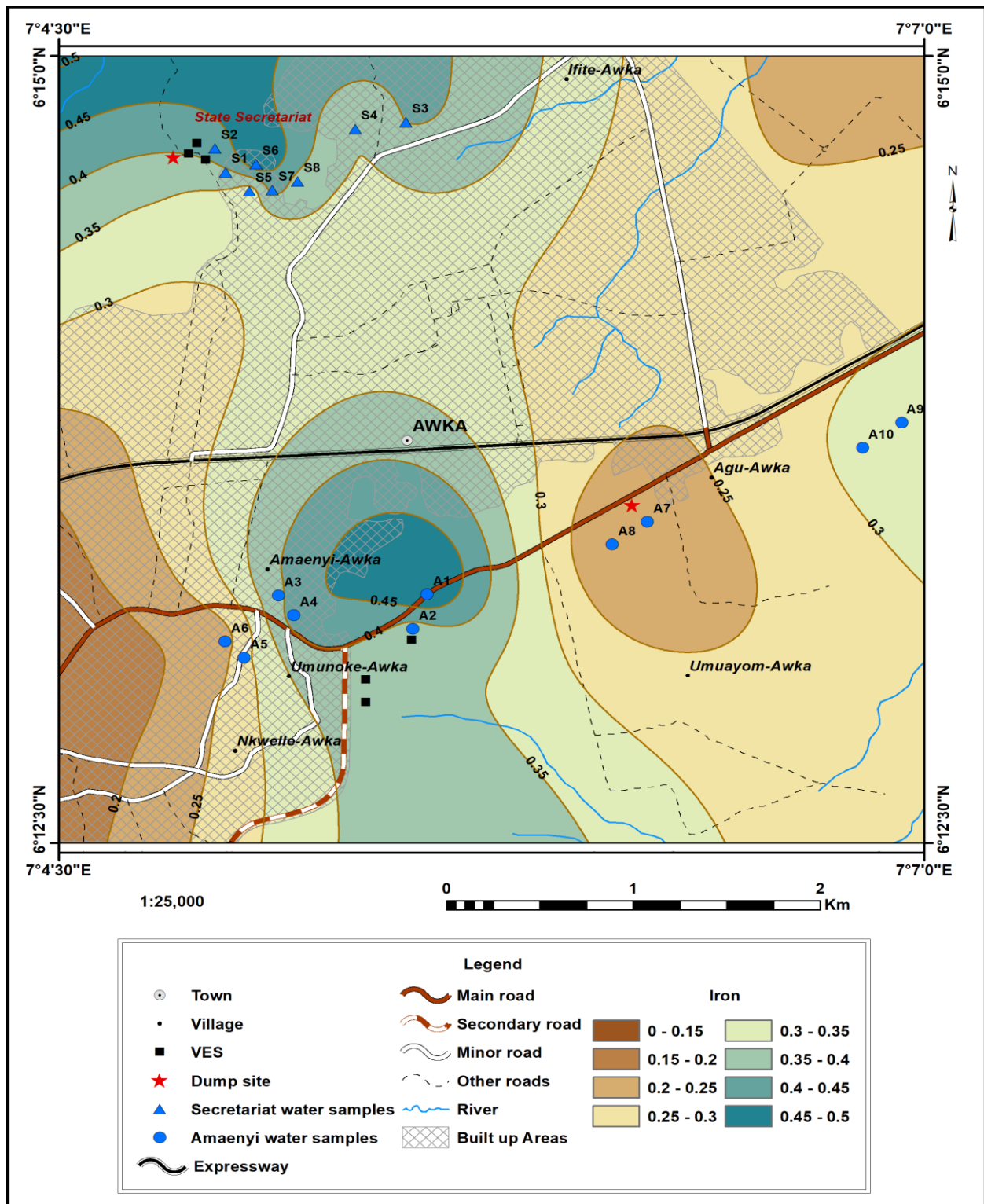


Fig.5: The distribution of the concentration of iron in the study area.

