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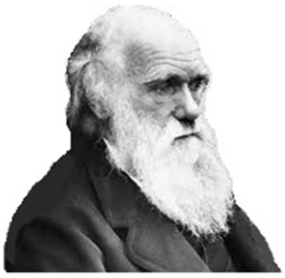

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Physico-chemical and Heavy Metal Assessment of Soil and Water in the Vicinity of Petrol Stations in Karu Local Government Area, Nasarawa State, Nigeria

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ABSTRACT

Soil and water exposure to petroleum at petrol filling stations is believed to induce physicochemical changes and heavy metal pollution thus, this study investigated the extent. Using standard procedures; soil samples were collected 20-30 m apart and at a depth of about 0 – 20 cm while, water samples were collected within 30 m of the stations. At 500 m away from the stations, samples were collected as control. Soil samples were analyzed for; pH (6.25±0.25 to 6.78±0.28), Temperature (29.0±0.49 to 30.5±0.71 °C), Total Dissolved Solids (358 ±1.00 to 620±1.00 mg/kg), Electrical conductivity (719±1.00 to 1248±1.20 µS/cm), Cation exchange capacity (6.80±0.30 to 11.2±0.30 mol/kg), Moisture content (3.50±0.30 to 7.00±0.30 %), Organic carbon (0.20±0.20 to 1.68±0.28 %) and heavy metal content (mg/kg): Cr (12.5±0.02 to 72.6±0.63), Cu (5.47±0.36 to 51.8±1.55), Fe (1525±25.10 to 2023±5.29), Ni (1.97±0.01 to 30.2±0.18), Mg (118±0.67 to 184±4.65), Mn (86.2±0.20 to 394±0.54), Pb (3.08±0.08 to 12.2±0.12) and Zn (12.4±0.46 to 157±0.70). Water samples were also analyzed for; pH (7.50±0.50 to 7.71±0.30), Temperature (30.0±1.00 to 30.7±0.70 °C), Total Dissolved Solids (33.0±1.00 to 48.0±1.00 mg/L), Electrical conductivity (66.0±1.00 to 98.0±1.00 µS/cm), Dissolved Oxygen (2.60±0.30 to 4.80±0.30 mg/L), Biological Oxygen Demand (6.25±0.25 to 14.2±0.20 mg/L), Turbidity (ND to 1.90±0.30 NTU) and Hardness (84.0±1.00 to 380±1.00 mg/L) and heavy metal content (mg/kg): Cr (0.187±0.004 to 0.257±0.002), Cu (0.101±0.012 to 0.112±0.008), Fe (ND to 0.019±0.007), Ni (ND to 0.020±0.002), Mg (6.06±0.203 to 6.63±0.105), Mn (0.057±0.002 to 0.360±0.004), Pb (0.042±0.000 to 0.072±0.001) and Zn (ND to 0.037±0.002). Even though, wide variability was observed in some instances, no significant impacts on soil and water were recorded as affirmed by their respective controls. In addition, determined parameters were on average within the

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acceptable threshold limits set by standard regulatory bodies like NESREA, DPR, NSDWQ and WHO except for EC, Fe and Mg in soil and Cr and Pb in water, in all samples.

***Keywords*:** Heavy metals, petrol stations, metal pollution, physico-chemical

1. INTRODUCTION

Over time, soil and water were thought as inexhaustible reservoirs for pollutants absorption thus, making many to adopt careless attitude towards our environment. With skyrocketing waste generation from advancing industrialization and rapid population growth [1], the conservation of soil and water has become a major concern [2]. Environmental pollution therefore has emerged as a global challenge, with much more bearing on developing countries where environmental sanitation practices and laws are neglected [3].

Water remains the most precious and inevitable resource for the survival of man and almost all other forms of life [4]. By this fact, a threat to water is therefore acknowledged as a threat to life [5]. Even though, water exist in abundance, covering 70 % of the earth surface, contamination and pollution of the fresh consumable fraction (0.3 %) of water has threatened its availability for human use [6]. Pollution of water is derived from natural and anthropogenic activities. Studies have agreed that anthropogenic activities nowadays contribute far more in polluting our water bodies and environment in general, than do natural causes [4].

Similarly, soil forms the bases which support all forms of life and as such, the concern for its pollution and the need for protection can never be overemphasized. Pollutants in soil are leached into water bodies through water percolation as such soil pollution is not just pollution of soil but technically water and the environment in general [2]. Pollutants discharged into the soil however, have complex chemical composition and in some instances improve soil fertility by increasing content of nitrogen, organic matter and cation exchange capacity [2]. Despite this good and maybe few others, there are endless negative effects of pollutants on environment and man in particular. Some pollutants are negatively impactful even at low concentrations and may not have any biological benefit like some toxic heavy metals. Heavy metals are directly linked to respiratory problems, kidney damage, and cancer [7].

