Environmental Science and Pollution Research
https://doi.org/10.1007/s11356-023-27622-w

RESEARCH ARTICLE

Pollution and risk assessment of phenolic compounds in drinking water sources from South-Western Nigeria

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Received: 8 November 2022 / Accepted: 9 May 2023

Abstract

This study reports the occurrence and risk assessment of 2,4-dinitrophenol (2,4-DNP), phenol (PHE), and 2,4,6-trichlorophenol (2,4,6-TCP) in drinking water sources in three south-western States in Nigeria (Osun, Oyo, and Lagos). Groundwater (GW) and surface water (SW) were collected during dry and rainy seasons of a year. The detection frequency of the phenolic compounds followed the trend Phenol > 2,4-DNP > 2,4,6-TCP. The mean concentrations of 2,4-DNP, Phenol, and 2,4,6-TCP in GW/SW samples from Osun State were 639/553 μg L−1, 261/262 μg L−1, and 169/131 μg L−1 during the rainy season and 154/7 μg L−1, 78/37 μg L−1, and 123/15 μg L−1 during the dry season, respectively. In Oyo State, the mean concentrations were 165/391 μg L−1 for 2,4-DNP and 71/231 μg L−1 for Phenol in GW/SW samples, respectively, during the rainy season. Generally, in the dry season, these values decreased. In any case, these concentrations are higher than those previously reported in water from other countries. The concentration of 2,4-DNP in water posed serious ecological risks to Daphnia on the acute scale while it was algae on the chronic scale. Estimated daily intake and hazard quotient calculations suggest that 2,4-DNP and 2,4,6-TCP in water pose serious toxicity concerns to humans. Additionally, the concentration of 2,4,6-TCP in water from Osun State in both seasons of the year and in both groundwater and surface water poses significant carcinogenic risks to persons ingesting water from these sources in the State. Every exposure group studied were at risk from ingesting these phenolic compounds in water. However, this risk decreased with increasing age of the exposure group. Results from the principal component analysis indicate that 2,4-DNP in water samples is from an anthropogenic source different from that for Phenol and 2,4,6-TCP. There is a strong need to treat water from GW and SW systems in these States before ingesting while assessing their quality regularly.

Keywords Environment · Groundwater · 2,4-Dinitrophenol · Carcinogenic · 2,4,6-Trichlorophenol · Hazard risks

Introduction

Due to phenolic compounds' carcinogenicity, neurotoxicity, mutagenicity, and endocrine-disrupting abilities, surveillance has been increased on them in the aquatic environment. Phenolic compounds such as Phenol, 2,4-dinitrophenol (2,4-DNP), and 2,4,6-trichlorophenol (2,4,6-TCP) are listed as priority pollutants in water by the United States Environmental Protection Agency (USEPA 2011). Phenolic compounds are organic chemicals with special structures consisting of an aromatic ring with one or more hydroxyl (–OH) functional groups. These –OH functionalities make phenolic compounds soluble in water, increasing their prevalence and easy transportation around surface water and in groundwater. Their presence has been reported across international borders and in places where they have never been used. A good example is the earth's pole (Jacob and Cherian 2013).

Responsible Editor: Xianliang Yi

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The presence of Phenol and 2,4-dinitrophenol in water stems from their massive utilisation in agricultural industries for the production of pesticides and fertilisers. 2,4-Dinitrophenol is also used in weight control pills (Gziut and Thomas 2022). Other sources of phenolic contamination in our water bodies are wastewater from industries such as textile, dyeing, and pharmaceutical (in the manufacture of personal care products). These phenolic compounds have the potential to bio-accumulate primarily because of their low biodegradability index (Zhou et al. 2017). This ability to bioaccumulate is amplified in the aquatic food chain (Al-Ahmari et al. 2018; Alharbi et al. 2018).

Phenolic compounds have caused a vast array of health challenges in humans, including endocrine disruption and toxicity to reproductive organs (Wolff et al. 2015; Zhang et al. 2017), alteration in growth and development, attack on the immune system (Goulart and Mascaro 2016), and carcinogenicity and neurotoxicity (Bolton and Dunlap 2017). Specifically, chlorophenols and nitrophenols are known to cause high fever, gastro-intestinal disturbances, cardiac arrest, headache, confusion and convulsions, histopathological alterations, genotoxicity (Chen et al. 2017; Lu et al. 2011), mutagenicity (Zhang et al. 2017), heart diseases, sarcoma, asthma (Igbinosa et al. 2013), lung cancer in living organisms (Honda and Kannan 2018), and thyroid-hormone disrupting effects (Hernández et al. 2020). One of such nitrophenols, 2,4-dinitrophenol (2,4-DNP), is noted to be the most noxious, having an LD_{50} around 30 mg kg^{-1} body weights in rats (Shea et al. 1983). 2,4-DNP is toxic at certain concentrations, and prolonged exposure to it through inhalation and skin absorption could affect the bone marrow, cause breakdown of the central nervous system, affect the cardiovascular system, cause cataracts, and increased metabolism resulting in fever, headache, profuse sweating, thirst, fatigue, and more. From animal studies, 2,4-DNP is teratogenic, mutagenic, and carcinogenic (Grundlingh et al. 2011). For 2,4,6-TCP, it is documented that it causes endocrine disruption and induces liver cancer, lymphomas, leukaemia, and hemangiosarcoma in rodents (Jung et al. 2004; McConnell et al. 1991; Program 1979). On the other hand, Phenol impacts water with unpleasant odour and taste, which reduces the quality and quantity of water available for human consumption (Yahaya et al. 2019). The hydrophobicity of these phenolic compounds, their ability to form free radicals, their low concentrations in water (usually at ng L^{-1}–μg L^{-1} levels), and the complexity of environmental matrices make them even more toxic, which makes monitoring of these pollutants necessary.

There are reports from China (Chen et al. 2021; Wang et al. 2020), Brazil (Ramos et al. 2021), Egypt (El-Naggar et al. 2022), South Africa (Yahaya et al. 2019), India (Kumar, 2018), and Malaysia (Al-Janabi et al. 2012) about the presence of these priority pollutants in their water bodies. A few countries, especially North America (USA and Canada) and Europe, have successfully tackled the problem of phenolic contamination in their water bodies. As a result, there have been very few reports of these chemical compounds in their water bodies since the last decade. In contrast, high concentrations of phenolics compounds have been found in a few countries in Asia and Africa, e.g., China, India, South Africa and Egypt, indicating some level of increasing industrialisation in these countries.

In addition, several developed countries have in place permissible concentration limits for the presence of these phenolic compounds in their water especially drinking water. Countries in Europe, for example, put the maximum level of chlorophenol in drinking water at 2 μg L^{-1} (WHO 2017), Canada at 2 μg L^{-1} (Warrington, 2021), India at 1 μg L^{-1} (Chand, 2018), China at 0.2 μg L^{-1} (Liu, 2009), Australia at 2 μg L^{-1} (Batley, 2014), and the World Health Organization (WHO) at 1 μg L^{-1} (WHO, 2017). The USEPA recommends 10 μg L^{-1} as the maximum concentration limit for 2,4-DNP in drinking water in the United States of America. It is even regarded as a priority pollutant by the Clean Water Act (Al-Mutairi 2010). While the USEPA has placed a maximum permissible limit of 1.0 mg L^{-1} for Phenol in wastewater, the WHO has 0.1 mg L^{-1} as its maximum permissible limit for the same in drinking water (Sonawane and Korake 2016). In Brazil, the Brazilian Potability Standard for drinking water set the maximum permissible level for 2,4,6-TCP at 200 ng L^{-1} (Sartori et al. 2012). However, there is a dearth of data on the presence of these phenolic compounds in water bodies and drinking water sources in Africa, even though these chemical compounds are vastly used in industries and particularly for agricultural purposes in the continent. Consequently, no limit has been determined for these priority pollutants in aquatic environments in African countries.

To make matters worse for millions of Africans, the major sources of drinking water are some of these aquatic environments, including streams, rivers, hand-dug wells, and boreholes. In fact, it is estimated that >50% of Africans use groundwater as their primary source of drinking water (https://businessday.ng/opinion/article/world-water-day-2022-where-are-we/). Water from these sources is usually not pre-treated before use. The quality of these drinking water sources from Africa and especially Nigeria, with respect to phenolic compounds, is relatively unknown.

Based on these observed gaps, this study aims to provide baseline data on the occurrence of some phenolic compounds [Phenol, 2,4-dinitrophenol (2,4-DNP), and 2,4,6-trichlorophenol (2,4,6-TCP)] in groundwater and surface water samples from three States in Southwestern Nigeria (Osun, Oyo, and Lagos States). Osun State is mainly an agricultural State, while the populace in Oyo State are government workers and as such it has several more urban areas than Osun State. Lagos State is one of the highly industrialized States in Nigeria and is regarded as a metropolitan State. Both Osun and Oyo States are closest to Lagos State in the Southwest of Nigeria. 2,4-DNP and Phenol were chosen based on their massive utilisation for agricultural purposes in this region of Nigeria, especially as constituents of fertilisers and pesticides, and also as component of paints while 2,4,6-TCP was selected since it is mainly a by-product of chlorination of water containing Phenol or certain aromatic acids, a process still being practiced in Nigeria. The choice of groundwater and surface water is because in most parts of Nigeria, especially in the Western region, groundwater and surface water are the primary potable water sources. Data from this study will be useful to policy-makers and water treatment professionals who will need them to develop guidelines and effective treatment strategies for the abatement of these chemical contaminants in water in Nigeria and the African continent.