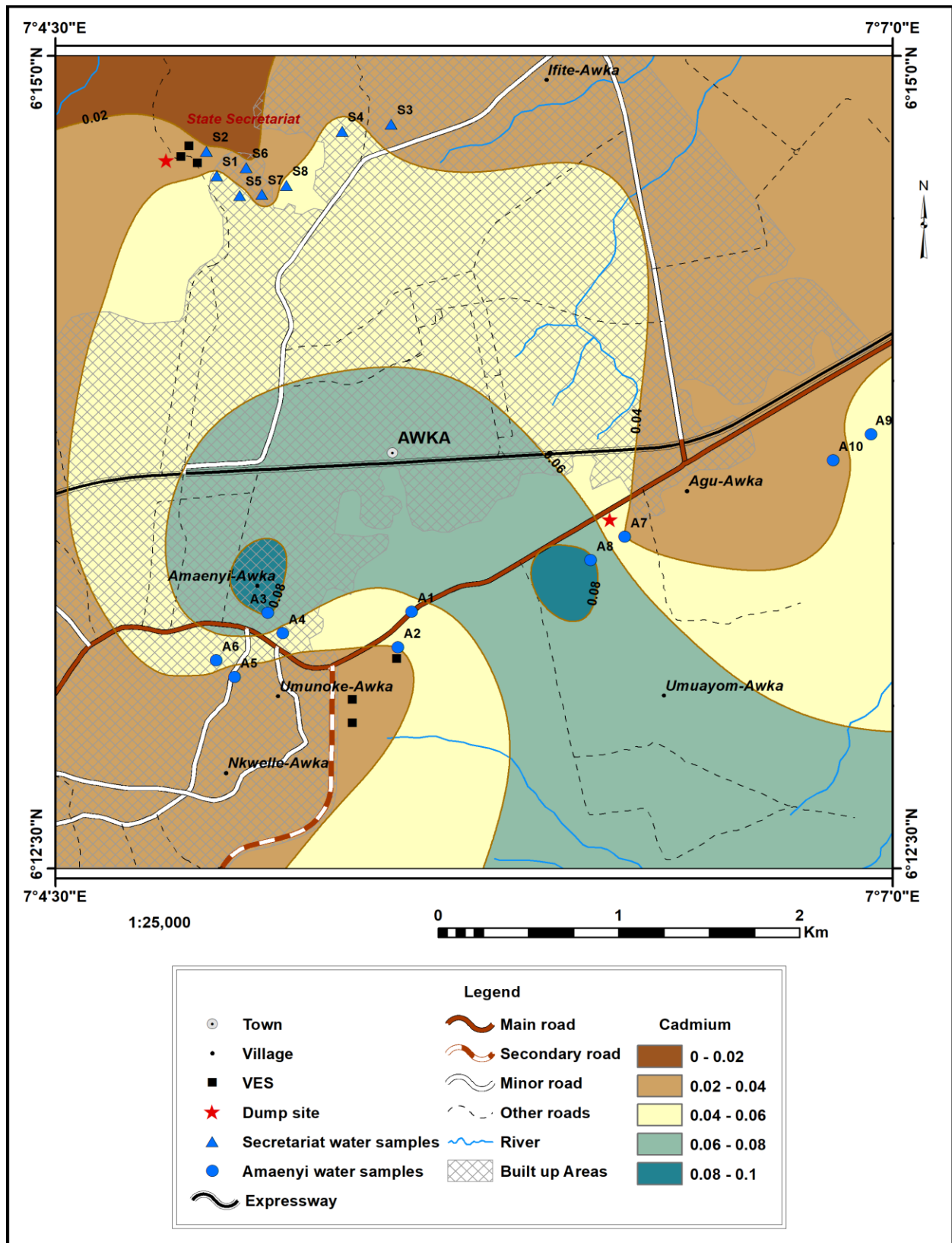


Fig.6: The distribution of cadmium in the study area

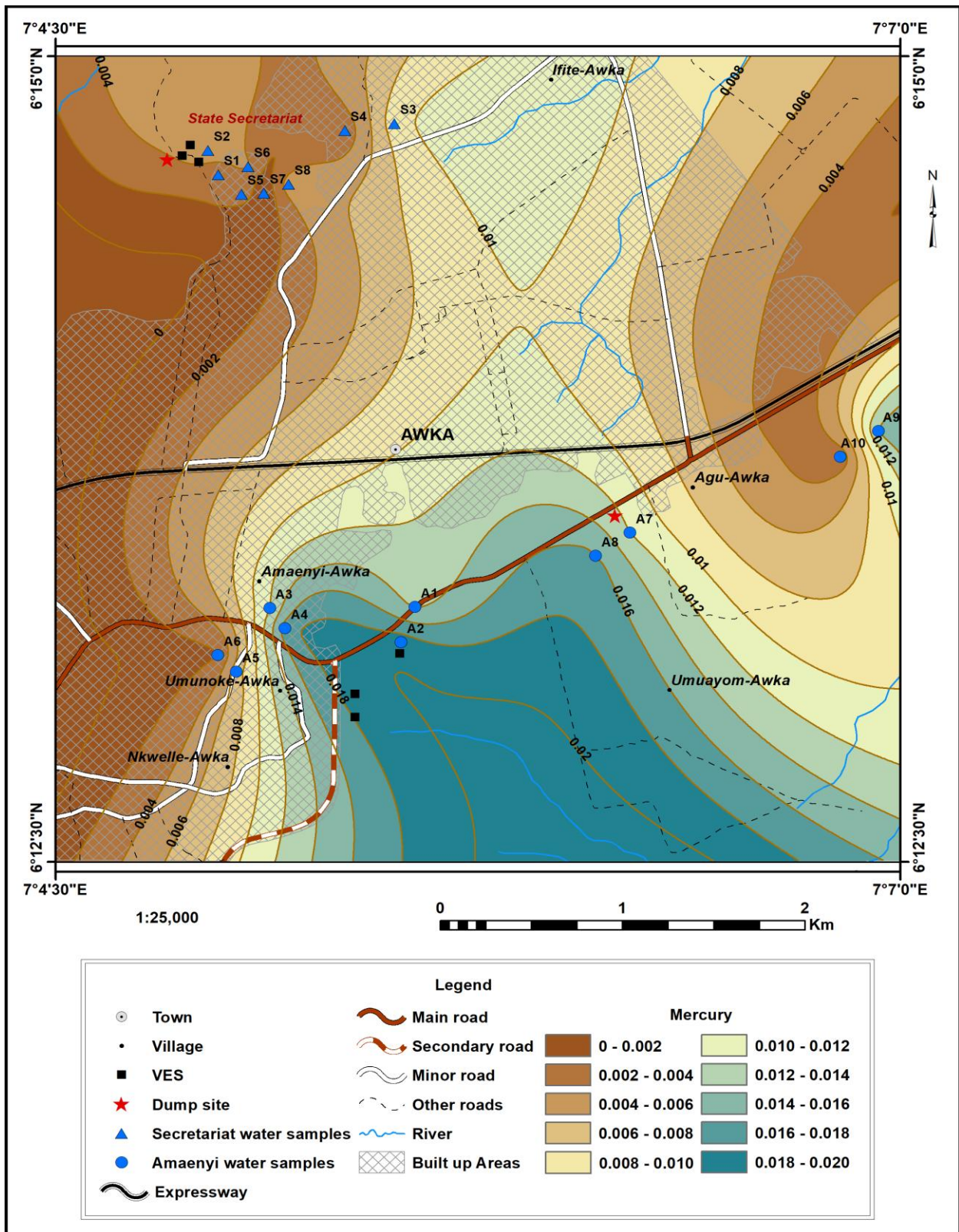


Fig.7: Distribution of Mercury in the study area

Lead concentration in samples range from 0 – 0.32ppm and 0 – 0.0359ppm with mean values of 0.006ppm and 0.007ppm in Amaenyi and State Secretariat areas respectively. The concentration of lead in samples S2, S6 and A1 exceeded the permissible guidelines. The spatial distribution of lead in the study (Fig.8) indicates the three samples with elevated lead concentration are located very close to the dumpsite underscoring their influence. The concentration of lead was observed to decrease with greater distance from the dumpsites. Lead is toxic even in trace amounts and are released into the environment through industrial and anthropogenic activities (Adekunle and Akinyemi, 2004)

