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Original Research Article

Effects of Selected Herbicides on Physicochemical Characteristics and Heavy Metal Concentrations in River Kaduna Water under Controlled Laboratory Conditions

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Abstract

Agricultural herbicide runoff poses severe ecological risks to tropical freshwater ecosystems. This study evaluated the comparative effects of low (1.0 mg/L) and high (10.0 mg/L) exposure concentrations of glyphosate, metolachlor, and 2,4-dichlorophenoxyacetic acid (2,4-D) on the physicochemical characteristics and heavy metal concentrations (Pb, Cd, and Zn) of River Kaduna water over a 6-week laboratory microcosm experiment. Water samples were monitored at weekly intervals for temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO), nitrate (NO_3-N), and phosphate (PO_4-P). Herbicide treatments induced significant ($p<0.05$) alterations in water quality dynamics. Glyphosate at 10.0 mg/L produced the largest increases in EC (1955.3±2.1 μS/cm) and TDS (977.67±1.5 mg/L), alongside a reduction in DO to 2.0±0.1 mg/L compared to the control (3.5±0.1 mg/L). Metolachlor significantly elevated phosphate levels (0.91–0.92 mg/L). Across treatments, lead (Pb) and cadmium (Cd) concentrations exceeded World Health Organization drinking water thresholds, with peak Pb reaching 0.364±0.03 mg/L under 2,4-D treatment and peak Cd reaching 0.021±0.0 mg/L under metolachlor treatment. Conversely, zinc (Zn) remained well within safety standards (0.002–0.088 mg/L). These results indicate that herbicide contamination degrades basic water quality parameters and promotes heavy metal mobilization in tropical surface waters.

Introduction

Herbicides, utilized in agricultural practices to control weeds, often find their way into aquatic environments through surface runoff and atmospheric deposition (Choudri et al., 2020). Globally, the intensification of agricultural practices has led to a significant increase in the use of herbicides for weed control (Choudri et al., 2020). While these chemicals are crucial for enhancing crop yields, their widespread application often results in unintended environmental consequences. Herbicide runoff from agricultural lands is a major non-point source of pollution, contaminating rivers, streams, and other aquatic environments (Wolfran et al., 2023).

Once in aquatic ecosystems, herbicides can cause stress within aquatic communities and radically alter community structure. They are designed to inhibit plant growth, and thus pose a direct threat to aquatic primary producers, such as algae, which form the base of the food web (Vonk et al., 2020). The disruption of algal communities can have cascading effects throughout the entire ecosystem, impacting biodiversity, nutrient cycling, and overall ecosystem functioning. Furthermore, the presence of herbicides and their degradation products in waterways can escape regulatory oversight, leading to long-term ecological damage and potential bioaccumulation in the food chain.

Glyphosate, Metolachlor, and 2,4-D are among the most commonly used herbicides in Nigeria. They are widely applied in various agricultural practices for weed control in crops such as maize, sorghum, cowpea, rice, sugarcane, cassava, and yam (Adeola et al., 2025). The widespread use of these herbicides in agricultural regions, including those surrounding River Kaduna, increases the likelihood of their presence in the river through runoff. These herbicides represent different modes of action, allowing for a comprehensive assessment of their combined and individual impacts on periphytic algal community structure. Their widespread use and documented aquatic toxicity make them highly relevant for a study investigating herbicide effects on river ecosystems in an agricultural region like Kaduna. River Kaduna is a significant water body flowing through Kaduna Metropolis, Nigeria. It serves as a vital resource for various human activities, including domestic water supply, irrigation for agriculture, and industrial uses (Shenpam et al., 2019). The extensive agricultural activities in the catchment area, coupled with documented pollution from agricultural runoff, strongly suggest the presence and potential impact of herbicides in River Kaduna. This makes it a relevant and representative location for investigating the effects of these chemicals on aquatic life.

Periphyton serves as a primary producer in freshwater ecosystems, utilizing sunlight to perform photosynthesis and produce organic material. This organic matter becomes a food source for a variety of invertebrates, which in turn supports higher trophic levels (Srivastava et al., 2019). The nutrient cycling facilitated by periphyton includes the uptake and processing of nutrients such as nitrogen and phosphorus, helping to regulate water quality by reducing nutrient loads (Zhang et al., 2020).

The assessment of heavy metals alongside herbicide exposure is important because aquatic organisms are rarely exposed to a single contaminant under natural conditions. Metals such as lead (Pb) and cadmium (Cd) may exert toxic effects on aquatic primary producers and potentially modify their responses to herbicide exposure. Determining their concentrations therefore provides important environmental context for interpreting changes observed in periphytic algal communities. This study evaluates the temporal effects of low (1.0 mg/L) and high (10.0 mg/L) exposure levels of glyphosate, metolachlor, and 2,4-D on the physicochemical traits and heavy metal concentrations (Pb, Cd, Zn) of River Kaduna water in a 42-day laboratory microcosm.