Materials and methods

Chemicals

Analytical standards of HPLC grades for Phenol, 2,4-Dinitrophenol (2,4-DNP), and 2,4,6-Trichlorophenol (2,4,6-TCP) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Methanol, ethyl acetate, dichloromethane, and acetonitrile were also obtained from Sigma-Aldrich (St. Louis, MO, USA). Similarly, other chemicals, such as concentrated hydrochloric acid, were obtained from Sigma-Aldrich (St. Louis, MO, USA) and were of analytical standard; ultrapure water was generated from a water purification system using Milli-Q Direct 8/16. The standard stock solutions of each analyte (20 mg L^{-1}) were prepared singly in ultrapure water and stored at 4 °C. Working solutions were spiked with 200 μg L^{-1} of the mixed phenolic compounds in the dilute stock solution prepared with ultrapure water.

Description of the study area

Osun, Oyo, and Lagos States belong to the tropical rainforest Biome in South-western Nigeria and lie between lat. 06° 30′ N and long. 04° 30′ E, lat. 7° 51′ N, and long. 3° 55′ E and lat. 6° 27′ N and 3° 24′ 23′ E, encompassing areas of approximately 14,875, 28,454, and 3,577 km^2, respectively. Coordinates for each sampling site is presented in the supporting information document (Table S1). The sampling States for this study are shown in Fig. 1.

Sample collection

Water samples from groundwater (hand-dug wells and boreholes) from 34 locations (Table S1) were collected using a polyethene bailer just below the water level (hand-dug well) and directly into sample bottles from the study area for 1 year, covering rainy and dry seasons. Similarly, surface water samples were randomly collected from 31 locations (Table S1) cutting across major rivers (Epe River in Lagos and Osun river in Osun State) and a water dam (Asejire in Oyo State). Samplings were done between April 2021 to March 2022, and each sample was collected in triplicate.

At each sampling site, samples of groundwater were taken ($n = 3$) and made into a composite. At the same time, for surface water, grab samples ($n = 3$) were collected from all the sampling sites in Osun, Oyo, and Lagos States, Nigeria, but not made into composites. Physicochemical analysis of samples

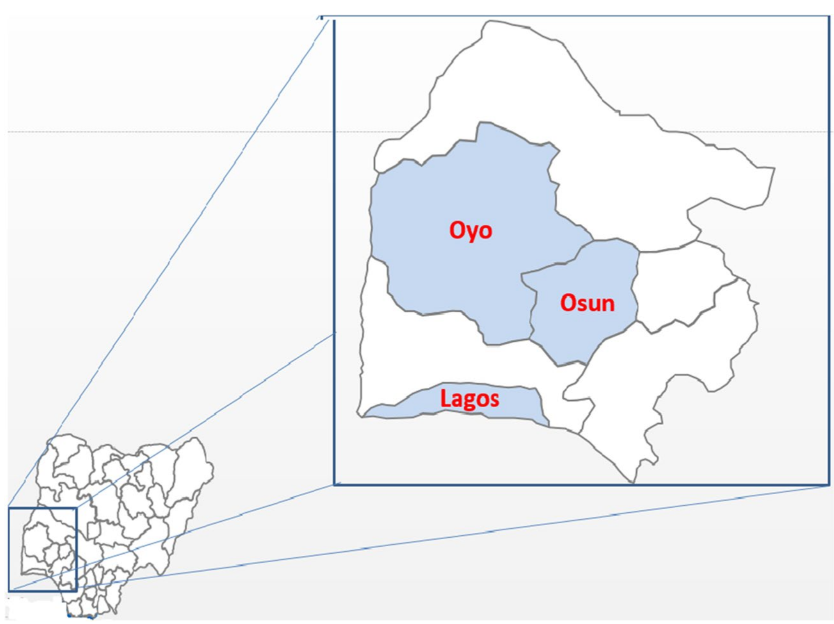

Fig. 1 The map of Southwestern States in Nigeria where the sampling campaign was conducted

was done with Hanna probe with capacity to measure pH and electrical conductivity, while total dissolved solids (TDS) were measured with a TDS meter. Results of some physicochemical analysis of these samples are shown in Table S2 (SI document).

Furthermore, the influence of seasonal variations on the amount and distribution of these phenolic compounds [2,4-dintrophenol (2,4-DNP); phenol; 2,4,6-trichlorophenol (2,4,6-TCP)] in water was studied. Three sampling campaigns (one for each State) were carried out during the rainy season (April to September 2021) and three also during the dry season (December to March 2022).

Groundwater and surface water samples (500 mL) from the field were stored in amber glass bottles already prewashed with methanol and ultrapure water and kept in ice packs to maintain the integrity of the samples. The samples were transported to the laboratory and stored at 4 °C. Extraction of analytes from water samples was done within 24 h.

Instrumental analysis

Prior to instrumental analysis, pre-treatment of samples was done using the solid phase extraction technique. Details of the procedure for this technique is provided in Section S1 (SI document). The quantification of the analytes in the reconstituted eluents was done using the high-performance liquid chromatography system with a UV detector (Agilent Series 1100). Analytes were separated using a C18 column (5 µm particle size, 250 × 4.6 mm i.d.), and all sample injections were done automatically by an autosampler. Methanol (HPLC grade) was used as the mobile phase at a flow rate of 0.5 mL/min [isocratic elution of water/methanol (30/70, v/v)]. The injection volume was 20 µL with a total run time of 17 min. The wavelength detector for the analytes was 220 nm.

Quality assurance and quality control

Procedural blanks were used to check for possible contamination and interferences from solvents and materials used in the extraction process. This was done with every extraction batch. The concentrations obtained from the procedural blanks were deducted from the known concentrations of the environmental samples. Methanol blank and midpoint calibration standard were injected after each batch analysis to check for discrepancies in instrumental response and carryover of the analytes of interest from prior injections. Quantification of analytes was carried out using the phenolic standards, and a standard calibration curve was obtained by analysing aqueous solutions containing the analytes of interest ranging from a concentration of 10 to 1000 µg L^{-1}.

Results suggest that standard deviations for data obtained were <20% for both types of water samples from Osun and Lagos States, <20% in groundwater samples from Oyo State, and 26% for Phenol from surface water in Oyo State. The instrumental quantification limit was determined at three times the signal-to-noise ratio using the standard deviation of the seven-point calibration intercepts divided by the slope, and the limit of quantification (LOQ) was calculated as ten times the ratio. The LOD ranged from 17 to 40 µg L^{-1}, and the coefficients of determination (r^2) of calibration curves were 0.999 for Phenol and 2,4-dinitrophenol and 0.998 for 2,4,6-trichlorophenol. The coefficients of determination as well as LOD and LOQ values are presented in Table S3.

Ecological risk assessment

The basis for the ecological risk assessment of phenolic compounds in this study is obtained from the US EPA ecological risk assessment framework (Chakraborty et al. 2016; Chen et al. 2014). The risk quotient (RQ) method was used to determine the toxicity levels of these phenolic compounds. The RQ is determined as follows:

$$RQ = \frac{MEC}{PNEC} \quad (1)$$

where RQ is the risk quotient; PNEC is the Predicted No Effect Concentration of compounds (µg/L) and MEC is the Measured Environmental Concentration of the compounds in water samples (µg/L). The PNEC is calculated for both acute and chronic tests using the EC_{50}/LC_{50} and NOEC, respectively, divided by an assessment factor (AF) (Wang et al. 2019a).

$$PNEC_{acute} = \left(EC_{50}/LC_{50} \text{ of three acute toxicity tests}\right)/AF_{acute} \quad (2)$$

$$PNEC_{chronic} = \text{NOEC in chronic tests}/AF_{chronic} \quad (3)$$

where EC_{50}/LC_{50} is the median effect/lethal concentration and NOEC is the no observed effect concentration.

The acute toxicity data (LC_{50} or EC_{50}) and chronic toxicity data (NOEC, LOEC, EC_{50}, and MATC) used in the current study for ecological risk assessment of Phenol, 2,4-DNP, and 2,4,6-TCP in three south-western states in Nigeria were obtained from existing literature, entailing three aquatic organisms [algae, invertebrates (*Daphnia*), and vertebrates (fishes)].

The ecological risk were grouped into three levels according to the RQ values with RQ >1 indicating a high ecological risk, RQ values between 0.1 < RQ < 1 signifying a median risk, and RQ < 0.1 suggesting a minimal environmental risk (Wang et al. 2019b).

Health risk assessment

The human risk is categorized into non-carcinogenic risk and carcinogenic risk. The non-carcinogenic risk (NCR) is calculated in terms of a hazard quotient (HQ) (Gerba 2019), where

$$HQ = CDI/RfD \tag{4}$$

RfD = oral reference dose (2,4,6-TCP = 1.1×10^{-2} mg kg^{-1} day^{-1}; 2,4-DNP = 2×10^{-3} mg kg^{-1} day^{-1}; phenol = 0.3 mg kg^{-1} day^{-1})

$$\text{But } CDI = (C \times DI \times EF \times ED)/(BW \times AT) \tag{5}$$

Where C = highest phenolic compound concentration found (mg L^{-1})

DI = daily intake (2.4 L day^{-1})

EF = exposure frequency (days/years)

ED = exposure duration (30 years for adult and 6 years for children as national upper bound time at one residence which is the 90th percentile)

BW = body weight (80 kg for adult and 30 kg for children), and

AT = averaging times in days (AT_{Adult} = 10950 days and $AT_{Children}$ = 2190 days) (EPA, 2015; Gerba 2019).

Moreover, the risk of cancer is calculated using

$$CR = CDI\ mg/kg/day * CSF\ mg/kg/day \tag{6}$$

where

CR = cancer risk

CSF = cancer slope factor which is 1.1×10^{-2} mg kg^{-1} day^{-1} for 2,4,6-TCP (Iris 2011). Phenol and 2,4-DNP are yet to have OSF values.