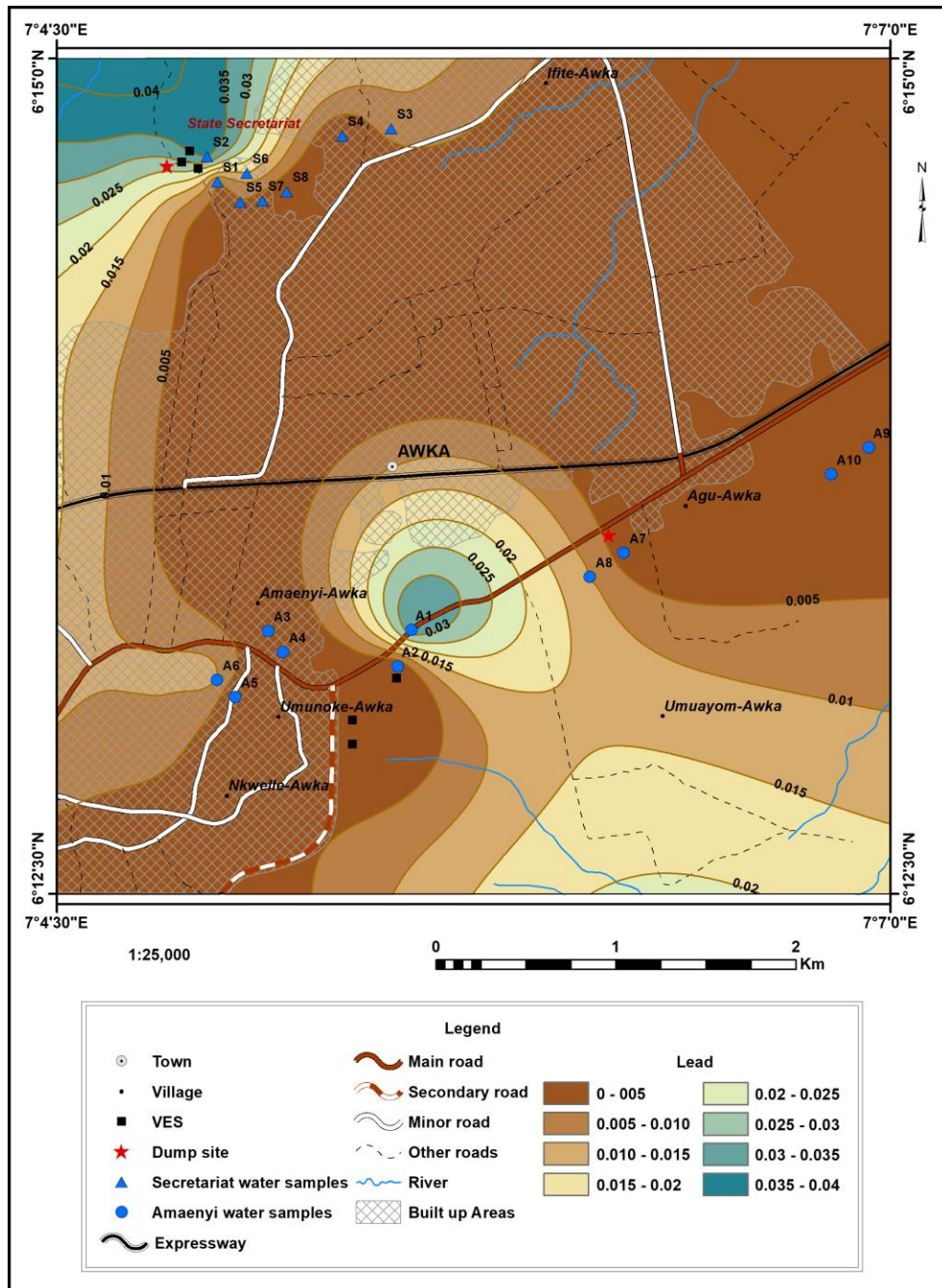


Fig.8: The spatial distribution of lead in the study area

### 4.3.1 Water Quality Index (WQI)

Water quality index was calculated using equations 1, 2, 3 and 4 from seven (7) physicochemical parameters. The results (Table 3) were classified according to Brown et al, (1972). The WQI in Amaenyi area rated the water samples as 20% excellent (A4 and A10), 30% good (A1, A5 and A6), 10% poor (A9), 20% very poor (A2 and A7) and 20% unfit for consumption (A3 and A8). Also the rating for State Secretariat area indicated 37.5% as very poor (S1, S2 and S5) while 62.5% were unfit for consumption (S3, S4, S6, S7 and S8). The deterioration in water quality can be associated with the effect of the dumpsites and other human activities. The water quality improved away from the dumpsites. However, the dumpsites are located in built-up areas and domestic sewage may also influence the water quality. Further, the dumpsite in the State Secretariat area is located on Nanka Formation which is composed mainly of sand. Sand being porous and permeable may enhance transport of contaminants. The acidic pH in the area attests the deterioration in water quality. Similar results were reported by Emecheta *et al.*, (2023) and Okolo *et al.*, (2018).

Table 3: WQI of Amaenyi and State Secretariat

Amaenyi		State Secretariat	
Samples	WQI	Samples	WQI
A1	48.29	S1	77.17
A2	92.30	S2	91.76
A3	103.30	S3	122.59
A4	19.65	S4	165.99
A5	35.12	S5	84.56
A6	30.38	S6	100.65
A7	78.61	S7	109.08
A8	106.81	S8	130.99
A9	50.30		
A10	17.67		

### 4.3.2 Heavy Metal Pollution Index (HPI)

The heavy metal pollution index was computed using equations 5 and 6 to further assess their role in groundwater pollution. The results (Table 4) were categorized according to Mohan *et al.*, (1996). The observed HPI values are < 100 in both dumpsites which indicates that the critical value has not been reached. However, the HPI values in samples in the study area range from 84.65 – 99.10 indicating highly contaminated groundwater. Anomalous values of HPI indicate groundwater contamination (Naseh *et al.*, 2018). Therefore, the dumpsites in the study area are major point sources of pollution to groundwater.

Table 4: Heavy metal Pollution Index (HPI) values for the various samples in Amaeyi and State Secretariat.