Materials and Methods

Study Area

The study is focused on River Kaduna (Figure 1), spanning Chikun and parts of Kaduna North Local Government Areas in Kaduna State, Nigeria, situated at approximately latitude 10°30 N and longitude 7°27 E. River Kaduna is one of the major tributaries of the Niger River in Nigeria. The catchment area of River Kaduna is characterized by intensive human activities including agriculture activities such as (rice, sugarcane, and vegetable farming), irrigation, industrial operations, urbanization, fishing, and livestock rearing. Agricultural practices around the river involve the use of herbicides and fertilizers which may enter the river through runoff. Industrial and domestic wastes from Kaduna metropolis are also discharged into the river, contributing to water pollution and ecological disturbance. The rationale for choosing the sampling site was to obtain a pollution gradient due to land use pattern.

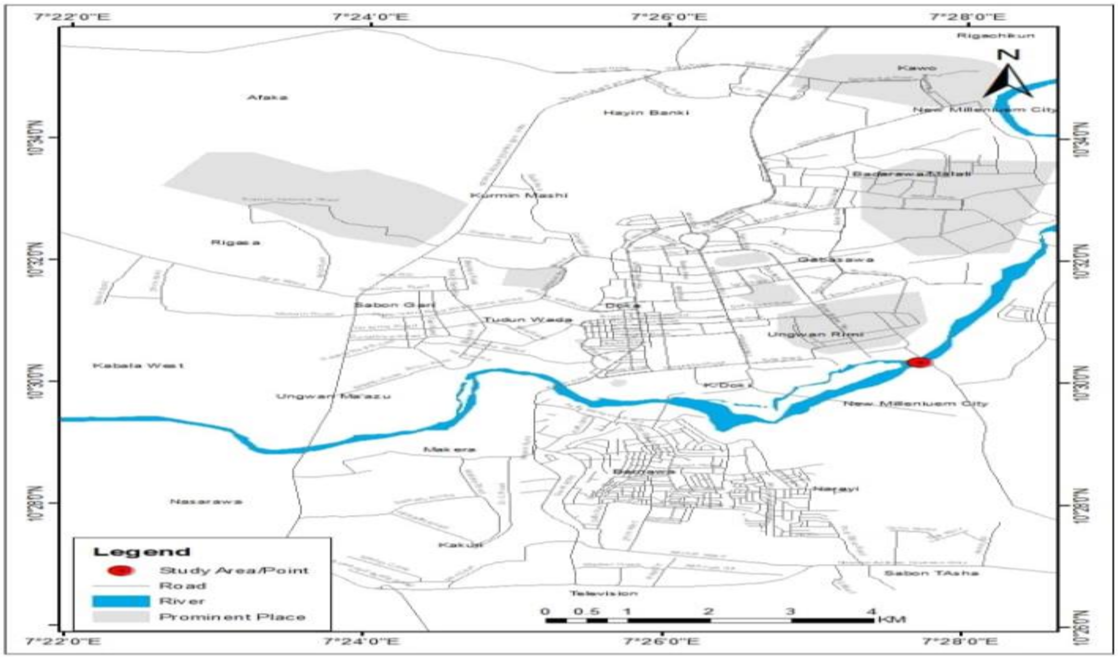

Figure 1: Map showing the study area

Source: (Koko, 2020)

Experimental Design

The experiment was conducted for six weeks under controlled laboratory conditions using 21 transparent glass jars as experimental units. The experiment was arranged as a completely randomized design which consisted of seven treatments with three independent replicates each (7 × 3 = 21). The treatments included a herbicide-free control and two concentrations (1.0 and 10.0 mg/L) of each of the three herbicides. The seven treatment groups were therefore: control, glyphosate 1.0 mg/L, glyphosate 10.0 mg/L, metolachlor 1.0 mg/L, metolachlor 10.0 mg/L, 2,4-D 1.0 mg/L, and 2,4-D 10.0 mg/L. Stock solutions were prepared by dissolving 0.5 g of each pure herbicide in 500 mL of distilled water, giving a stock concentration of 1,000 mg/L. The low concentration (1.0 mg/L) was obtained by adding 0.5 mL of stock solution to 499.5 mL of water containing periphytic algal samples, while the high concentration (10.0 mg/L) was prepared using 5.0 mL of stock solution in 495 mL of water containing the algal samples (Lozano et al., 2017). The control received the same water and periphyton treatment but no herbicide. An equal quantity of periphytic algae (10ml) was introduced into each experimental unit to ensure uniformity among treatments. Periphytic algal samples were examined microscopically before herbicide exposure (Day 0) and subsequently at 7-day intervals (Days 7, 14, 21, 28, 35, and 42), while water samples from each experimental unit were analyzed for physicochemical parameters and heavy metal concentrations using standard analytical procedures.