Metals and metalloid elements with high specific density and relative atomic weight greater or equal to 5 g/cm^3 and 40.04 respectively, are regarded as heavy metals [8]. Heavy metals have emerged as a threatening class of pollutant due to their wide array of negative impacts and increasing presence in the environment due to technological advancement. Despite their being toxic, nondegradable, bioaccumulative and persistent in the environment, some are visibly harmful even at extremely low (trace) concentrations [8 & 9]. Following these features of heavy metals regarding their presence in the environment, it has become imperative to periodically assess their pollution potential. Heavy metals include but are not limited to Cadmium (Cd), lead (Pb), copper (Cu), chromium (Cr) and zinc (Zn), Iron (Fe), Manganese (Mn), Nickel (Ni) (Ande 2023b). Theses potentially toxic elements endanger human and animal health by entering water, soil, plant and food chain [10]. Presence of heavy metals in soil has great impact on the physicochemical parameters and fertility of soil. For water, some of the common parameters include; Turbidity, pH, Total Dissolved Solids (TDS), Hardness, Biological Oxygen Demand (BOD) and Dissolved Oxygen [11]. Meanwhile, for soil they include; pH, cation exchange capacity, Organic Matter and Moisture content [12]. The impact

on these parameters depends on the water and soil types, initial condition and amount of the contaminant present within the soil [13]. When these elements enter the ecosystem, they are prone to migrate, accumulate and concentrate for a long period of time in aquatic organisms, destroying the ecological balance, and affecting human health through food chain and drinking water, causing global concern [14]. This happens even more when the accumulation of these potentially toxic elements in soil and water exceeds the safety threshold; thus, threatening ecological balance and human health. The pathways through which these heavy metals get to humans have been highlighted in Figure 1. Meanwhile, the threshold values of some of these potentially toxic metals in water and soil are presented in Table 1.

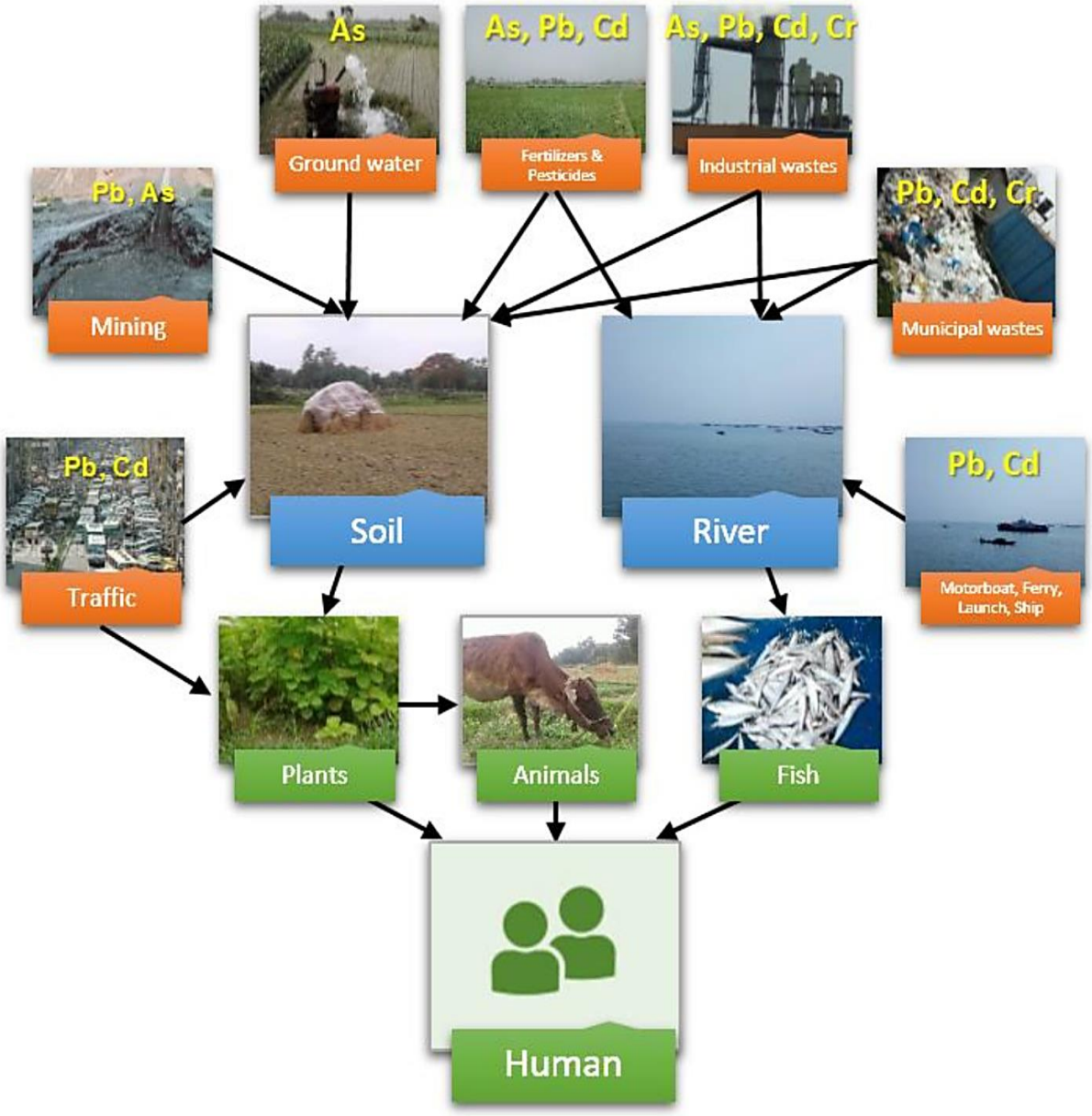

Figure 1. Pathways through which heavy metals gain accesses to man

Table 1. The WHO / NESREA Standard for Heavy Metal in Soil and Water [15]