AMAENYI		STATE SECRETARIAT	
Samples	HPI	Samples	HPI
A1	98.06	S1	98.84
A2	97.91	S2	99.05
A3	97.82	S3	98.61
A4	97.91	S4	98.85
A5	98.73	S5	98.89
A6	84.65	S6	99.08
A7	98.34	S7	99.10
A8	97.58	S8	98.73
A9	98.09		
A10	98.97		

#### 4.3.3 Contamination Factor (Cd)

Equations 7 and 8 were used to compute the contamination factor for the heavy metals. The resultant Cd values (Table 5) were grouped into three categories as follows: Cd < 1 (low), Cd = 1 - 3 (medium) and Cd > 3 (high) according to Nasrabadi (2015). The computed values for Cd provide insights into the level of contamination by these trace elements. The Cd rated all samples in the study area < 1 indicating low contamination except sample A1 which was > 3 indicating high degree of contamination. The anomalous Cd value of A1 may not entirely be attributed to the dumpsite but other anthropogenic sources too. The present result is in a manner similar to the report of Yari and Sobhanardakani (2016).

Table 5: Contamination index (Cd) for the various samples in Amaenyi and State Secretariat areas

Sample	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
Cd	3.39	-0.04	0.14	0.11	-1.67	-1.11	-0.94	0.91	-0.53	-1.97
Sample	S1	S2	S3	S4	S5	S6	S7	S8		
Cd	-2.32	0.65	0.27	-2.82	-1.69	-1.59	-3	-2.62		

#### 4.3.4 Metal Evaluation Index (MEI)

Metal evaluation index (MEI) focuses on heavy metals in water samples used for estimating the quality (Edet *et al.*, 2003). It was calculated using equation 9 following Mohan *et al.*, (1996). The index classify water as HEI < 400 (low pollution), HEI = 400 - 800 (moderate pollution), HEI > 800 (high pollution). The computed result is shown in Table 6. In Amenyi, the computed MEI ranges from 14.9 - 52.05, with a mean value of 30.19 while in State Secretariat 15.45 - 36.7 with a mean value of 22.60. The results in the present study are < 400, indicating low heavy metal pollution. Heavy metals generally have no useful effects in the body system. Long-term

exposure may cause acute health hazards (Mominulet *al.*, 2018). The heavy metal pollution indices show high value for some of the samples indicating contaminated groundwater. The present result is similar to the report of Reddy and Sunitha (2023).

Table 6: Metal Evaluation index (MEI) for the various samples in Amaenyi and State Secretariat areas

Sample	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	<b>Mean</b>
MEI	52.05	27.89	37.28	30.11	17.42	24.48	24.47	45.68	27.61	14.9	<b>30.19</b>
Sample	S1	S2	S3	S4	S5	S6	S7	S8			
MEI	22.02	36.7	24.06	18.44	21.72	22.53	15.45	19.91			<b>22.60</b>

#### 4.4 Biological Parameter

The sources of microbes in water are human and animal excreta, although there are other sources that may also be significant (WHO, 2010). The detection of each pathogenic organism in water is technically difficult, time consuming and expensive and therefore, not used for routine water testing procedures. Instead, indicator organisms are routinely used to assess the microbiological quality of water and provide an easy, rapid and reliable indication of the microbiological quality of water. Thus, the presence of coliform in water is taken, as an indication of the presence of pathogenic organisms.

Total coliform count (TCC) values ranges from  $0.2 \times 10^1$  cfu/ml to  $2.2 \times 10^1$  cfu/ml in Amaenyi and  $1.0 \times 10^1$  cfu/ml to  $1.5 \times 10^1$  cfu/ml in State Secretariat, with mean values of  $1.12 \times 10^1$  cfu/ml and  $1.24 \times 10^1$  cfu/ml respectively. In Amaenyi, the values for samples A1, A4, A5, A6, A9 and A10 and samples S5 and S8 in the State Secretariat were within the NSDWQ permissible limit. However, samples A2, A3, A7 and A8 as well as S1, S2, S3, S4, S6 and S7 in Amaenyi and State Secretariat areas respectively exceeded the permissible limit. The WHO guideline was exceeded by all the samples in the study area. The indication is that groundwater in study area are biologically polluted.

The spatial distribution of coliform in the study area (Fig. 9) showed that high concentration was observed in areas surrounding the dumpsites (A2 A3 and A8) with a decrease in concentration away from them. Similar trend was reported by Abbas *et al.* (2023) and Kristantiet *al.* (2022).