Sample Collection

A bulk sample was collected once between 8a.m and 10a.m at the beginning of the experiment which lasted for six weeks from July 2025 to August 2025. Water samples were collected in two-liter jars, securely sealed to prevent contamination during transportation, placing the jars in an ice chest. These samples were transported to the Biology Department Laboratory of Ahmadu Bello University, Zaria, and the Central Laboratory of Bayero University, Kano, for comprehensive analysis of both biological and physicochemical parameters.

Digestion of Water Samples

The digestion of the water sample was carried out by the method described by Eneji et al. (2017) without modification. A 25 mL of water sample was measured and 5.0 mL of concentrated HNO_3 (73 % w/w) was added, shaken and heated to about

110 ◦C in a conical flask until the water reduced to 20.0 mL. Another 5.00 mL of Conc. HNO_3 was added and further concentrated to solubilize particulate matter content until it became clear. The sample was allowed to cool; thereafter, a little quantity of distilled water was added and filtered through a filter paper. The filtrate was made up to mark in a 50 mL volumetric flask then transferred to plastic sample bottle and covered.

Physicochemical Analysis of Water

Physicochemical parameters, including pH, temperature, electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO), phosphate, and nitrate, were determined using standard analytical methods. pH, temperature, EC, and TDS were measured using calibrated Palintest Micro 800 and Wagtech WE30120 meters. Dissolved oxygen was determined by the Azide-modified Winkler method following APHA (2017). Phosphate and nitrate concentrations were analysed using the Stannous Chloride colorimetric method and Palintest Photometer 7500, respectively, following standard procedures (Gupta, 2007). All colorimetric measurements were based on photometric determination, where colour intensity was directly proportional to the concentration of the respective analyte (Zaky, 2015).

Analysis of Heavy Metal

Selected heavy metals (Pb, Zn, Cd, and Cu) were determined using a BUK 235 Atomic Absorption Spectrophotometer (AAS). Water samples (100 mL) were digested with HNO_3, H_2SO_4, and $HClO_4$ on a hot plate at 100°C until complete digestion, then cooled, filtered, and diluted to 100 mL with distilled water following the method of Sadiq et al. (2022). The AAS was calibrated using appropriate metal standards and a reagent blank before analysis. Metal concentrations were determined at their respective wavelengths using appropriate hollow cathode lamps.

Data Analysis

Data are presented as mean ± standard deviation (n=3). Differences among treatments and control over time were analyzed using one-way Analysis of Variance (ANOVA) followed by Duncan's Multiple Range Test (p<0.05) in IBM SPSS Statistics.

Results

Physicochemical and Heavy Metals Parameters for Metolachlor Treatments

Metolachlor exposure significantly increased EC, TDS, and phosphate levels relative to the control (p<0.05) (Table 1a and b). Low (1.0 mg/L, S1) and high (10.0 mg/L, S2) metolachlor treatments increased EC from 298.67±3.5 µS/cm in the control to 468±3.6–471.67±1.5 µS/cm in S1 and 504±6.0–509.00±2.0 µS/cm in S2. TDS increased from 147±2.6 mg/L in the control to 232.33±1.5–237.00±0.0 mg/L in S1 and 251.00±0.0–254.67±1.5 mg/L in S2. Dissolved oxygen declined from 3.5±0.10 mg/L in the control to 3.1±0.10–3.2±0.06 mg/L in S1 and 2.6±0.10–2.7±0.06 mg/L in S2, with the greater reduction occurring under S2. Phosphate increased from 0.82±0.01 mg/L in the control to 0.91±0.00–0.92±0.01 mg/L in S1, while S2 recorded 0.83±0.00–0.84±0.00 mg/L. Cd ranged from 0.019±0.06–0.021±0.00 mg/L in S1 and 0.006±0.00–0.007±0.00 mg/L in S2, while Pb ranged from 0.105±0.10–0.117±0.10 mg/L in S1 and 0.170±0.10–0.178±0.07 mg/L in S2. This showed significant difference between the groups. Both Cd and Pb exceeded their WHO limits, whereas Zn remained below the WHO limit, ranging from 0.011±0.01–0.014±0.00 mg/L in S1 and 0.086±0.00–0.088±0.00 mg/L in S2.

Treatments with the same letter are not significantly different. Values are mean ±SD of three replications. Key: pH =Hydrogen ion, EC = Electrical conductivity, TDS = Total dissolved solids, PO_4-P = Phosphate, NO_3-N = Nitrate, DO = Dissolved oxygen, Zn =Zinc, Cd= Cadmium, Pb= Lead, WHO STD = World Health Organization Standard, ns = Not significant, ** Highly significant (p<0.01), * = significant (p<0.05).