Parameters	WHO/NESREA	
	Soil (mg/Kg)	Water (mg/L)
Fe	0.5-50 /100	0.3/1.0
Zn	95 /95	5.0/3.0
Ni	50-10 /40	0.02 /0.02
Pb	0.01 /50	0.01/0.1
Cu	100-200 /100	2.0 /1.0
Cr	0.05 /50	0.05/0.05
Cd	1-3 /1	0.003/0.003
Mn	- /1500	0.4 /0.4

Nigeria as a country has depended greatly on oil exploration as a major economic resource [16]. Petroleum refineries and depots are regarded as major sources of air pollutants; particulate matter (PM), nitrogen oxides (NOx), carbon monoxides (CO), hydrogen sulphide (H_2S), sulphur oxides (SOx) and heavy metals. Heavy metals are allegedly agents of reproductive problems in humans and animals [16]. Energy generation from varying products of fossil fuel has led to the petroleum industry development with accompanying retail stations. Common among the retails are the premium motor spirit filling stations where it is sold alongside lubricating oils of different kinds [17]. Petroleum is generally thought of in terms of crude oil products but also includes all liquid, gaseous, and solid hydrocarbons.

Proliferation of petroleum retailing stations around residential and commercial areas has been witnessed recently. This significantly raised the level of petroleum products being disposed indiscriminately into the environment and has led to soil contamination, affecting both surface and underground water. In many petroleum filling stations, mini motor servicing workshops are situated. In such workshops, activities for example change of oil fluids (oil, transmission, and brake types) cleaning, painting and car washing are carried. Such servicing activities are accompanied by dismantling of motor parts, spillage of spent and fresh oils thus, releasing contaminants including the heavy metals [18]. Aside servicing, petroleum spillage is a frequent recurring phenomenon during discharge of petroleum products into the underground reservoir. Of these two major instances petroleum and allied heavy metals find their way into the environment. By this, petroleum exploration and use has joined the other anthropogenic activities like mining, agricultural and industrial waste discharges as major contributors to heavy metals pollution of the environment [13]. Several studies have developed an integral assessment of soil and water qualities linked to human health and potential risks posed by heavy metal pollutants in the environments [19].

Therefore, the release of heavy metals from oil and gas wastes has become a matter of grave concern as they present a spectrum of human health and environmental challenges, when not managed properly. As earlier mentioned, these heavy metals when inhaled or ingested can impact neurological and kidney damage as well as cause cancer [20]. They also impact the physicochemical properties of soil and water and by extension the organisms that live within and agriculture. It is found that the key approach to addressing pollution of the environment due to these pollutants is simply prevention. This pollution can be prevented through proper handling (storage, transportation and waste management), to avoid reckless and indiscriminate release or discharge of contaminant into soil, water and environment in general. Therefore, it is of great significance to deepen the pollution assessment and risk assessment of these potentially toxic elements in soil and water around oil production plants, storage sites and retailing stations such as filling station.