The HQ of the non-carcinogenic risk is categorized as HQ >1, indicating a high non-carcinogenic risk, while HQ <1 indicates non-carcinogenic risk. The carcinogenic risk, however, is categorized into negligible risk ($CR < 10^{-6}$), possibility of cancer ($CR > 10^{-6}$), and unacceptable risk ($CR > 10^{-4}$) (Zhou et al. 2017). The CR was calculated for all the phenolic compounds with CSF for the compounds in water as found in the literature ((EPA), 2002; IB and Assessment 1993).

Due to the simultaneous presence of these phenolic compounds, the hazard index (HI), which predicts the potential harm caused from exposure to more than one chemical via the sum of the individual hazard quotients for each chemical, was also used in this study:

$$HI = \text{sum of hazard quotients} \tag{7}$$

If HI is >1.0, then the water is unsafe for drinking. The closer the HI value is to 1.0, the more unsafe the drinking water is.

Statistical analysis

Statistical analyses were carried out using the Statistical Package for The Social Sciences (SPSS Statistics23; IBM Corporation, Cornell, NY, USA) and Origin (OriginLab 9.1). The variation in the concentrations between the urban and rural sampling sites in Osun, Oyo, and Lagos States was determined by the Kruskal-Wallis test; furthermore, nonparametric Spearman correlation informed us about the relationship between the concentrations of the phenolic compounds, statistical significance was set at *p* value less than 0.05. Multivariate statistical analysis was carried out using the principal component analysis (PCA) software, which was used to further interrogate the significant association between the phenolic compounds. The principal component analysis is a vastly used multivariate statistical method of analysis in environmental studies (Adesanya et al. 2020; Ogunlaja et al. 2019). It has been established as an instrument for the identification of contamination sources and also used substantially to confirm the association between diverse environmental variables and/or total variability of a data set (Awolusi et al. 2018; Bolujoko et al. 2022; Ogunlaja et al. 2019).

Results and discussions

Occurrence of phenolic compounds in surface water and groundwater

From Fig. 2A–D, it is generally observed that the frequency of detection of these phenolic compounds was higher in the rainy season than in the dry season with the highest detection frequencies found in water samples from Osun State and the lowest found in those from Lagos State.

Phenol was more frequently detected in water samples from the different sampling sites in the three States (Osun, Oyo, Lagos) with as much as 100% detection frequency

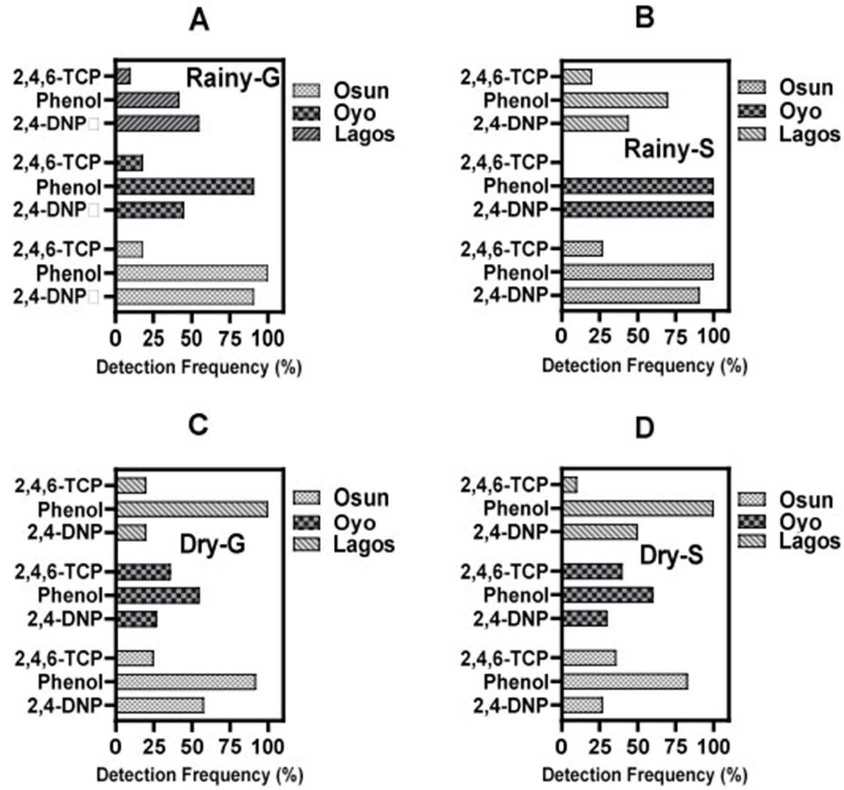

Fig. 2 Detection frequency of phenolic compounds in water samples collected from Osun, Oyo, and Lagos States in Nigeria (Rainy-G = rainy season groundwater samples; Rainy-S = rainy season surface water samples; Dry-G = dry season groundwater samples; Dry-S = dry season surface water samples)

(Fig. 2A–D) irrespective of the season of the year (rainy or dry season) or the source of the water (groundwater or surface water). However, in most cases, phenol had higher detection frequencies in surface water samples than in groundwater samples. 2,4,6-TCP is the least frequently detected phenolic compound in water samples from all three States (≤50% detection frequencies) for both seasons. Nonetheless, from the raw data obtained (not presented), the presence of 2,4,6-TCP in groundwater samples from most sample sites in Oyo State was below the limit of detection.

Figure 3 shows the box plots for the median, maximum, and minimum concentrations of the various phenolic compounds in the water samples collected from the three States. From Fig. 3, it is observed that data for the presence of Phenol and 2,4,6-TCP in water samples from Osun State during the rainy season have a high level of agreement for both surface water and groundwater samples indicating that the concentrations of these phenolic compounds in samples collected from the different sites in this State are within close range. Data for samples from the other two States (Oyo and Lagos) during the rainy season generally have lower levels of agreement. However, data variability is reduced in the dry season except for data from Osun State (Fig. 3).

The median concentration values for these phenolic compounds are higher in the rainy season than in the dry season from samples from Osun State, but the reverse is the case with the samples from Oyo and Lagos States.

Considering the mean concentration values of these phenolic compounds in water samples from the different sites in the various States, we note that 2,4-DNP has the highest mean values for both seasons (rainy and dry seasons) and in both groundwater and surface water (Fig. 4A–D). Apparently, the mean concentrations of 2,4-DNP in groundwater samples were higher than those for surface water samples from the three States for both seasons (rainy and dry). The exception to these observations is water samples collected during the rainy season in Oyo State (Fig. 3).

This observation with mean concentrations is because of the increase in farming activities in Nigeria during this season which requires the application of fertilisers, pesticides, and herbicides. 2,4-DNP being an essential constituent of pesticides and foliage fertilisers applied to farmlands during the rainy season is washed off into water bodies and percolate into groundwater (Luo et al. 2014; Ramos et al. 2021; Zhong et al. 2018). The mean concentration levels of 2,4-DNP in water samples from Osun State are higher during the rainy season for this reason since the State is known mainly for agriculture. Furthermore, during this season, there is an increase in stormwater across the three States' discharge that increases the level of 2,4-DNP in water (Yahaya et al. 2019).

Analysis for the presence of 2,4,6-TCP in most groundwater and surface water samples during the rainy season in Oyo and Lagos States indicates concentrations that are below the detection limit. However, 2,4-DNP was found

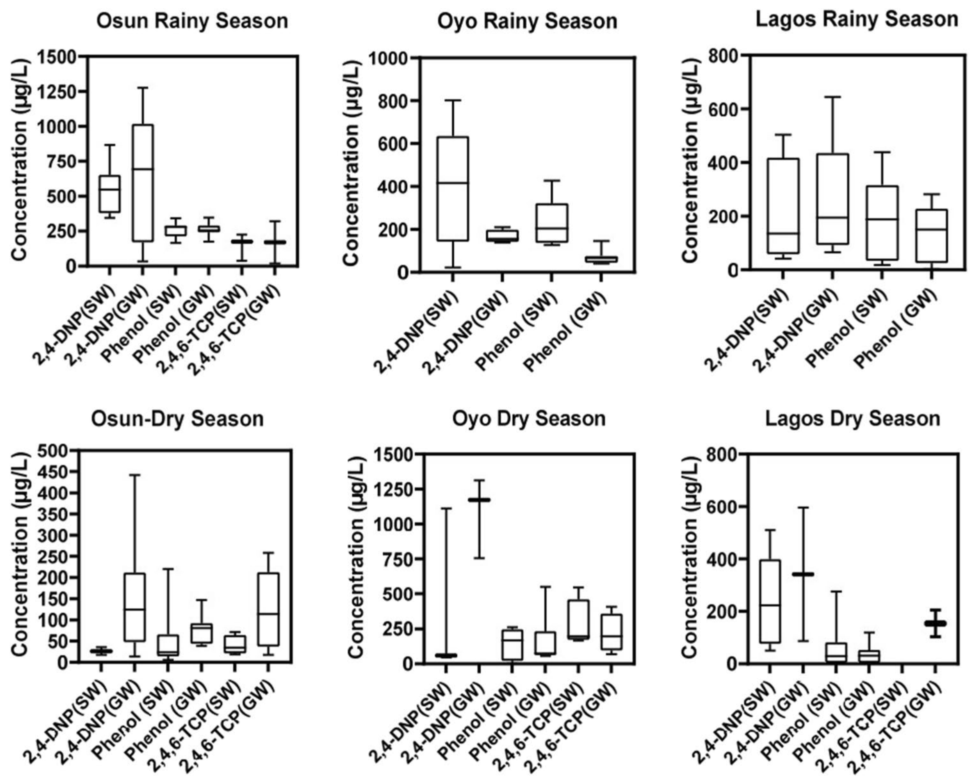

Fig. 3 Box plots for median, maximum, and minimum concentrations of phenolic compounds in water samples collected from Osun, Oyo, and Lagos States in Nigeria (SW = surface water; GW = groundwater; 2,4-DNP = 2,4-Dinitrophenol; 2,4,6-TCP = 2,4,6-Trichlorophenol)