Physicochemical and Heavy Metals Parameters for Glyphosate Treatments

Glyphosate exposure significantly altered EC, TDS, dissolved oxygen, nitrate, phosphate, and heavy-metal concentrations relative to the control (p<0.05) (Table 2a and b). Low (1.0 mg/L, G1) and high (10.0 mg/L, G2) glyphosate treatments increased EC from 298.67±3.5 µS/cm in the control to 585.67±5.1–

589.00±3.0 µS/cm in G1 and 1952.33±2.5–1955.3±2.0 µS/cm in G2. TDS increased from 147±2.6 mg/L in the control to 297.00±1.5–299.33±0.5 mg/L in G1 and 976.33±1.5–977.67±0.5 mg/L in G2. Significant difference was observed between the groups. Dissolved oxygen declined from 3.5±0.10 mg/L in the control to 2.8±0.10–2.9±0.06 mg/L in G1 and 2.0±0.10–2.1±0.06 mg/L in G2. Nitrate changed from 27.63±0.55 mg/L in the control to 27.03±0.25–27.30±0.20 mg/L in G1 and 30.90±0.10–31.10±0.10 mg/L in G2. Phosphate increased from 0.82±0.01 mg/L in the control to 0.92±0.00–0.93±0.01 mg/L in G1, while G2 recorded 0.83±0.00–0.84±0.00 mg/L. Cd decreased from 0.011±0.00 mg/L in the control to 0.002±0.00–0.002±0.02 mg/L in G1 and 0.004±0.00–0.005±0.00 mg/L in G2. Pb decreased from 0.438±0.06 mg/L in the control to 0.320±0.10–0.341±0.06 mg/L in G1 and 0.220±0.00–0.236±0.05 mg/L in G2, although all treatment values remained above the WHO limit of 0.01 mg/L. Zn increased from 0.002±0.01 mg/L in the control to 0.007±0.00–0.008±0.00 mg/L in G1 and 0.009±0.00–0.010±0.00 mg/L in G2. Significant difference was observed among the treatments.

Treatments with the same letter are not significantly different. Values are mean ±SD of three replications. Key: pH =Hydrogen ion, EC = Electrical conductivity, TDS = Total dissolved solids, PO_4-P = Phosphate, NO_3-N = Nitrate, DO = Dissolved oxygen, Zn =Zinc, Cd= Cadmium, Pb= Lead, WHO STD = World Health Organization Standard, ns = Not significant, ** Highly significant ($p<0.01$), * = significant ($p<0.05$).

Physicochemical and Heavy Metals Parameters for 2,4-D Treatments

2,4-D exposure significantly altered EC, TDS, nitrate, phosphate, and heavy-metal concentrations relative to the control ($p<0.05$) (Table 3a and b). Low (1.0 mg/L, D1) and high (10.0 mg/L, D2) 2,4-D treatments increased EC from 298.67±3.5 µS/cm in the control to 1068.67±3.5–1072.00±2.0 µS/cm in D1 and 1070.33±1.5–1074.00±1.0 µS/cm in D2. TDS increased from 147±2.6 mg/L in the control to 533.00±1.0–536.00±1.0 mg/L in D1, while D2 recorded 193.00±1.0–195.00±1.0 mg/L. Significant difference was observed between the groups. Dissolved oxygen increased from 3.5±0.10 mg/L in the control to 3.8±0.10–3.9±0.06 mg/L in D1 and 3.8±0.10–3.9±0.06 mg/L in D2. Nitrate increased from 27.63±0.55 mg/L in the control to 30.00±0.20–30.10±0.10 mg/L in D1, while D2 recorded 28.00±0.20–28.10±0.10 mg/L. Phosphate decreased from 0.82±0.01 mg/L in the control to 0.63±0.01–0.64±0.00 mg/L in D1, whereas D2 recorded 0.82±0.00–0.84±0.00 mg/L. Statistical difference was observed between the groups. Zn increased from 0.002±0.01 mg/L in the control to 0.054±0.01–0.058±0.00 mg/L in D1, while D2 recorded 0.003±0.00–0.006±0.00 mg/L. Cd ranged from 0.005±0.01–0.006±0.00 mg/L in D1 and 0.004±0.07–0.010±0.07 mg/L in D2, with values exceeding the WHO limit of 0.003 mg/L. Pb decreased from 0.438±0.06 mg/L in the control to 0.232±0.10–0.239±0.12 mg/L in D1 and 0.345±0.00–0.364±0.03 mg/L in D2, but remained above the WHO limit of 0.01 mg/L. Significant difference was observed among the treatments

Treatments with the same letter are not significantly different. Values are mean ±SD of three replications. Key: pH =Hydrogen ion, EC = Electrical conductivity, TDS = Total dissolved solids, PO_4-P = Phosphate, NO_3-N = Nitrate, DO = Dissolved oxygen, Zn =Zinc, Cd= Cadmium, Pb= Lead, WHO STD = World Health Organization Standard, ns = Not significant, ** Highly significant ($p<0.01$), * = significant ($p<0.05$).