Study Area

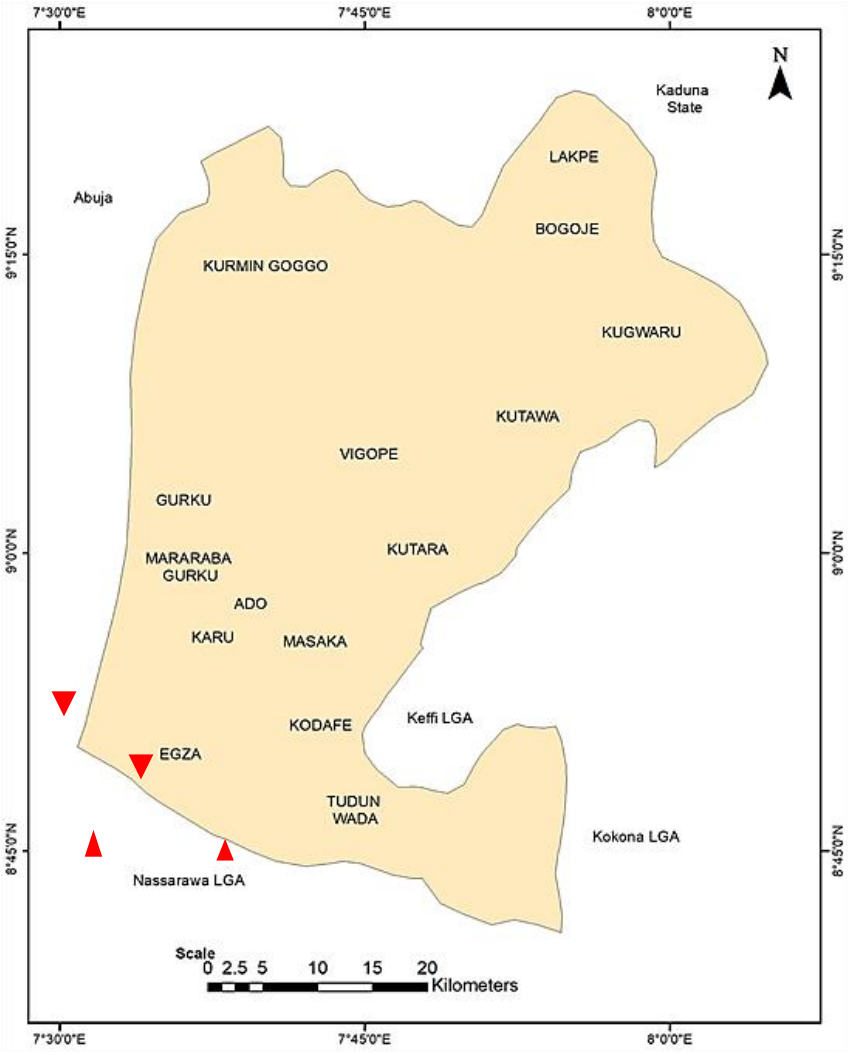

Figure 2. Map of Karu Local Government Area, showing sample locations

Petroleum filling stations within Karu Local Government Area of Nasarawa State, North Central Nigeria were considered for the studies. Nasarawa State is geographically coordinated by an area of 2,640 km^2 and lying between latitude 8° 32′ and 10° 0′ north and longitude 7° 42′ east. Meanwhile, Karu local government has an area of 2,640 km^2 and lies between latitude 9.0469 and longitude 7.7636. Karu Local Government is an urban area in the North Central region of Nigeria, with some parts stretching into the boundaries of the Federal Capital Territory (FCT). The proximity of the major urban settlement of Karu to Abuja makes them part of the development corridors of the Federal Capital Territory. It consist of some major areas such as: Ado, New Nyanya, Mararaba, Newkaru, Masaka and some fast growing areas such as one man village and new Karshi [21]. Karu has two distinct seasons; wet (rainy) and dry seasons. The temperature, rainfall and humidity patterns follow closely, the pattern of two dominant tropical air masses, leading to the emergence of distinct climatic regimes. Temperature during the dry season (November-April) can be as high as 27.5 °C and 37 °C. March is a critical month during which temperature is usually highest, ranging from 35 °C to 37 °C. The maximum temperature ranges from 23.5 °C to 36 °C and is registered in the wet season (May-October). Daily range is reduced to about 7 °C illustrating the moderating influence of cloud cover and these patterns however vary with elevation [22]. The map of the study area showing the sample points is presented in Figure 2.

2. METHODOLOGY

2. 1. Sample Collection

Random sampling technique was adopted and soil and water samples were collected around four different filling stations within Karu Local Government Area, Namely; AYM Shafa (Mararaba), NNPC (Ado), Enyo (Karu) and Total Energies (Masaka). The soil samples were coded, S1, S2, S3 and S4 respectively. Meanwhile the water samples were coded W1, W2, W3 andW4 respectively. The controls were both coded CTRL. Triplicate soil samples were collected within each sampling spot of about 20-30 m apart, using a clean stainless steel trowel. Samples were obtained at a depth of about 0 – 20 cm, soil samples were mixed thoroughly to homogenize. An amount of 20 g was properly labelled and wrapped in a clean aluminum foil, placed in a clean polythene bag and transported to Joseph Sarwuan Tarkaa Chemistry laboratory Makurdi for further analysis.

Similarly, triplicate water samples were collected within each sampling spot of about 20 - 30 m apart. Soil and water (Tap water) samples were collected 500 m away from the vicinity of the main sampling points and regarded as control. Soil and water samples were stored in a freezer to minimize sample degeneration until used.

2. 2. Soil sample preparation and digestion

After screening the soil to remove debris, drying and pulverizing, then sieving with a 2 mm mesh, 2 g of the soil was introduced into a digestion flask and 20 mL of Nitric-hydrochloric acids (Sigma Aldrich, India) in the ratio of 1:3 was added to the samples. This was allowed to sit for 24 hours in a fume cupboard. After that, the entire mixture was heated till the solution becomes clear, allowed to cool, and then filtered into a 100 mL volumetric flask using a Whatman filter paper. The solution was made up to mark using deionized water. This procedure

was repeated for all the soil samples. The clear supernatant solutions were transferred to a set of plastic vials to assess the concentrations of Cr, Cu, Fe, Ni, Mg, Mn, Pb and Zn in soil.

2. 3. Water Sample Digestion

To ensure organic matter and prevention of interferences during heavy metal analysis, 20 mL of the water samples were treated with drops of Nitric acid, filtered, and stored at 4 °C pending metal analysis.