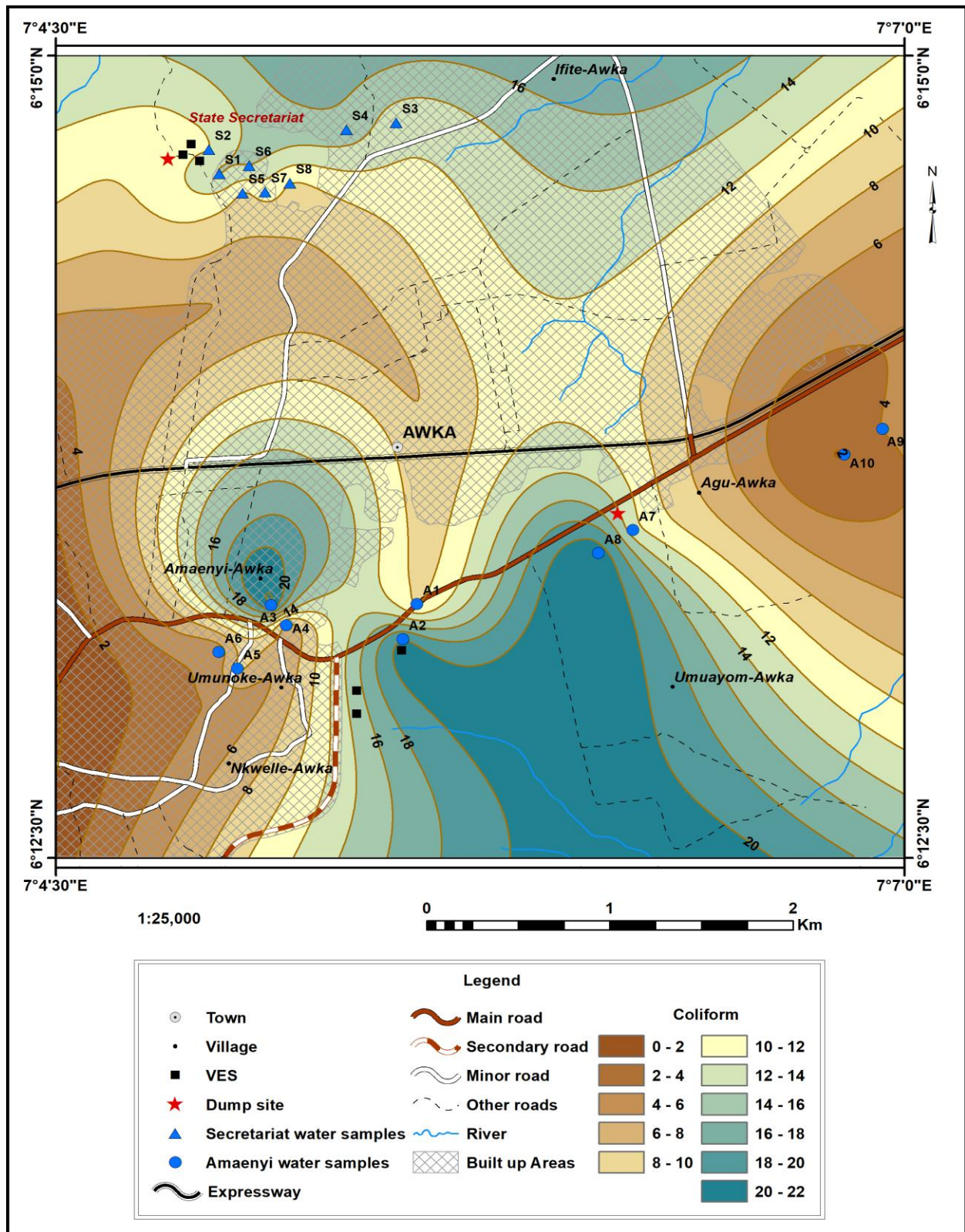


Fig.9: The distribution of coliform bacteria in the study area

#### 4.5 Correlation of analyzed parameters in groundwater

Pearson correlation analysis was generated to assess the relationships between parameters dissolved in groundwater. The results are shown in Tables 7 and 8. A correlation of  $r < 0.5$  was interpreted as weak,  $r = 0.5 - 0.7$  as medium and  $r = 0.8 - 1$  as strong interrelationships. Total hardness had strong positive relationship with bicarbonate in the two areas indicating temporal hardness. However, it was observed that total hardness and bicarbonate were also positively strongly correlated with sulphate and calcium in Amaenyi area indicating permanent hardness in groundwater. It can be said that the positive relationship of total hardness, bicarbonate, calcium, sulphate, mercury, and nitrate indicate similar input sources. Total dissolved solids is majorly influenced by the presence of sodium, potassium and cadmium hence the strong positive relationship especially in the Amaenyi area. Also, the strong positive relationship which existed between lead, chloride and magnesium may indicate input from lead batteries in Amaenyi dumpsite. Furthermore, a strong positive relationship existed between BOD, DO1 and DO5 linking the input source to decay of organic matter. COD and BOD equally exhibited a medium positive correlation in Amaenyi area. Therefore, correlation analysis indicates most of the variations are elucidated by the anthropogenic pollutants predominantly from the waste dumpsites. The present result is in manner similar to that reported by Selvakuma *et al.*, (2007).