Discussion

Herbicide application significantly influenced the physicochemical characteristics and heavy metal concentrations of River Kaduna water. Water temperature remained relatively stable throughout the experimental period, indicating that the applied herbicides had no direct effect on thermal conditions. This agrees with previous studies reporting that environmental temperatures are primarily controlled by climatic factors, while temperature mainly influences herbicide degradation and toxicity rather than being affected by herbicide application itself (Ukwenya et al., 2023). The reduction in pH observed in glyphosate-treated samples is attributable to the acidic nature of glyphosate and its degradation products, which release proton-donating functional groups during mineralization (Gandhi, 2021).

Table 1a: Mean ± SD Physicochemical Parameters and Heavy Metals Treated with Metolachlor Herbicide, July 2025

		Week 1		Week 2		Week 3	
Parameter	Control	S1	S2	S1	S2	S1	S2
TEMP (˚C)	23.5±0.10^{ab}	23.20±0.10^{c}	23.10±0.10^{cd}	23.3±0.10^{b}	23.1±0.10^{c}	23.4±0.10^{b}	23.2±0.10^{c}
pH	7.63±0.10^{d}	8.07±0.01^{b}	8.05±0.02^{c}	8.07±0.01^{b}	8.04±0.01^{c}	8.06±0.01^{b}	8.04±0.02^{b}
EC (µS/cm)	298.67±3.5^{f}	468±3.6^{e}	504±6.0^{d}	470±2.0^{e}	506.67±1.5^{d}	470.67±1.5^{e}	504.33±1.5^{d}
DO (mg/L)	3.5±0.10^{b}	3.2±0.10^{c}	2.7±0.10^{d}	3.1±0.10^{c}	2.7±0.10^{e}	3.2±0.06^{c}	2.7±0.06^{e}
TDS (mg/L)	147±2.6^{g}	233.33±1.5^{e}	252.67±3.1^{d}	234.33±1.5^{e}	252.67±1.5^{d}	234.00±1.0^{e}	251.67±1.5^{d}
NO_3-N (mg/L)	27.63±0.55de	33.15±0.35^{a}	27.10±0.26^{ef}	32.90±0.20^{a}	27.10±0.10^{e}	33.03±0.15^{a}	27.06±0.20^{e}
PO_4-P (mg/L)	0.82±0.01b	0.92±0.01^{a}	0.83±0.01^{b}	0.91±0.0^{a}	0.84±0.0^{b}	0.91±0.0^{a}	0.84±0.0^{b}
Zn (mg/L)	0.002±0.01^{d}	0.011±0.01^{c}	0.088±0.00^{a}	0.011±0.0^{c}	0.088±0.0^{a}	0.013±0.0^{c}	0.086±0.0^{a}
Cd (mg/L)	0.011±0.00^{b}	0.019±0.06^{a}	0.007±0.03^{bc}	0.020±0.0^{a}	0.007±0.0^{b}	0.021±0.0^{a}	0.007±0.0^{b}
Pb (mg/L)	0.438±0.06^{c}	0.117±0.13^{b}	0.178±0.07^{b}	0.117±0.1^{b}	0.175±0.1^{b}	0.112±0.0^{b}	0.173±0.1^{b}

Table 1b: Mean ± SD Physicochemical Parameters and Heavy Metals Treated with Metolachlor Herbicide, July 2025

	Week 4		Week 5		Week 6		WHO STD
Parameter	S1	S2	S1	S2	S1	S2	
TEMP (˚C)	23.2±0.1^{c}	23.1±0.1^{c}	23.4±0.1^{b}	23.2±0.1^{c}	23.5±0.1^{a}	23.2±0.1^{b}	23–35
pH	8.06±0.0^{b}	8.05±0.0^{b}	8.08±0.0^{b}	8.05±0.0^{c}	8.07±0.0^{b}	8.05±0.0^{c}	6.5–8.5
EC (µS/cm)	469.67±1.5^{e}	504.00±1.0^{d}	471.33±2.5^{e}	509.00±2.0^{d}	471.67±1.5^{e}	508.33±1.5^{d}	≤1000
DO (mg/L)	3.1±0.1^{c}	2.6±0.1^{e}	3.1±0.1^{c}	2.6±0.1^{e}	3.1±0.1^{c}	2.7±0.1^{e}	≥5.0
TDS (mg/L)	232.33±1.5^{e}	251.00±1.0^{d}	236.00±1.0^{e}	254.67±1.5^{d}	237.00±1.0^{e}	254.00±1.0^{d}	≤500
NO_3-N (mg/L)	33.10±0.1^{a}	26.97±0.1^{f}	33.00±0.2^{a}	27.13±0.1^{e}	33.00±0.1^{a}	27.20±0.1^{e}	≤50
PO_4-P (mg/L)	0.91±0.0^{a}	0.83±0.0b^{c}	0.91±0.0^{a}	0.83±0.0^{b}	0.91±0.0^{a}	0.83±0.0^{b}	≤0.3
Zn (mg/L)	0.013±0.0^{c}	0.087±0.0^{a}	0.013±0.0^{c}	0.087±0.0^{a}	0.014±0.0^{c}	0.087±0.0^{a}	≤3.0
Cd (mg/L)	0.019±0.0^{a}	0.006±0.0^{b}	0.020±0.0^{a}	0.007±0.0^{b}	0.019±0.0^{a}	0.007±0.0b^{c}	≤0.003
Pb (mg/L)	0.105±0.1^{d}	0.170±0.1^{cd}	0.110±0.1^{d}	0.171±0.1^{cd}	0.107±0.1^{d}	0.170±0.1^{cd}	≤0.01