2. 4. Metal Analysis

Flame Atomic Absorption Spectrophotometer (iCE 3000 Series, Thermo Scientific, Germany), was employed following standard procedure to determine the heavy metals. Wavelength of absorption for the metals, used in the procedure were; 248.3 (Fe), 279.5 (Mn), 357.9 (Cr), 324.8 (Cu), 283.3 (Pb), 213.9 (Zn), 285.2 (Mg), 228.8 (Cd), and 232 (Ni) nm.

2. 5 Physicochemical Parameters of Soil and Water

2. 5. 1. Determination of pH of soil and water

The pH of the soil and the water were determined using a pH meter.

2. 5. 2. Cation exchange capacity of soil

An amount of 10 g of soil sample was introduced in a 500 mL beaker, containing 250 mL of NH_4OH, and shaken thoroughly for 30 minutes. It was allowed to stand for 24 hours then filtrated into a plastic bottle. The residue was repeatedly washed with ethanol to remove the excess NH_4OH, and then washed with about 30 mL of NaCl solution to leach out NH_4^+ [23]. The CEC was then calculated thus;

$$\text{CEC (cmol /kg) of Soil} = \frac{\text{VB} - \text{VS} \times \text{N} \times 100\text{mcf}}{\text{S}}$$

where:
VB = volume of the blank,
VS = Sample volume,
N = NaOH's normality,
S = weight of sample,
mcf = moisture correction factor

2. 5. 3. Organic Matter of soil

The soil sample was oven dried and heated at a temperature of 400 °C overnight, to burn off organic matter. The sample was weighed and weight loss of soil sample was measured and the amount of organic matter was recorded.

$$\text{OM} = C \times 1.72$$

where:
C = Carbon

1.72 is a constant.

2. 5. 4. Moisture content of soil

An amount of 50 g of soil sample was oven dried and heated at a temperature of about 105 °C [24]. The weight of the dried soil was reweighed and calculated using the equation below:

$$\text{MC} = \frac{\text{Weight of moist soil (M)} - \text{Weight of dry soil (D)}}{\text{Weight of dry soil (D)}}$$

2. 5. 5. Turbidity of water

Turbidity was measured using a portable turbid meter.

2. 5. 6. Total Dissolved Solids (TDS)

An amount 50 mL of sample of filtered water was oven-dried in a beaker for 5hrs at 105 °C. To determine the TDS, the weight difference between the oven-dried content and the empty beaker was used to estimate the TDS [25].

$$\text{Total dissolve solid (mg/L)} = \frac{(\text{W2}-\text{W1})\text{mg}\times 1000}{\text{mL of filtrate used}}$$

2. 5. 7. Hardness

To a 250 mL conical flask, 25 mL of each water sample was measured into and to it, 3 mL of ammonium chloride in concentrated ammonia buffer was added alongside 2 drops of Eriochrome black T indicator. It was then titrated against 0.01M EDTA solution until there was a color change from, violet to blue [26].

$$\text{Hardness in mg/L } CaCO_3 = \frac{[v\times m\times 1000]}{mL\ of\ sample\ used}$$

2. 5. 8. Biological Oxygen Demand (BOD) and Dissolved Oxygen (DO)

Inside a 1000 mL volumetric flask, 10 mL of the water sample was added alongside 2 mL of ferric chloride solution, magnesium sulfate, and phosphate buffer and the entire solution made up to 1 liter mark with deionized water. The samples were analyzed immediately as day zero (D0) and on the fifth day (D5) [27].

$$\text{BOD} = \frac{\text{D0}-\text{D5}}{\text{Dilution Factor}}$$

2. 6. Analysis of Potentially Toxic Element

Atomic Adsorption Spectrophotometer (AAS) was used to determine the presence and concentration of Cr, Cu, Fe, Ni, Mg, Mn, Pb and Zn in water and soil samples, following standard methods.

3. RESULTS

The physicochemical properties of soil and water within the study site are presented in Table 2 and 3 respectively. In all instances, CTRL represents the control samples while; S1, S2, S3 and S4 represent the others. Physicochemical properties of soil and water are known to be influenced by the presence of contaminants. In a related study, it was agreed that pollutants, particularly heavy metals from solid waste, increase significantly the soil physicochemical parameters [2], which also agreed with other studies [28 & 29]. For the soil parameters, all except electrical conductivity was seeing to go beyond the acceptable limit in all the sample sites including the control.