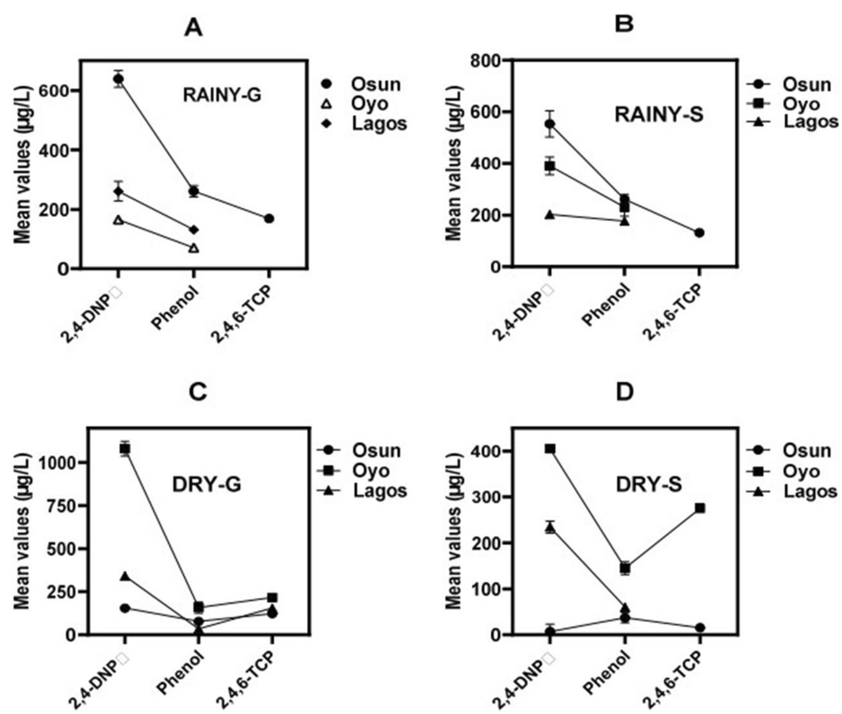

Fig. 4 Plots of mean concentration values of phenolic compounds in water samples from Osun, Oyo, and Lagos States in Nigeria (Rainy-G = rainy season groundwater samples; Rainy-S = rainy season surface water samples; Dry-G = dry season groundwater samples; Dry-S = dry season surface water samples)

in less amounts in water samples from Oyo and Lagos States with the latter being the least. This is especially so because Lagos State is a metropolitan city with very few agricultural activities.

Precisely, the mean concentrations of 2,4-DNP in groundwater (639.2 µg L^{-1}) and surface water (553.4 µg L^{-1}) from Osun State were highest among the three States during the rainy season (Fig. 4A, B). It should be noted that 2,4-DNP in the groundwater samples from Osun State had a mean concentration of 154.2 μg L^{-1} while Phenol and 2,4,6-TCP had mean concentrations of 77.7 μg L^{-1} and 122.9 μg L^{-1}, respectively, during the dry season. The mean concentrations 639.2 μg L^{-1} for 2,4-DNP, 261 μg L^{-1} for Phenol, and 169 μg L^{-1} for 2,4,6-TCP in groundwater samples during the rainy season were observed from this State (Fig. 4A, B). The mean concentrations for 2,4-DNP, Phenol, and 2,4,6-TCP in surface water samples in Osun are 553 μg L^{-1}, 261 μg L^{-1}, and 146 μg L^{-1}, respectively, during the rainy season and 25 μg L^{-1}, 42 μg L^{-1}, and 40 μg L^{-1} during the dry season, respectively.

However, in the dry season, analysis of groundwater and surface water samples from Oyo State for the presence of 2,4-DNP gave the highest mean concentration values of 1080 μg L^{-1} and 405 μg L^{-1}, respectively (Fig. 4C, D). Basically, groundwater samples from Oyo State had mean concentration values of 1080 μg L^{-1} for 2,4-DNP, 157 μg L^{-1} for Phenol, and 216 μg L^{-1} for 2,4,6-TCP during the dry season. In the rainy season, the mean concentration values are 165.3 μg L^{-1} for 2,4-DNP and 71 μg L^{-1} for Phenol. There were no mean concentration values for 2,4,6-TCP in groundwater samples from this State in the rainy season because results were all below detection limits for this phenolic compound. For surface water samples, the mean concentration values were 405 μg L^{-1} for 2,4-DNP, 145 μg L^{-1} for Phenol, and 275.6 μg L^{-1} for 2,4,6-TCP during the dry season. Furthermore, the mean concentration values were 391 μg L^{-1} for 2,4-DNP and 171 μg L^{-1} for Phenol during the rainy season (Fig. 4A–D).

The mean concentration values for these phenolic compounds in groundwater samples from Lagos State in the rainy season are 260 and 131 μg L^{-1} for 2,4-DNP and phenol, respectively; in the dry season 341.6, 34.3, and 154 μg L^{-1} for 2,4-DNP, Phenol, and 2,4,6-TCP respectively. For surface water samples collected from this State, the mean concentrations for 2,4-DNP and Phenol were 203 and 177 μg L^{-1} in the rainy season and 235 and 60 μg L^{-1} in the dry season, respectively (Fig. 4A–D). The mean concentrations for 2,4,6-TCP in groundwater and surface water samples from this State were not reported because it was observed that ca. 98% of the samples had below detection limit concentrations of this phenolic compound.

Although 2,4-DNP had the highest mean concentration values in the water samples studied, the concentrations of phenol in these samples were also significantly high. This might not be unconnected with the increasing use of personal care products by millions of Nigerians, most especially as disinfectants and sunscreens, hair dyes, and relaxers. These products are known to contain Phenol. Furthermore, the biodegradation of substituted phenolic compounds by microorganisms in the aqueous soil phase may result in the formation of Phenol (Preda et al. 2018). However, there is generally a decrease in the maximum concentrations of the three phenolic compounds in water samples during the dry season except for samples from Oyo State where the reverse is the case. This is because samples from this State were collected a day after a heavy rainfall across the State during a season regarded to be dry.

Even though the concentrations of phenolic compounds in groundwater samples were higher in urban areas than in rural areas, statistical analysis (not shown) indicate that there is no significant difference ($p < 0.05$) in these concentrations, which suggests that people living in both urban and rural areas in these States are equally exposed to any potential risk associated with the concentration of these phenolic compounds in their water bodies when ingested.

There was an impact of seasonal variation on the quality of water samples collected. Groundwater samples from Oyo and Lagos States show more toxicity to algae, *Daphnia*, and fish in the dry season (Fig. 3) than in the rainy season due to the higher maximum concentration of these phenolic compounds. In contrast, samples from Osun State show a reverse trend. This is likely because, from our observation, there are more hand-dug wells in Osun State than in Oyo and Lagos States. It is known that surface runoff readily contaminates hand-dug wells (which are usually shallow). Consequently, these phenolic compounds can easily be transported to hand-dug wells during the rainy season (Ibrahim et al. 2021). However, groundwater samples from Oyo and Lagos were from boreholes, often below the water table and not easily polluted by transported chemicals.

The concentrations of phenolic compounds obtained in this study are significantly higher than those previously reported from other countries worldwide, as shown in Table 1. In some cases, 2,4,6-TCP concentrations were higher than WHO-set limits of 200 μgL^{-1} for its presence in drinking water (Angelino and Gennaro 1997; EPA and Technology 2015; Organization 1994; WHO 2003). In fact, the mean concentrations of 2,4-DNP and 2,4,6-TCP reported in this study are >200-fold higher than those found in the Buffalo River of Eastern Cape South Africa (Yahaya et al. 2019), one of the very few reports from Africa.

Multivariate statistics: principal component analysis

The results of the principal component analysis (PCA) for the parameters studied in groundwater and surface water samples from Osun, Oyo, and Lagos States are summarized in Table 2. The preliminary results of the Kaiser-Meyer-Olkin (KMO) test (≥0.5) and Bartlett sphericity tests ($p < 0.001$) indicate that the data qualify for structure detection, and this further validates the results of the PCA. For groundwater samples from Osun State, three principal components dominated the PCA, accounting for 82.7% of the total variance. The first principal component (PC1) explained 41.5%

Table 1 Concentrations of phenolic compounds in water sources from different countries

Country	Matrix	Phenol*	2,4-DNP*	2,4,6-TCP*	Reference
China	River	<LOD-3.84	<LOD-2.69	<LOD-2.48	Chen et al. (2021)
Egypt	River	<LOD-0.109	0.0914	0.0029–0.046	El-Naggar et al. (2022)
Brazil	Groundwater	--	0.43	0.08–25.9	Ramos et al. (2021)
Singapore	River	0.3	0.45	---	Tang et al. (2014)
Poland	Groundwater	---	---	0.06–0.89	Michałowicz et al. (2011)
Malaysia	Treated water	---	---	1–5	Al-Janabi et al. (2012)
South Africa	Dam	0.14	0.774	0.46	Nthunya et al. (2019)
WHO	Drinking water	1000	-	200	
Nigeria†	Groundwater	261	1080	216	This study
Nigeria†	River	261	553.4	275	This study

*Values are in micrograms per litre

†Mean concentration values

Table 2 Rotated component matrix for variables in groundwater and surface water samples from Osun and Oyo States