Table 2a: Mean ± SD Physicochemical Parameters and Heavy Metals Treated with Glyphosate Herbicide, July 2025

		Week 1		Week 2		Week 3	
Parameter	Control	G1	G2	G1	G2	G1	G2
TEMP (˚C)	23.5±0.10^{ab}	23.03±0.06^{d}	23.46±0.06^{ab}	23.1±0.10^{c}	23.4±0.10^{b}	23.1±0.10^{c}	23.5±0.06^{ab}
pH	7.63±0.01^{d}	8.19±0.01a	7.45±0.01^{f}	8.19±0.01^{a}	7.45±0.01^{f}	8.19±0.01^{a}	7.45±0.01^{d}
EC (µS/cm)	298.67±3.5^{f}	585.67±5.1^{c}	1954±7.9^{a}	587.67±2.5^{c}	1952.33±2.5^{b}	588.33±2.1^{c}	1954.3±1.5^{a}
DO (mg/L)	3.5±0.10^{b}	2.8±0.10^{d}	2.0±0.10^{e}	2.9±0.06^{d}	2.0±0.06^{f}	2.8±0.06^{d}	2.1±0.06^{f}
TDS (mg/L)	147±2.6^{g}	298±2.6^{c}	976±5.3^{a}	298.33±1.5^{c}	976.33±1.5^{a}	298.00±1.0^{c}	976.00±1.0^{a}
NO_3-N (mg/L)	27.63±0.55^{de}	27.03±0.25^{f}	31.00±0.20^{b}	27.13±0.15^{e}	31.00±0.10^{b}	27.20±0.20^{e}	30.96±0.15^{b}
PO_4-P (mg/L)	0.82±0.01^{b}	0.93±0.01^{a}	0.83±0.01^{b}	0.92±0.0^{a}	0.84±0.0^{b}	0.92±0.0^{a}	0.83±0.0^{bc}
Zn (mg/L)	0.002±0.01^{d}	0.007±0.01^{cd}	0.009±0.01^{c}	0.007±0.0^{c}	0.008±0.0^{c}	0.007±0.0^{c}	0.009±0.0^{c}
Cd (mg/L)	0.011±0.00^{b}	0.002±0.02^{c}	0.004±0.05^{bc}	0.002±0.0^{b}	0.004±0.0^{b}	0.002±0.0^{c}	0.005±0.0^{bc}
Pb (mg/L)	0.438±0.06^{c}	0.341±0.06^{a}	0.236±0.05^{ab}	0.332±0.1^{a}	0.231±0.1^{ab}	0.329±0.1^{a}	0.227±0.0^{ab}

Table 2b: Mean ± SD Physicochemical Parameters and Heavy Metals Treated with Glyphosate Herbicide, July 2025