#### CONCLUSION

Hydrochemical assessment of groundwater in the vicinity of Amaenyi and State Secretariat dumpsites was carried out to determine the influence on water quality. The result indicated that TDS, EC and the major ions were within the permissible limit of the guidelines although some of the heavy metals (Fe, Pb, Hg and Cd) exceeded the limit. The coliform group exceeded the permissible limit indicating biological pollution. Also, the results of the various water quality indices (WQI, Cd, HPI and MEI) indicated highly contaminated groundwater. Finally Pearson correlation analysis was used to interpret the relationships among the parameters. Strong positive correlation was observed between parameters such as BOD, DO1 and DO5, bicarbonate, total hardness, sodium, cadmium and sulphate indicating the effect of anthropogenic activities especially from the waste dumpsites. Presence of pathogenic microbes and hazardous chemicals in groundwater deteriorate quality and may pose serious threat to public health.

Table 7: Pearson's correlation coefficient for Amaenyi

	<i>pH</i>	<i>EC</i>	<i>Th</i>	<i>Cl<sup>-</sup></i>	<i>HCO<sub>3</sub><sup>3-</sup></i>	<i>SO<sub>4</sub><sup>2-</sup></i>	<i>NO<sub>3</sub><sup>-</sup></i>	<i>Ca<sup>2+</sup></i>	<i>Mg<sup>2+</sup></i>	<i>Na<sup>+</sup></i>	<i>K<sup>+</sup></i>	<i>TDS</i>	<i>DO1</i>	<i>DO5</i>	<i>BOD</i>	<i>COD</i>	<i>Cd</i>	<i>Hg</i>	<i>Fe</i>	<i>Coli</i>	<i>Pb</i>	
<i>pH</i>	1																					
<i>EC</i>	0.36	1																				
<i>Th</i>	-0.42	-0.79	1																			
<i>Cl<sup>-</sup></i>	-0.52	0.16	-0.19	1																		
<i>HCO<sub>3</sub><sup>-</sup></i>	-0.54	-0.78	0.87	-0.23	1																	
<i>SO<sub>4</sub><sup>2-</sup></i>	-0.20	-0.88	0.84	-0.30	0.70	1																
<i>NO<sub>3</sub><sup>-</sup></i>	-0.17	-0.85	0.70	-0.37	0.76	0.83	1															
<i>Ca<sup>2+</sup></i>	-0.25	-0.74	0.65	-0.41	0.73	0.74	0.59	1														
<i>Mg<sup>2+</sup></i>	-0.21	0.04	-0.43	0.80	-0.36	-0.25	-0.24	-0.24	1													
<i>Na<sup>+</sup></i>	-0.24	0.18	0.17	0.31	0.22	-0.11	-0.03	-0.08	0.002	1												
<i>K<sup>+</sup></i>	-0.08	0.18	0.06	0.37	0.06	-0.05	0.01	-0.22	0.19	0.89	1											
<i>TDS</i>	-0.09	0.33	0.03	0.16	0.13	-0.21	-0.09	-0.10	-0.08	0.96	0.86	1										
<i>DO1</i>	0.40	0.34	0.10	-0.27	-0.14	-0.13	-0.10	-0.33	-0.57	0.27	0.13	0.30	1									
<i>DO 5</i>	0.34	0.10	0.23	-0.32	0.09	-0.004	0.19	-0.21	-0.54	0.34	0.19	0.34	0.92	1								
<i>BOD</i>	0.61	0.39	-0.12	-0.21	-0.33	-0.11	-0.01	-0.55	-0.31	0.23	0.40	0.30	0.75	0.70	1							
<i>COD</i>	0.49	0.57	-0.57	-0.03	-0.52	-0.40	-0.19	-0.55	0.11	-0.02	0.21	0.17	0.26	0.19	0.64	1						
<i>Cd</i>	-0.07	0.37	0.03	0.19	-0.10	-0.12	-0.15	-0.15	-0.11	0.68	0.53	0.70	0.60	0.51	0.40	0.23	1					
<i>Hg</i>	0.44	0.11	-0.13	0.07	-0.42	0.18	0.13	-0.30	0.18	-0.02	0.28	0.01	0.33	0.25	0.68	0.59	0.37	1				
<i>Fe</i>	0.02	-0.04	-0.19	0.41	-0.19	0.11	0.01	0.02	0.65	0.30	0.59	0.28	-0.5	-0.48	-0.04	0.10	0.05	0.40	1			
<i>Coli</i>	-0.04	0.20	0.14	0.18	-0.01	0.02	0.16	-0.46	-0.15	0.51	0.59	0.49	0.61	0.61	0.75	0.46	0.65	0.58	0.002	1		
<i>Pb</i>	-0.50	0.10	-0.27	0.83	-0.17	-0.27	-0.26	-0.14	0.82	0.14	0.14	0.08	-0.37	-0.38	-0.39	0.13	0.23	0.05	0.33	0.004	1	