	Osun GW			Osun SW			Oyo GW			Oyo SW		Lagos GW		Lagos SW	
	1	2	3	1	2	3	1	2	3	1	2	1	2	1	2
DNP	0.15	0.05	**0.94**	0.03	−0.01	**0.96**	0.29	0.29	**0.80**	−0.24	**0.75**	−0.08	**0.75**	0.18	**0.76**
PHE	−0.16	**0.91**	0.09	0.03	**0.70**	−0.02	0.24	**0.84**	0.16	0.09	***0.57***	*−0.73*	0.20	−0.02	0.39
TCP	0.37	0.66	−0.20	−0.10	*−0.52*	0.17	0.08	0.09	*−0.90*	−0.09	**0.76**	0.05	*−0.72*	−0.02	*−0.78*
pH	***0.51***	0.27	***−0.56***	−0.14	**0.66**	0.24	−0.01	**0.85**	−0.03	0.30	***0.51***	**0.76**	0.32	**0.70**	0.30
EC	**0.99**	0.02	0.03	**1.00**	0.21	0.03	**0.98**	0.10	0.03	**0.98**	−0.01	**0.55**	−0.39	**0.93**	−0.08
TDS	**0.98**	0.02	0.03	**1.00**	0.01	−0.01	**0.97**	0.13	0.10	**0.98**	−0.02	**0.65**	−0.11	**0.97**	−0.02
Eigen values	2.490	1.348	1.121	2.012	1.207	1.004	2.552	1.358	1.192	2.109	1.703	1.993	1.254	2.395	1.371
% Total variance	41.51	22.47	18.69	33.53	20.12	16.73	42.54	22.63	19.86	35.15	28.38	33.21	20.90	39.92	22.85
% Cumulative	41.51	63.98	82.66	33.53	53.65	70.38	42.54	65.17	85.03	35.15	63.53	33.21	54.11	39.92	62.77

Extraction method: principal component analysis. Rotation method: Varimax with Kaiser (bold figures indicate values ≥ 0.5); Figures in bold are those above acceptable threshold limit of 0.50

of the total variance and showed very high loadings of 0.99 and 0.98 for electrical conductivity (EC) and total dissolved solids (TDS), respectively. Similar high loadings ≥0.97 for EC and TDS were also observed for other water samples (groundwater and surface water) from Oyo State (Table 2; Fig. 5). High PCA loadings found in water samples (both groundwater and surface water) in Osun and Oyo States suggest a very strong association between EC and TDS, and hence similar sources and factors contributing to the values of both EC and TDS from water samples from the two States. This is expected because of the relationship between EC and TDS, and previous reports which show a similar strong correlation between EC and TDS (Thirumalini and Joseph 2009; Sa'ad et al. 2021). For groundwater samples from Osun State, there is an association between Phenol and 2,4,6-TCP in the PC2 analysis shown in Table 2. This suggests a quasi-independent behaviour within the group, which is further corroborated by a large distance between the two phenolic compounds (PHE and TCP) in Fig. 5A and confirming they are from different sources. There is also an association between phenol and pH in Osun surface water and Oyo groundwater samples which suggests that these two components (phenol and pH) have a similar source in water samples from these States.

The pH loading of 0.51 for groundwater samples from Osun State (Fig. 5A) is not as high as that for EC and TDS, suggesting that the pH of water samples from this State is influenced by pollution from different sources. Likewise, the PCA results for Osun surface water (SW) showed that it had three principal components significantly dominated by EC and TDS in PC1. This accounts for 33.5% of the total variance with very high loadings of ≥0.99 indicating a strong relationship between EC and TDS (Fig. 5B) influenced by a common factor.

The PC2 value for Osun State groundwater samples consist of a high loading of 0.91 for Phenol (PHE) and a relatively moderate loading of 0.66 for 2,4,6-TCP (TCP). Also, PC2 values (for surface water samples) for Osun State were dominated by pH and PHE with loadings of 0.66 and 0.70, respectively, accounting for 20.1% of the total variance. The

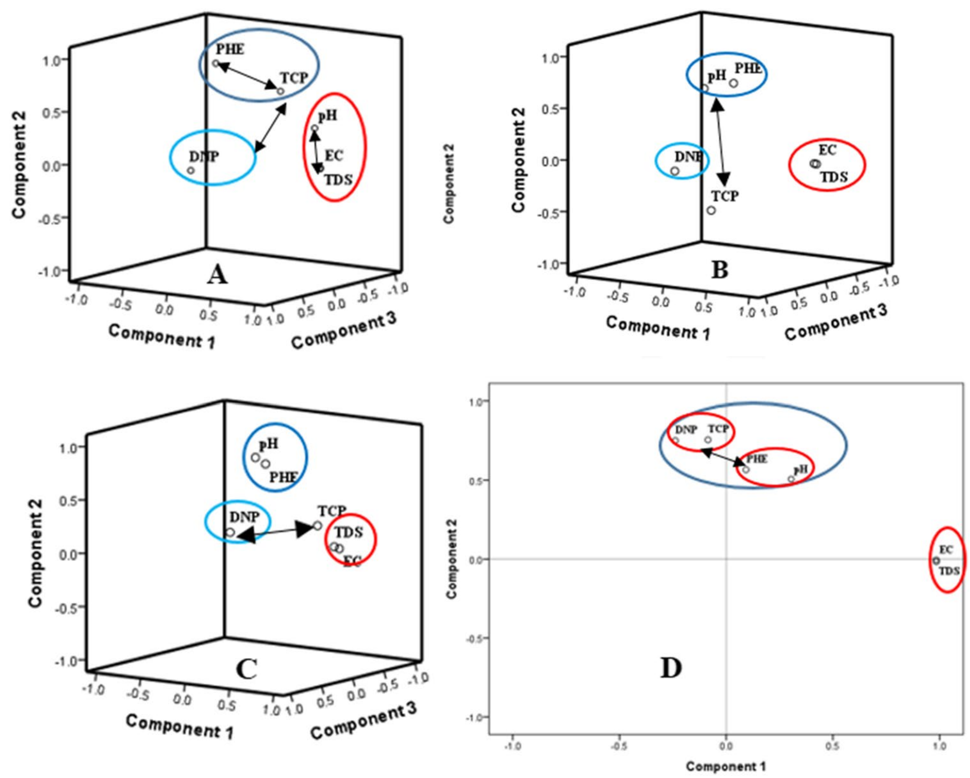

Fig. 5 PCA loading 3D plot for studied parameters in Osun State (**A**) groundwater samples (PC1 vs PC2 vs PC3); (**B**) surface water samples (PC1 vs PC2 vs PC3); Oyo (**C**) groundwater samples (PC1 vs PC2 vs PC3); and (**D**) surface water samples (PC1 vs PC2)

PC3 for groundwater samples is dominated only by 2,4-DNP accounting for 18.7% of the total variance with high loadings of 0.94. This is confirmed in Fig. 5A, indicating that 2,4-DNP is from a source different from those of PHE and TCP. The loading of −0.56 for pH indicates that 2,4-DNP and pH have different sources. Like the groundwater samples, the PC3 for surface water samples from this State is dominated significantly by 2,4-DNP with a loading of 0.96 accounting for 16.7% of the total variance (Fig. 5A), also indicating that 2,4-DNP is from a source different from phenol and 2,4,6-TCP.

Similarly, the physico-chemical parameters of groundwater samples from Oyo State were dominated by three principal components. PC1, PC2, and PC3 were best represented by EC and TDS, EC and PHE, and pH and DNP accounting for 42.5, 22.6, and 19.9% of the total variance respectively (Table 2). The negative high loading of −0.90 for TCP (Fig. 5C) and its large distance with 2,4-DNP indicate that it is from a different source. Nonetheless, surface water samples from this State (Oyo) were described by two principal components (PC1 and PC2). Like with Osun State groundwater and surface water samples, PC1 was dominated by EC and TDS accounting for 35.2% of the total variance, while PC2 was dominated by 2,4-DNP, PHE, 2,4,6-TCP, and pH with loadings of 0.75, 0.57, 0.76, and 0.51, respectively, accounting for 28.4% of the total variance. The relatively low loadings of PHE and pH suggest the influence of a different factor through a similar source as shown in Fig. 5D.

Likewise, Table 2 summarizes the results of the PCA for groundwater and surface water samples obtained from Lagos State. Data from the PCA also showed that PHE did not contribute significantly ($p \leq 0.05$) to the total variance observed in the parameters studied.

The groundwater PCA result was represented by two principal components responsible for a cumulative variance of 54.1% with pH, EC, and TDS dominating PC1 accounting for 33.2% of the total variance. EC and TDS were also correlated in PC1 even though not as strong as the association seen in water samples from Osun and Oyo States (Fig. 6A). The PC2 for Lagos groundwater is dominated significantly by DNP with a loading of 0.75 accounting for 20.9% of the total variance. The surface water PCA result was equally represented by two principal components responsible for a cumulative variance of 62.8% with pH, EC, and TDS dominating the PC1 accounting for 39.9% of the total variance, and 2,4-DNP with a loading of 0.76 dominating the PC2 accounting for 22.9% of the total variance (Fig. 6B).