	Week 4		Week 5		Week 6		WHO STD
Parameter	G1	G2	G1	G2	G1	G2	
TEMP (˚C)	23.1±0.1^{c}	23.4±0.1^{b}	23.2±0.1^{c}	23.5±0.1^{ab}	23.3±0.1^{b}	23.5±0.1^{a}	23–35
pH	8.19±0.0^{a}	7.45±0.0^{e}	8.19±0.0^{a}	7.45±0.0^{e}	8.19±0.0^{a}	7.45±0.0^{e}	6.5–8.5
EC (µS/cm)	586.67±2.0^{c}	1955.0±2.0^{a}	589.00±3.0^{c}	1954.3±3.5^{a}	588.33±2.5^{c}	1955.3±2.1^{a}	≤1000
DO (mg/L)	2.8±0.1^{d}	2.0±0.1^{f}	2.8±0.1^{d}	2.0±0.1^{f}	2.8±0.1^{d}	2.0±0.1^{f}	≥5.0
TDS (mg/L)	297.00±1.0^{c}	976.33±1.5^{a}	299.33±1.5^{c}	977.00±2.0^{a}	299.00±1.0^{c}	977.67±1.5^{a}	≤500
NO_3-N (mg/L)	27.30±0.2^{e}	30.90±0.1^{b}	27.20±0.1^{e}	31.10±0.1^{b}	27.20±0.2^{e}	31.06±0.1^{b}	≤50
PO_4-P (mg/L)	0.92±0.0^{a}	0.83±0.0^{bc}	0.92±0.0^{a}	0.83±0.0^{b}	0.92±0.0^{a}	0.83±0.0^{b}	≤0.3
Zn (mg/L)	0.008±0.0^{c}	0.010±0.0^{c}	0.007±0.0^{c}	0.009±0.0^{c}	0.008±0.0^{c}	0.010±0.0^{c}	≤3.0
Cd (mg/L)	0.002±0.0^{b}	0.005±0.0^{b}	0.002±0.0^{c}	0.004±0.0^{bc}	0.002±0.0^{c}	0.004±0.0^{bc}	≤0.003
Pb (mg/L)	0.320±0.1^{ab}	0.220±0.0b^{cd}	0.324±0.1^{ab}	0.223±0.0b^{cd}	0.320±0.1^{ab}	0.223±0.0b^{cd}	≤0.01

Table 3a: Mean ± SD Physicochemical Parameters and Heavy Metals Treated with 2, 4-D Herbicide, July 2025

		Week 1		Week 2		Week 3	
Parameter	Control	D1	D2	D1	D2	D1	D2
TEMP (˚C)	23.5±0.10^{ab}	23.4±0.10^{b}	23.6±0.10^{a}	23.4±0.10^{b}	23.6±0.10^{a}	23.4±0.10^{b}	23.6±0.10^{a}
pH	7.63±0.01^{d}	7.61±0.01^{e}	7.62±0.01^{de}	7.63±0.01^{d}	7.60±0.01^{e}	7.62±0.01^{c}	7.61±0.01^{c}
EC (μS/cm)	298.67±3.5^{f}	1068.67±3.5^{b}	1070.33±1.5^{b}	1069.67±1.5^{b}	1072.33±2.5^{b}	1070.0±1.0^{b}	1072.6±1.5^{b}
DO (mg/L)	3.5±0.10^{b}	3.8±0.10^{a}	3.8±0.10^{a}	3.9±0.06^{a}	3.8±0.06^{a}	3.8±0.06^{a}	3.9±0.06^{a}
TDS (mg/L)	147±2.6^{g}	533.33±3.1^{b}	193.33±1.5^{f}	535±1.0^{b}	195±1.0^{f}	534.00±1.0^{b}	194.00±1.0^{f}
NO_3-N (mg/L)	27.63±0.55^{de}	30.00±0.20^{c}	28.00±0.20^{d}	30.00±0.10^{c}	28.00±0.10^{d}	30.10±0.10^{c}	28.10±0.10^{d}
PO_4-P (mg/L)	0.82±0.01^{b}	0.63±0.01^{c}	0.83±0.01^{b}	0.63±0.0^{d}	0.83±0.0^{bc}	0.64±0.0^{d}	0.83±0.0^{bc}
Zn (mg/L)	0.002±0.01^{d}	0.055±0.01^{b}	0.003±0.00^{cd}	0.054±0.0^{b}	0.004±0.0^{cd}	0.056±0.0^{b}	0.005±0.0^{cd}
Cd (mg/L)	0.011±0.00^{b}	0.005±0.01^{bc}	0.010±0.07^{bc}	0.006±0.0^{b}	0.004±0.0^{b}	0.006±0.0^{bc}	0.004±0.0^{bc}
Pb (mg/L)	0.438±0.06^{c}	0.239±0.12^{ab}	0.364±0.03^{a}	0.236±0.1^{ab}	0.355±0.0^{a}	0.236±0.1^{ab}	0.350±0.0^{a}

Table 3b: Mean ± SD Physicochemical Parameters and Heavy Metals Treated with 2, 4-D Herbicide, July 2025