Table 2. Physicochemical properties of the soil samples

Parameters	S1 Mean±S.D	S2 Mean±S.D	S3 Mean±S.D	S4 Mean±S.D	CTRL Mean±S.D	NESREA
pH	6.57±0.16	6.25±0.25	6.45±0.25	6.78±0.28	6.20±0.30	6.0-8.0
Temp (°C)	30.5±0.71	30.1±0.50	29.9±0.52	29.0±0.49	29.7±0.50	20-30
TDS (mg/kg)	358 ±1.00	434±1.00	359±1.01	620±1.00	492±1.00	1000-2000
EC (µS/cm)	723±1.00	874±1.00	719±1.00	1248±1.20	720±1.00	100-500
CEC(mol/kg)	6.80±0.30	7.60±0.30	11.2±0.30	6.80±0.30	4.80±0.30	5-15
Moisture Content (%)	3.50±0.30	6.00±0.31	3.50±0.30	7.00±0.30	6.50±0.30	10-30
Organic Carbon (%)	0.20±0.20	1.68±0.28	0.44±0.54	0.24±0.54	0.16±0.36	2.5

SD = Standard Deviation S = Soil Sample (S1, S2, S3 and S4)

Table 3. Physicochemical properties of the water smples

Parameters	W1 Mean±S.D	W2 Mean±S.D	W3 Mean±S.D	W4 Mean±S.D	CTRL Mean±S.D	NESREA
pH	7.50±0.50	7.57±0.50	6.78±0.25	7.71±0.30	6.82±0.20	6.8-8-5
Temp (°C)	30.0±1.00	30.0±1.00	30.7±0.70	30.0±1.00	28.93±0.50	20-30
TDS (mg/L)	33.0±1.00	44.0±1.00	44.0±1.00	48.0±1.00	23.58±1.22	500-1000
EC (µS/cm)	66.0±1.00	88.0±1.00	98.0±1.00	94.0±1.00	67.55±0.50	10-100
DO (mg/L)	4.80±0.30	2.82±0.25	2.84±0.35	2.60±0.30	2.63±0.32	5-8
BOD (mg/L)	6.25±0.25	12.3±0.30	14.2±0.20	14.1±0.30	14.10±0.30	30
Turbidity (NTU)	BLD	0.70±0.20	0.10±0.20	1.90±0.30	BLD	5-20
Total Hardness (mg/L)	84.0±1.00	200±1.00	380±1.00	240±1.00	189±0.70	100-200

SD = Standard Deviation W = Water Sample (W1, W2, W3 and W4) BLD = below detection

Table 4. Heavy metals concentrations in the soil samples (mg/kg)

Metal	S1 Mean±S.D	S2 Mean±S.D	S3 Mean±S.D	S4 Mean±S.D	CTRL Mean±S.D	DPR	NESREA
Cr	12.5±0.02	15.0±0.11	72.6±0.63	21.2±0.27	14.1±0.11	100	50
Cu	5.47±0.36	7.40±0.03	51.8±1.55	6.98±0.15	4.78±0.17	36	100
Fe	1587±2.66	1525±25.10	2023±5.29	1651±41.20	1545±8.28	500	100
Ni	1.97±0.01	2.23±0.01	30.2±0.18	2.24±0.02	2.37±0.03	35	40
Mg	161±0.36	184±4.65	118±0.67	162±2.13	138±0.79	≤100	100
Mn	89.4±0.43	86.2±0.20	394±0.54	99.2±0.43	204±0.56	476	1500
Pb	3.08±0.08	12.2±0.12	4.30±0.03	6.32±0.06	4.39±0.18	85	50
Zn	12.4±0.46	32.6±2.29	157±0.70	46.5±0.35	11.3±0.33	50	95

SD = Standard Deviation; S = Soil Sample (S1, S2, S3 and S4); DPR = Department of Petroleum Resources; NESREA = National Environmental Standards and Regulation Enforcement Agency

Table 5. Heavy metals concentrations in the water samples (mg/L)

Metals	W1 Mean±S.D	W2 Mean±S.D	W3 Mean±S.D	W4 Mean±S.D	CTRL Mean±S.D	NSDWQ	WHO
Cr	0.187±0.004	0.225±0.010	0.239±0.010	0.257±0.002	0.047±0.001	0.05	0.05
Cu	0.101±0.012	0.112±0.008	0.110±0.007	0.111±0.008	0.100±0.01	1.0	2.0
Fe	BLD	0.019±0.007	BLD	BLD	BLD	0.3	0.3
Ni	BLD	0.020±0.002	0.012±0.000	0.011±0.000	BLD	0.02	0.02
Mg	6.63±0.105	6.27±0.065	6.62±0.066	6.06±0.203	5.25±0.03	20	30
Mn	0.057±0.002	0.360±0.004	0.067±0.001	0.086±0.008	0.020±0.01	0.2	0.4
Pb	0.045±0.003	0.057±0.002	0.042±0.000	0.072±0.001	0.01±0.01	0.01	0.01
Zn	BLD	0.037±0.002	BLD	BLD	BLD	3.0	5.0

SD = Standard Deviation; W = Water Sample (W1, W2, W3 and W4); BLD = below detection; NSDWQ = Nigerian Standard for Drinking Water Quality

4. DISCUSSION

The pH values of the studied soil samples were slightly acidic but within normal soil pH range (6.0-8.0), designated by NESREA. The soil samples have pH values ranging between 6.25±0.25 and 6.78±0.28, which were not reasonably different from the pH value of the control