Hierarchical cluster analysis

Cluster analysis (CA) was performed on the selected physicochemical parameters and phenolic compound concentrations in both groundwater and surface water samples. The results are represented by the dendrograms (Figs. 7 and 8). The degree of association between the variables (physicochemical

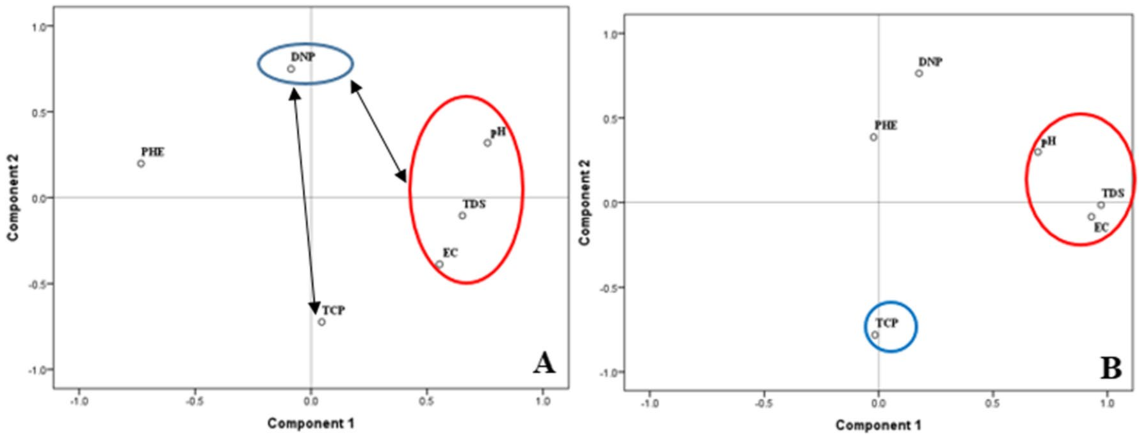

Fig. 6 PCA loading 3D (PC1 vs PC2) plot for parameters studied in Lagos (**A**) groundwater and (**B**) surface water samples, respectively

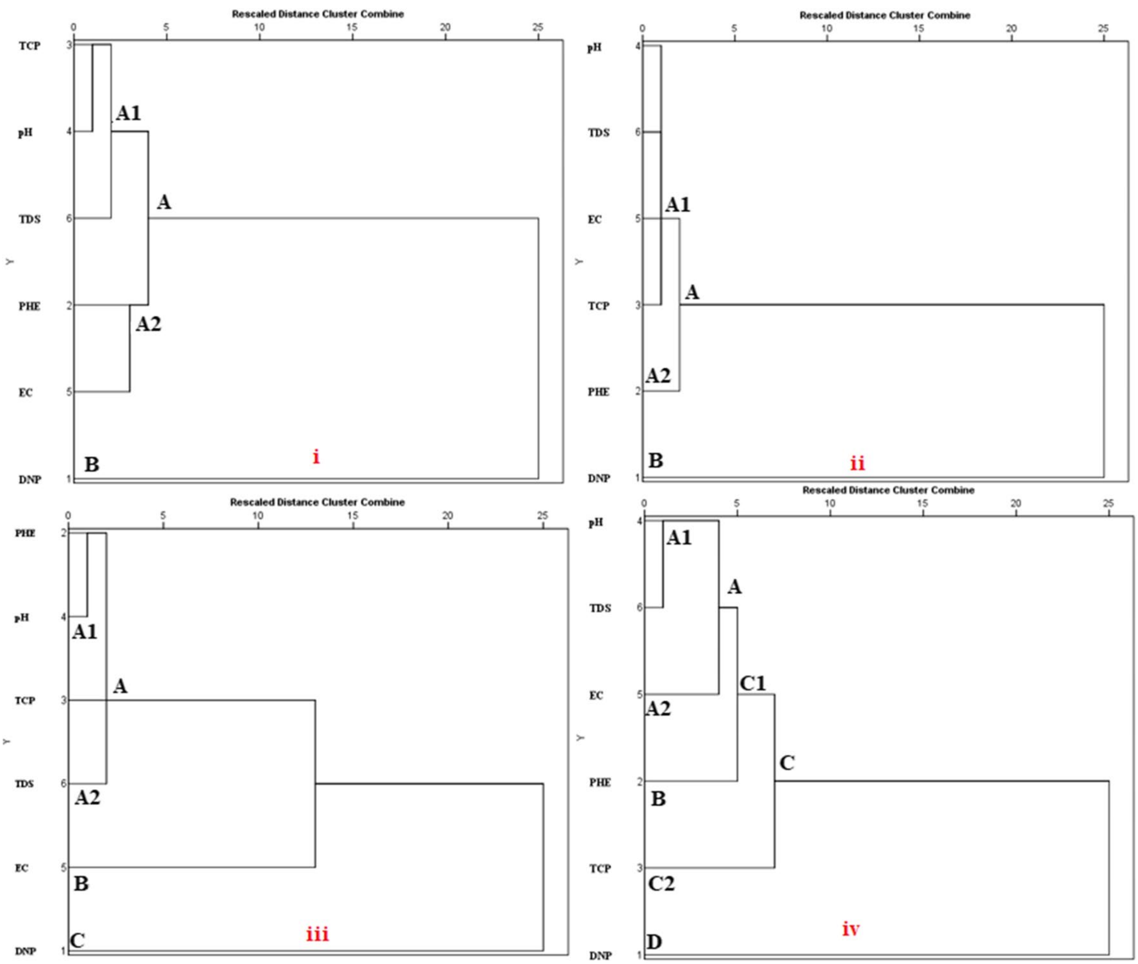

Fig. 7 Hierarchical cluster analysis dendrogram showing the relationship between phenolic compounds and physicochemical properties in Osun (groundwater (i) and surface water (ii)) and Oyo (groundwater (iii) and surface water (iv) Samples

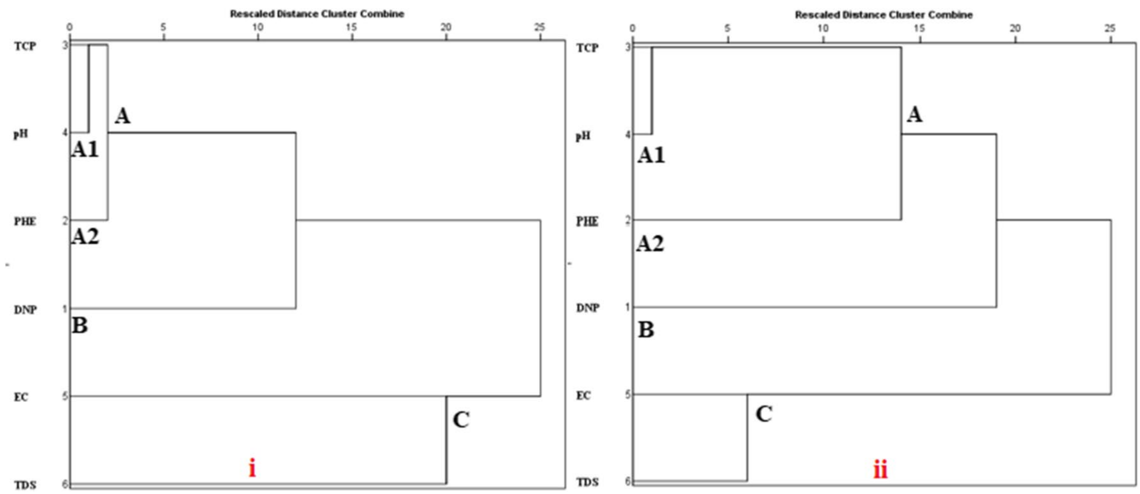

Fig. 8 Hierarchical cluster analysis dendrogram showing the relationship between phenolic compounds and physicochemical properties in Lagos State groundwater (i) and surface water (ii) samples

parameters and phenolic compound concentrations) is depicted by the distance between clusters in the dendrogram. The dendrogram further corroborates the results of the PCA.

Figure 7(i,ii) shows that the CA results for Osun groundwater and surface water samples were grouped into two main clusters (A and B). For Osun groundwater, cluster A contains two lower clusters, A1 (TDS, pH and TCP) and A2 (EC and PHE). pH and TCP were joined together at a shorter distance, suggesting a common origin, but pH and TCP were joined together at a relatively high level confirming the influence of another factor. Similarly, A2 (EC and PHE) was joined together at another relatively higher level than A1 (TDS, pH and TCP), suggesting the influence from similar sources. Furthermore, the CA result for Osun groundwater also contained a stand-alone cluster B (DNP) that joined cluster A at a higher distance. Similarly, the proximity in the dendrogram between EC and TDS in Fig. 7(ii–iv) suggests a form of similarity in distribution patterns in water samples and corroborated the PCA results.

In addition, Fig. 7iv shows that the studied variables in Oyo surface water samples were grouped into four main clusters. However, the clustering pattern was less distinct in comparison to others. Furthermore, Fig. 7(i–iv) shows a consistent wide distance between DNP and every other studied variable, indicating the influence of a different anthropogenic source.

Although Fig. 8(ii) shows significant associations between the physico-chemical properties and phenolic compounds in surface water samples from Lagos State at higher distances compared to what is seen in Fig. 8(i), the similarity in the cluster pattern suggests a similar anthropogenic source of contamination for both groundwater and surface water in Lagos State except for DNP with large distances from other two phenolic compounds (as seen with the PCA). This indicates the influence of an entirely different anthropogenic source of DNP. In Oyo surface water samples, there is a close association between 2,4-DNP and 2,4,6-TCP and this is suggestive of the fact that they are both from similar origin and have the same influencing factors. The similarity in the PCA with reference to pH, EC, and TDS between Osun groundwater and surface water also suggests similarity in the contributing factors, and hence similar sources of pH, EC, and TDS (Fig. 8A, B). Although data from the PCA showed that groundwater from Osun and Oyo States had more multiple sources of contamination than other samples, the analysis showed that 67 to 100% of groundwater samples had more multiple sources of contamination compared to surface water samples from the three States. However, for Lagos groundwater and surface water samples, there was no correlation between the phenolic compounds and the physico-chemical properties (pH, EC, and TDS) as seen from the loadings. This shows that the physico-chemical factors were not the determining factors for the presence of phenolic compounds in Lagos water samples but other variables (Fig. 8). 2,4-DNP was not associated with any other phenolic compound and physico-chemical properties except in Oyo surface water.

Ecological risk assessment

The ecological risk assessment for 2,4-Dinitrophenol, Phenol, and 2,4,6-Trichlorophenol was calculated based on the risk quotient (RQ) for minimum and maximum measured environmental concentrations for surface water and groundwater samples from the three States. Data obtained are presented in Tables S4 and S5.