	Week 4		Week 5		Week 6		WHO STD
Parameter	D1	D2	D1	D2	D1	D2	
TEMP (˚C)	23.4±0.1^{b}	23.6±0.1^{a}	23.5±0.1^{ab}	23.6±0.1^{a}	23.5±0.1^{a}	23.6±0.1^{a}	23–35
pH	7.63±0.0^{c}	7.61±0.0^{d}	7.63±0.0^{d}	7.62±0.0^{d}	7.63±0.0^{d}	7.62±0.0^{d}	6.5–8.5
EC (μS/cm)	1071.6±1.5^{b}	1074.0±1.0^{b}	1072.0±2.0^{b}	1073.0±2.0^{b}	1071.3±1.5^{b}	1073.0±1.0^{b}	≤1000
DO (mg/L)	3.8±0.1^{a}	3.8±0.1^{a}	3.8±0.1^{a}	3.8±0.1^{a}	3.8±0.1^{a}	3.8±0.1^{a}	≥5.0
TDS (mg/L)	533.00±1.0^{b}	193.00±1.0^{f}	536.00±1.0^{b}	195.00±1.0^{f}	536.00±1.0^{b}	195.00±1.0^{f}	≤500
NO_3-N (mg/L)	30.10±0.1^{c}	28.10±0.1^{d}	30.00±0.1^{c}	28.00±0.1^{d}	30.10±0.1^{c}	28.00±0.1^{d}	≤50
PO_4-P (mg/L)	0.63±0.0^{d}	0.84±0.0^{b}	0.63±0.0^{d}	0.82±0.0^{bc}	0.63±0.0^{d}	0.82±0.0^{bc}	≤0.3
Zn (mg/L)	0.058±0.0^{b}	0.005±0.0^{cd}	0.056±0.0^{b}	0.006±0.0^{cd}	0.056±0.0^{b}	0.005±0.0^{cd}	≤3.0
Cd (mg/L)	0.006±0.0^{b}	0.004±0.0^{b}	0.006±0.0^{bc}	0.004±0.0^{bc}	0.006±0.0^{bc}	0.004±0.0^{bc}	≤0.003
Pb (mg/L)	0.232±0.1^{abc}	0.345±0.0^{a}	0.235±0.1^{abc}	0.346±0.0^{a}	0.234±0.1^{abc}	0.345±0.0^{a}	≤0.01

Such changes are ecologically important because pH influences nutrient availability and the solubility of heavy metals, with lower pH increasing the bioavailability of metals such as lead and cadmium (Pérez et al., 2011).

Electrical conductivity (EC) and total dissolved solids (TDS) increased following herbicide exposure, particularly in glyphosate and 2,4-D treatments, indicating increased ionic concentrations in the water. These increases are likely associated with dissolved ions from herbicide formulations, degradation products, and the mobilization of soil salts and associated metals. Similar increases have been reported in River Kaduna and other agricultural watersheds affected by agrochemical runoff (Onoyima, 2022).

Dissolved oxygen (DO) declined following herbicide application, with the greatest reduction occurring in glyphosate-treated water. The decrease may be attributed to reduced photosynthetic activity of aquatic primary producers and increased microbial respiration during herbicide degradation, leading to greater biological oxygen demand. Metolachlor caused moderate reductions in DO, whereas 2,4-D produced comparatively smaller effects, suggesting lower disruption of aquatic microbial and algal communities (Lozano et al., 2017).

Nitrate concentrations remained within the WHO permissible limit for drinking water, whereas phosphate concentrations were comparatively elevated. Increased phosphate levels may enhance eutrophication, promoting excessive growth of algae and cyanobacteria and contributing to fluctuations in dissolved oxygen. Similar observations have been reported for herbicide-contaminated freshwater systems where nutrient enrichment alters ecosystem functioning and aquatic food-web dynamics (Cornish, 2023).

Heavy metal analysis revealed that lead and cadmium concentrations exceeded the WHO guideline values in most treatments, whereas zinc remained within acceptable limits. Elevated lead and cadmium concentrations are likely associated with agricultural runoff, industrial discharges, urban wastewater, and changes in water chemistry following herbicide application that enhance metal mobility. The lower pH observed in glyphosate treatments may have further increased the solubility and bioavailability of these metals. Although zinc concentrations remained relatively low, combined exposure to multiple metals may still pose ecological risks to aquatic organisms.

Overall, the findings demonstrate that herbicide application can alter key physicochemical characteristics of freshwater systems and influence heavy metal dynamics. These changes may reduce water quality, increase metal bioavailability, and create conditions that threaten aquatic ecosystem health, emphasizing the need for effective management of agricultural runoff and continuous monitoring of freshwater resources.

Conclusion

This study demonstrates that glyphosate, metolachlor, and 2,4-D alter the water quality profile of River Kaduna. High exposure concentrations increase electrical conductivity and total dissolved solids, suppress dissolved oxygen levels, and promote the mobilization of lead and cadmium beyond WHO permissible limits. Glyphosate exerted the largest influence on physical ionic metrics, whereas metolachlor and 2,4-D significantly affected nutrient balance and lead mobilization, respectively. These findings highlight the need to monitor agricultural chemical runoff to protect freshwater ecosystems and downstream users.

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Author Contribution

All authors contributed to the conceptualization, methodology, data collection, analysis, interpretation of results, manuscript preparation, critical revision, and approval of the final manuscript.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the research, authorship, and publication of this manuscript.

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