(6.20±0.30). Acidic soil impairs plants nutrient uptake and increase the availability of aluminum which can also be toxic to plants [16]. Acidic soil however favours the availability of manganese which is also a plant nutrient. Acidity of soil is associated with cations such as hydrogen (H^+), aluminium (Al^{3+}), and iron (Fe^{2+}) or Fe^{3+}). On the other hand, basicity is promoted by cations such as; potassium (K^+), sodium (Na^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}), through their formation of bases. Water on the other hand, has pH ranging from 6.78±0.25 to 7.71±0.30 which is also within the NESREA designation of normal water (6.8-8-5). Water from the respective sampling points is more drawn to neutral side of the pH scale, compared to the soil. The pH of the water ranged between 6.78±0.25 and 7.71±0.30, which was not in any way significantly different from the control (6.82±0.20). In all cases, the pH values of the samples were within the acceptable limit designated by NESREA. Even though, pH has no direct impact on consumption, it is an important operational parameter as it is indicative of pollution potential [30]. It is understood that water with low pH (7 or less) is more potentially corrosive and might lead to release of metals when allowed to pass through metal pipes. Similarly, a slightly lower pH was reported from filling stations and auto mechanic workshops by [31].

Temperature of the soil and the water obtained from the vicinity of the filling stations were not different from those of the controls and were in the range of 29.0±0.49 - 30.5±0.71 °C. On average, the temperature values were at maximum and slightly above the Permissible limit (20 – 30 °C) of NESEREA, for both soil and water. Similar temperature ranges were reported by [32], and [31], in studies of soil and water in the vicinity of petrol filling stations and auto mechanic workshops in Abeokuta Metropolis, Nigeria and Bamenda-City, North West Region of Cameroon respectively. This high temperature recorded in the study area can be attributed to the atmospheric temperature of the place. Temperature has a positive correlation with the rate of some biological and chemical processes thus; the soil and water will be good for agricultural and aquatic activities.

TDS is a measure of total ion dissolved in a solution. The TDS values of the soil and water within the vicinity of the petrol filling stations were all within the NESREA permissible limits of ≤ 2000 and ≤ 1000 mg/kg respectively. The TDS values of the soil ranged from 358 ±1.00 to 620±1.00 mg/kg whereas, that of water ranged from 33.0±1.00 to 48.0±1.00 mg/kg which correspond to that reported by [30]. The control water sample and the rest of the water samples showed no reasonable difference except for S4 sample point which was a bit higher.

Soil electric conductivity (EC) in the vicinity of the petrol filling stations were found to be above the permissible limit set by NESREA (100-500 µS/cm). The values ranged from 719±1.00 to 1248±1.20 µS/cm; the control was not much different from the values of S1, S2 and S3 however, great difference was noticed in S4. This also, corresponds to the trend recorded earlier in TDS. EC is the measure of the ionic activity of a solution in terms of its ability to transmit current.

Hence, the result of this study can be attributed to the uptake of soluble electrolytes from spilled petroleum products at the stations. High electrical conductivity indicates high availability of nutrients in soil which further implies high negative charge sites in the soil, holding up a great deal of cations. Water on the other hand has electrical conductivity values not different from the control (67.55±0.50 µS/cm), which were all within the acceptable limit of NESREA (10 – 100 µS/cm). The EC of the water samples range from 66.0±1.00 to 98.0±1.00 µS/cm. The presence of oil in water reduces EC [30] hence, might be the reason for the low witnessed EC in water.

Turbidity values of the water samples ranged from BLD - 1.90±0.30 NTU, and in all the sampling points together with the control, turbidity values were quite low, and far lower than the maximum permissible limit set by NESREA (20 NTU), indicating good water quality. Even though, turbidity per se, has no health implication regarding consumption however, excessive turbidity causes staining and blockage of fittings [30].

Dissolve oxygen (DO) in the sampling point, W1 demonstrated reasonably high value, higher than all the rest, which were not different within themselves. Although, all the values are still lower than the minimum threshold value set by NASREA (5 – 8 mg/L). The low DO values ranging from 2.60±0.30 to 4.80±0.30; indicate that the study area will poorly support activities of aerobic organism [30]. Furthermore, the ecosystem might be upset thereby encouraging the development of septic conditions and subsequent production of anaerobic conditions in the groundwater [33].

In addition, water that is saturated with oxygen tastes fresh to human palates although, water with high DO levels speed up corrosion in water pipes [30].

Biochemical oxygen demand BOD of the water samples ranged from 6.25±0.25 to 14.2±0.20 mg/L, while that of the control was 14.10±0.30 mg/L. The BOD values were all within the acceptable limit of ≤ 30 mg/L set by NESREA.

Hardness of water is a function of the concentrations of magnesium and calcium ions present in the water as well as other ions like sulphate, chloride and hydrocarbonate [31]. The hardness value of the study area was examined and found to be greatly varied, ranging from 84.0±1.00 to 380±1.00 mg/L. All sampling points except W2 and the control fell within the acceptable range (100-200 mg/L) by NESEREA. Hardness value for W1 (84.0±1.00 mg/L) was found to be lower than the minimum of the prescribed acceptable range (100-200 mg/L) by NESEREA. Meanwhile, W3 and W4 were all above the threshold, with a reasonable difference and a trend W3 > W4. However, all the samples showed values reasonably above the WHO limit of 75 mg/L [31]. The high hardness values in W3 and W4 might be an indication of permanent hardness.