In Osun State, the ecological risk to three trophic level,s algae, *Daphnia*, and Fish from the concentration of 2,4-DNP,

Table 3 Non-cancer and cancer risk assessments for phenolic compounds in groundwater samples from Osun, Oyo, and Lagos States, Nigeria

State	Season	PC	CDI_{NCR}	HQ_{NCR}	LoR_{NCR}	HQ_{CR}	LoR_{CR}
Osun	Rainy	2,4-DNP	0.03831	19.6	High	**	**
		Phenol	0.01038	0.03	Low	**	**
		2,4,6-TCP	0.0096	24	High	1.06×10^{-4}	High
	HI	43.2					
	Dry	2,4-DNP	0.01314	6.6	High	**	**
		Phenol	0.00426	0.01	Low	**	**
		2,4,6-TCP	0.00339	8.5	High	3.73×10^{-5}	High
	HI	15.1					
Oyo	Rainy	2,4-DNP	0.0063	3.2	High	**	**
		Phenol	0.00435	0.015	Low	**	**
		2,4,6-TCP	*	*	*	*	*
	HI	3.2					
	Dry	2,4-DNP	0.03939	19.7	High	**	**
		Phenol	0.01656	0.06	Low	**	**
		2,4,6-TCP	0.01221	30.5	High	1.34×10^{-4}	High
	HI	50.3					
Lagos	Rainy	2,4-DNP	0.01932	9.7	High	**	**
		Phenol	0.00846	0.03	Low	**	**
		2,4,6-TCP	0.00225	5.6	High	2.48×10^{-5}	High
	HI	15.3					
	Dry	2,4-DNP	0.01788	8.9	High	**	**
		Phenol	0.00357	0.012	Low	**	**
		2,4,6-TCP	0.00615	15.4	High	6.77×10^{-5}	High
	HI	24.3					

HQ hazard quotient, *NCR* non-carcinogenic risk, *CR* carcinogenic risk, *PC* phenolic compound, *LoR* level of risks

*No values

**There are no values or because there is currently no CSF for 2,4-DNP and Phenol

Phenol, and 2,4,6-TCP in groundwater and surface water is high and even much higher during the rainy season than in the dry season. This trend is reversed for water samples from Lagos State as seen from the RQ_{acute} and $RQ_{chronic}$ values in Tables 3 and 4. Samples from Oyo State show a similar ecological risks trend to Algae, *Daphnia*, and Fish like that from Lagos State.

Comparing the risk from the three phenolic compounds, 2,4-DNP pose the highest toxicity risk to the three aquatic lives, followed closely by 2,4,6-TCP, with Phenol being the least with moderate ecological risk. On the acute scale (RQ_{acute}), *Daphnia* is more at risk than either Algae or Fish (Tables S4 and S5) in both rainy and dry seasons for groundwater and surface water. Conversely, on the chronic scale ($RQ_{chronic}$), Algae and Fish are more susceptible to toxicity from the three phenolic compounds in both groundwater and surface water during the rainy and dry seasons.

In comparing the RQ values of water samples during both seasons, groundwater samples from Oyo and Lagos States show higher RQ values compared to the RQ values obtained from surface water in the same States during the dry season. The reverse is the case for samples from Osun State in the same season. However, during the rainy season, the RQ values obtained from groundwater samples in Osun and Lagos States were higher than those obtained for the surface water in these two States. Nonetheless, samples from Oyo State showed a reverse trend in the rainy season. This may suggest that the presence of these chemicals may, on the one hand, hinder algal growth, which appears to be a positive development, but on the other hand, harm the health of people drinking from such polluted water in the long term. The higher ecological risks posed by 2,4-DNP compared to that of Phenol or 2,4,6-TCP is in tandem with its high mean concentrations in water samples collected across the three States.

In general, it is observed that 2,4-DNP toxicity impacts *Daphnia* more than Algae and Fish on the acute scale (RQ_{acute}) while Algae is the most impacted on the chronic scale ($RQ_{chronic}$). In general, 2,4-DNP in water samples collected around these Southwestern States in Nigeria pose more ecological risk to aquatic life—Algae, *Daphnia*, and Fish—than either phenol or 2,4,6-TCP. This can be seen

Table 4 Non-cancer and cancer risk assessments for phenolic compounds in surface water samples from Osun, Oyo, and Lagos States, Nigeria

State	Season	PC	CDI_{NCR}	HQ_{NCR}	LoR_{NCR}	HQ_{CR}	LoR_{CR}
Osun	Rainy	2,4-DNP	0.02601	13.0	High	**	**
		Phenol	0.01026	0.03	Low	**	**
		2,4,6-TCP	0.00672	16.8	High	7.39×10^{-5}	High
	HI	29.8					
	Dry	2,4-DNP	0.00108	0.5	Low	**	**
		Phenol	0.0066	0.02	Low	**	**
		2,4,6-TCP	0.00216	5.4	High	2.38×10^{-5}	High
	HI	5.9					
Oyo	Rainy	2,4-DNP	0.02406	12.0	High	**	**
		Phenol	0.01281	0.04	Low	**	**
		2,4,6-TCP	*	*	*	*	*
	HI	12.1					
	Dry	2,4-DNP	0.03333	16.7	High	**	**
		Phenol	0.00786	0.03	Low	**	**
		2,4,6-TCP	0.01638	40.9	High	1.8×10^{-5}	High
	HI	57.6					
Lagos	Rainy	2,4-DNP	0.01509	7.5	High	**	**
		Phenol	0.01317	0.04	Low	**	**
		2,4,6-TCP	0.00579	14.5	High	6.37×10^{-5}	High
	HI	22.1					
	Dry	2,4-DNP	0.0153	7.7	High	**	**
		Phenol	0.00828	0.03	Low	**	**
		2,4,6-TCP	0.0084	21	High	9.24×10^{-5}	High
	HI	28.7					

HQ hazard quotient, *NCR* non-carcinogenic risk, *CR* carcinogenic risk, *PC* phenolic compound, *LoR* level of risks

*No values

**There are no values or because there is currently no CSF for 2,4-DNP and Phenol

from the higher RQ values for 2,4-DNP compared with those for phenol or 2,4,6-TCP. The susceptibility of *Daphnia* to acute toxicity from 2,4-DNP found in these water samples when compared to Algae and Fish is expected because of its lower organisation level, without well-developed mechanisms to ameliorate toxicity imposed on them from the environment. The potential acute and chronic toxicity risks posed by groundwater and surface water bodies reported in this study are likely to increase if water treatment involves chlorination (Michałowicz and Duda 2007), as is still the case in many developing countries in the world. Although a published study reported by Michałowicz and Duda suggests that the concentrations of Phenol in water samples posed the most negligible toxicity to algae, *Daphnia*, and Fish when compared with 2,4-DNP and 2,4,6-TCP (Michałowicz and Duda 2007), this is not obvious from this study. It, thus, implies that the concentration of Phenol may determine its level of toxicity to aquatic life since the concentration of Phenol in water samples in this study far exceeds those reported by Michałowicz and Duda (2007).

Human exposure and health risk assessments

Human exposure

Groundwater is a major source of drinking water for the populace in Nigeria (Danert and Healy 2021). In some impoverished areas in these States studied, which are typically in the rural settings, surface water suffices as a source of drinking water. Hence, it is crucial to determine the amount of human exposure to these phenolic compounds when ingesting water from these sources. The human exposure to phenolic compounds in this study was assessed using the estimated daily intake (EDI; $\mu g\ kg^{-1}$ bw day^{-1}) based on the United States Exposure Factors Handbook (USEPA, 2011). The population was grouped into infants (<1 year old), toddlers (1–3 years old), children (4–11 years old), teenagers (12–21 years old), and adults (≥21 years old).

$$\text{EDI water}\left(\mu g\ kg^{-1}\ \text{bw day}^{-1}\right) = (C \times D)/BW \qquad (8)$$

where C is the concentration of the analyte in water (μg L^{-1}), D is the daily water consumption rate (L day^{-1}), and BW is the body weight (kg). The median and maximum concentrations were used to calculate the EDI. The daily water consumption rate (D) and body weight used for calculating the EDI were as follows: infants (1 L day^{-1}, 9.2 kg), toddlers (0.9 L day^{-1}, 13.8 kg), children (1.3 L day^{-1}, 31.8 kg), teenagers (2.4 L day^{-1}, 71.6 kg), and adults (3.1 L day^{-1}, 80 kg) (USEPA, 2011). The Environmental Protection Agency of the United States gave a Provisional Peer-Reviewed Toxicity Value of 0.002 mg kg^{-1} day^{-1} for 2,4-DNP from drinking water (EPA 2007). The non-fatal lowest observed adverse effect level (LOAEL) for 2,4-DNP is put at 0.9–2.0 mg kg^{-1} day^{-1} while its fatal doses are given as 3.0–7.0 mg kg^{-1} day^{-1} for 3–14 days (Przybyla et al. 2021). However, because 2,4,6-TCP is considered a carcinogenic compound, a no significant risk level (NSRL) of 10 μg day^{-1} was assigned to it (https://oehha.ca.gov/chemicals/246-trichlorophenol). Phenol is not known to be toxic but can alter the taste of water.

The median and maximum concentrations for these phenolic compounds in groundwater and surface water samples collected from the different States are provided in Table S6.

Considering Fig. 9 obtained from maximum concentrations of the phenolic compounds, the EDI values of 2,4-DNP in groundwater samples from the different States both in the rainy and dry seasons are below the LOEAL and fatal doses already prescribed but are higher than the Provisional Peer Reviewed Toxicity Value of 0.002 mg kg^{-1} day^{-1} (Fig. 9A, D). This is even so when median values 2,4-DNP was used for EDI calculations for both seasons (Fig. 10A, C). Similarly, the EDI values for 2,4,6-TCP in the groundwater samples from Osun and Lagos States during the rainy season are far higher than the prescribed threshold limit of 10 μg day^{-1} when maximum concentrations were used for EDI calculations (Fig. 9C). This is similarly true for groundwater samples from Oyo State during the dry season (Fig. 9F). However, with median concentration values, only EDI values from Oyo State were beyond the 2,4,6-TCP prescribed threshold limit during the dry season as values obtained in the rainy season were below the detection limit (Fig. 10E). However, in the dry season, the EDI values for 2,4,6-TCP were lower than the threshold limit.