Table 8: Pearson's correlation coefficient for State Secretariat

	<i>pH</i>	<i>EC</i>	<i>TH</i>	<i>Cl<sup>-</sup></i>	<i>HCO<sub>3</sub><sup>-</sup></i>	<i>SO<sub>4</sub><sup>2-</sup></i>	<i>NO<sub>3</sub></i>	<i>Ca<sup>2+</sup></i>	<i>Mg<sup>2+</sup></i>	<i>Na<sup>+</sup></i>	<i>K<sup>+</sup></i>	<i>TDS</i>	<i>DO1</i>	<i>DO5</i>	<i>BOD</i>	<i>COD</i>	<i>Cd</i>	<i>Hg</i>	<i>Fe</i>	<i>Coli</i>	<i>Pb</i>	
<i>pH</i>	1																					
<i>EC</i>	0.66	1																				
<i>TH</i>	0.17	-0.17	1																			
<i>Cl</i>	-0.36	0.05	-0.26	1																		
<i>HCO<sub>3</sub></i>	0.27	-0.10	0.88	-0.33	1																	
<i>SO<sub>4</sub><sup>2-</sup></i>	-0.54	-0.29	0.31	0.04	0.37	1																
<i>NO<sub>3</sub></i>	-0.77	-0.58	0.18	0.16	0.14	0.83	1															
<i>Ca<sup>2+</sup></i>	0.54	0.54	-0.08	0.35	-0.04	-0.66	-0.82	1														
<i>Mg<sup>2+</sup></i>	-0.51	-0.48	-0.36	0.03	-0.14	-0.02	0.24	-0.15	1													
<i>Na<sup>+</sup></i>	-0.58	-0.20	-0.20	0.89	-0.20	0.15	0.35	0.19	0.44	1												
<i>K<sup>+</sup></i>	0.68	-0.07	0.48	-0.45	0.51	-0.43	-0.51	0.32	-0.31	-0.54	1											
<i>TDS</i>	-0.82	-0.70	-0.19	0.23	-0.13	0.34	0.43	-0.23	0.70	0.51	-0.37	1										
<i>DO1</i>	-0.08	-0.18	0.81	-0.09	0.81	0.58	0.57	-0.36	-0.08	0.08	0.07	-0.12	1									
<i>DO5</i>	-0.62	-0.86	0.19	-0.32	0.06	0.46	0.70	-0.85	0.21	-0.14	-0.04	0.46	0.23	1								
<i>BOD</i>	-0.33	-0.82	0.56	-0.30	0.63	0.47	0.54	-0.50	0.27	-0.05	0.35	0.45	0.55	0.72	1							
<i>COD</i>	-0.26	0.07	-0.08	0.47	-0.25	0.16	0.50	-0.31	-0.08	0.41	-0.51	-0.27	0.33	0.06	-0.24	1						
<i>Cd</i>	-0.27	-0.22	-0.02	-0.002	0.18	0.09	-0.13	0.28	0.53	0.25	-0.04	0.72	-0.14	-0.07	0.25	-0.71	1					
<i>Hg</i>	-0.12	-0.18	0.75	-0.45	0.57	0.51	0.49	-0.57	-0.21	-0.31	0.01	-0.16	0.78	0.47	0.43	0.22	-0.22	1				
<i>Fe</i>	0.29	0.08	-0.06	-0.14	-0.27	-0.47	-0.09	-0.15	-0.23	-0.26	0.17	-0.61	-0.01	0.09	-0.24	0.59	-0.85	0.14	1			
<i>Coliform</i>	0.03	-0.07	0.34	0.46	0.30	-0.19	0.10	0.29	0.19	0.57	0.10	-0.12	0.50	-0.22	0.11	0.50	-0.16	0.08	0.30	1		
<i>Pb</i>	0.44	0.59	0.20	0.12	-0.02	-0.01	-0.10	0.06	-0.87	-0.25	0.04	-0.82	0.17	-0.29	-0.46	0.51	-0.80	0.24	0.51	0.06	1	

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