The number of exchangeable cations per unit mass of dry soil which perform a major function in soil fertility is known as cation exchange capacity (CEC) [2]. The cation exchange capacity of the soil samples were all within the acceptable range except for S4 which was lower than the minimum of the range of 5 - 15 mol/kg set by NESEREA. The reasonable content of exchangeable cations in the soil implies the presence of ions such as; Calcium (Ca), Sodium (Na), Magnesium (Mg) and Potassium (K). Cation exchange capacity also relies on other parameters like; pH, clay and organic matter (OM) contents of soil [2]. Soil with low CEC content is subject to leaching and may certainly yield insufficient nutrient ions like Ca, Na, Mg, K and low organic matter.

Moisture content of soil generally ranges between 6.84 - 21.89 % [34]. Looking at the result of the study, S1 and S3 have the same value of moisture content (3.50±0.30 %) whereas; S2 and the CTRL have somewhat similar value (6.00±0.31 and 6.50±0.30 respectively). The moisture content of S4 (7.00±0.30 %), on the other hand was slightly above the rest however, all the values were below the minimum of the acceptable limit set by NESEREA.

Organic carbon is the preserved carbon in organic matter and its presence in soil help rise the capacity to accumulate exchangeable cations in soil, which serve as nutrient to plants. The percentage of organic carbon content in all the soil samples which ranged between 0.16±0.36 to 0.44±0.54 % were far lower than the threshold of 2.5 %, except for S2 which was quite close

(1.68±0.28). The fertility of the soil around the study sites therefore is not high and might need to be boosted for a good yield.

The metal concentrations determined in the various soil samples are presented in Table 4. Concentrations in mg/kg were in the respective ranges for; Cr (12.5±0.02 to 72.6±0.63), Cu (5.47±0.36 to 51.8±1.55), Fe (1525±25.10 to 2023±5.29), Ni (1.97±0.01 to 30.2±0.18), Mg (118±0.67 to 184±4.65), Mn (86.2±0.20 to 394±0.54), Pb (3.08±0.08 to 12.2±0.12) and Zn (12.4±0.46 to 157±0.70). The concentrations of Cr, Ni, Mn, and Pb were within the DPR and NESREA acceptable threshold limits. In contrast, all soil samples had the concentrations of Mg and Fe above the DPR and NESREA permissible limits. Levels of Zn and Cu were within safe concentrations except for levels detected in soil sample S3. Soil samples from location S3 contained the highest concentrations of Cr, Cu, Fe, Ni, Mn, and Zn hence, the most polluted site. The control samples had values within the ranges observed for the study points thus, confirming less impact of the exposure except for S3 which has highly significant difference.

The metal concentrations in the drinking water samples from the study area were investigated and results are presented in Table 5. The water samples were found to contain Cr (0.187±0.004 to 0.257±0.002), Cu (0.101±0.012 to 0.112±0.008), Fe (BLD to 0.019±0.007), Ni (BLD to 0.020±0.002), Mg (6.06±0.203 to 6.63±0.105), Mn (0.057±0.002 to 0.360±0.004), Pb (0.042±0.000 to 0.072±0.001) and Zn (BLD to 0.037±0.002). The Fe and Zn levels in water samples W1, W3, and W4 were not detected; Ni was not detected in W1. The water samples contained safe amounts of Zn, Mg, Fe, and Cu as stipulated by the NSDWQ and WHO. Ucheana *et al*., reported unsafe Pb concentrations, safe Zn and Mg concentrations in water samples collected from some urban centers in Enugu state, Nigeria [35]. However, Cr and Pb levels were above the NSDWQ and WHO threshold of 0.05 and 0.01 mg/L, respectively. The exposure to high Cr and Pb amounts in the drinking water could lead to carcinogenic and non-carcinogenic health issues [36]. The concentrations of Mn and Ni in W2 were above the 0.2 and 0.02 mg/L concentrations recommended by NSDWQ and WHO. With regards to the control samples, it can be inferred that there is varied influence on the water due to activities within the stations as the controls have values within the acceptable limits.

5. CONCLUSION

No serious physicochemical changes were observed between the exposed sampling points and the controls even though variations existed. Hence, it suffices to say there is yet little or no influence of the anthropogenic activities in the petrol filling stations on the soil and water in the particular study areas. More also, all the studied physicochemical parameters for the soil and water seemed to be either below or within the acceptable threshold limits set by NESREA, except for the electrical conductivity of the soil which was reasonably above in all sampling points, including the control.

This further confirms less impact of the petroleum chemical products and the activities within petrol filling stations on the physicochemical properties of the soil and water within the vicinity. Similar instance is observed in the heavy metal concentration of the soil as only Fe and Mg were seeing to be above the threshold in all sampling points including the control. Water on the other hand had Cr and Pb concentrations above the limits however, thus time the values of the control were within permissible limits. This therefore infers that, the metals may possibly have been contributed by the activities within the stations.

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