The trend observed for EDI values of 2,4-DNP in surface water for the different States and in rainy and dry seasons is similar to that observed for groundwater as earlier described. However, the EDI values of the former are lower than the latter (Figs. 9, 10, 11, and 12). Just like with groundwater, the EDI values for 2,4,6-TCP in surface water are higher than the prescribed threshold limit of 10 μg day^{-1} in most cases and this is more so in the dry season than in the rainy season when maximum concentrations of the phenolic compound (2,4,6-TCP) was used for the calculation of EDI values (Fig. 11C, F).

When the median values of the concentrations of phenolic compounds were used to calculate the EDI values for surface water, it is observed that EDI values for 2,4-DNP calculated for infants and toddlers for Osun State were higher than the

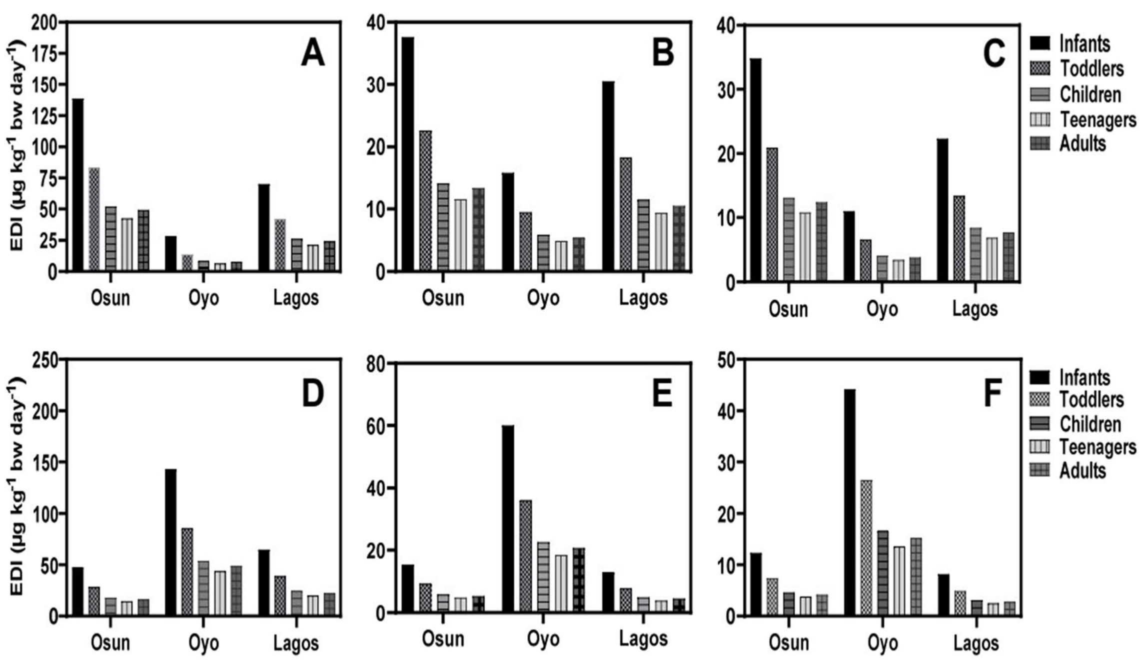

Fig. 9 Estimated daily intake (EDI) calculated with the maximum concentration values of (**A**) 2,4-Dinitrophenol, (**B**) Phenol, (**C**) 2,4,6-Trichlorophenol in groundwater during rainy season, (**D**) 2,4-Dinitrophenol, (**E**) Phenol, and (**F**) 2,4,6-Trichlorophenol in groundwater during the dry season for various exposure groups in Osun, Oyo, and Lagos States, Nigeria

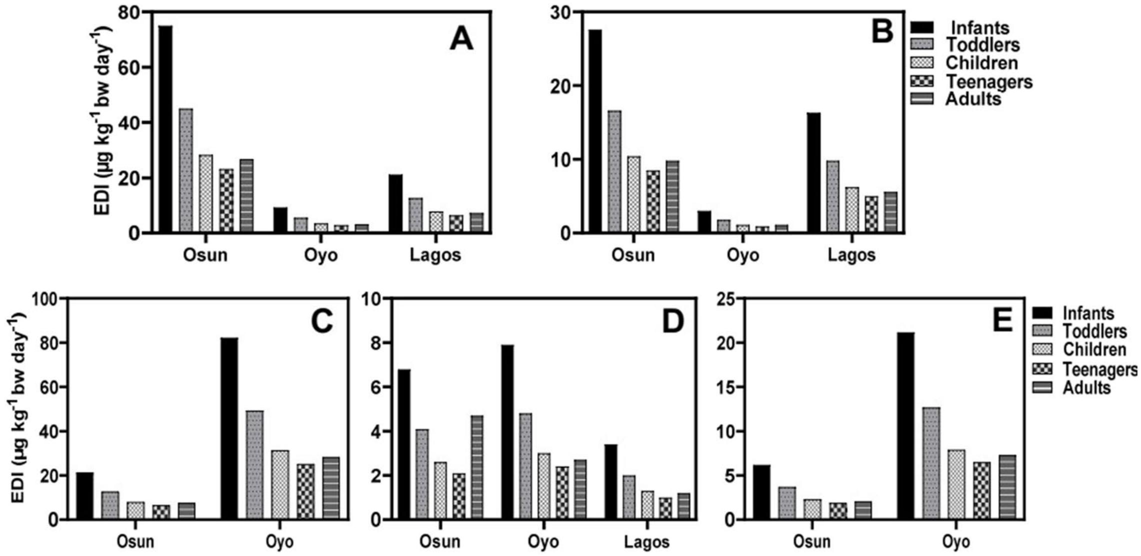

Fig. 10 Estimated daily intake (EDI) calculated with the median concentration values of (**A**) 2,4-Dinitrophenol, (**B**) Phenol in groundwater during rainy season, (**C**) 2,4-Dinitrophenol, (**D**) Phenol, (**E**) 2,4,6-Trichlorophenol in groundwater during the dry season for various exposure groups in Osun, Oyo, and Lagos States, Nigeria

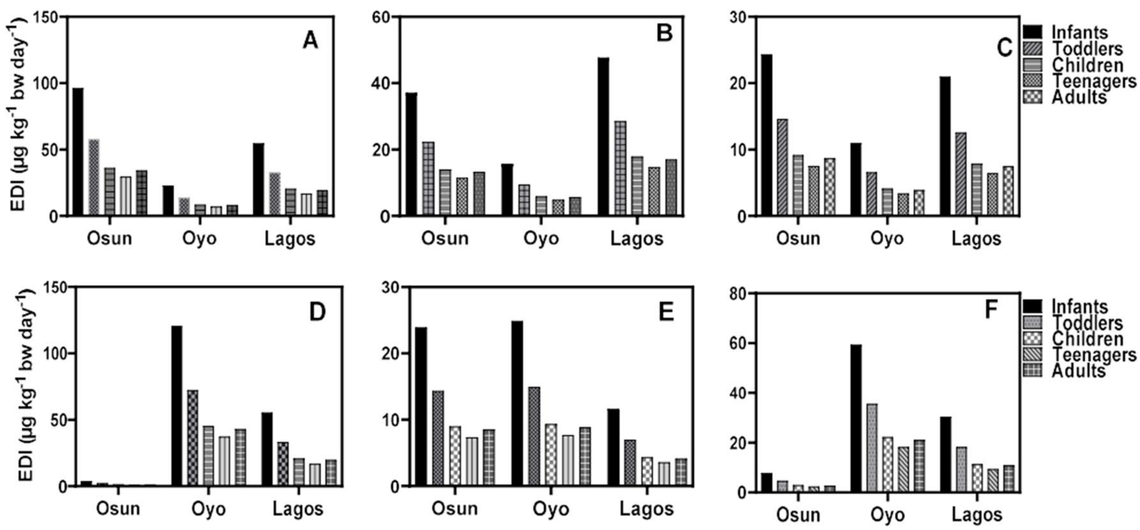

Fig. 11 Estimated daily intake (EDI) calculated with the maximum concentration values of (**A**) 2,4-Dinitrophenol, (**B**) Phenol, (**C**) 2,4,6-Trichlorophenol in surface water during rainy season, (**D**) 2,4-Dinitrophenol, (**E**) Phenol, (**F**) 2,4,6-Trichlorophenol in surface water during the dry season for various exposure groups in Osun, Oyo, and Lagos States, Nigeria

Provisional Peer-Reviewed Toxicity Value of 0.002 mg kg^{-1} day^{-1} during the rainy season (Fig. 12A) as well as those for Lagos and Oyo States in the dry season (Fig. 12D). However, the EDI values were lower than the LOAEL and fatal doses prescribed. These same population groups (infants and toddlers) are also at risk with the concentration of 2,4,6-TCP in surface water from Osun and Oyo States during rainy and dry seasons, respectively (Fig. 12C, F). Generally, the EDI values for these phenolic compounds in surface water decreased in the dry season (Fig. 12D–F) than in the rainy season (Fig. 12A–C).

Generally, it is observed that EDI values decreased with the increasing age of the exposure group. The EDI values were highest for infants and lowest for teenagers across the three States. However, there is no statistical difference between EDI values for children, teenagers, and adults. Water samples from Osun State provided the highest EDI values across all exposure groups for 2,4-DNP, Phenol, and 2,4,6-TCP during the rainy season (Figs. 9, 10, 11, and 12). During the dry season, the EDI values for all three phenolic compounds decreased for Osun and Lagos States but

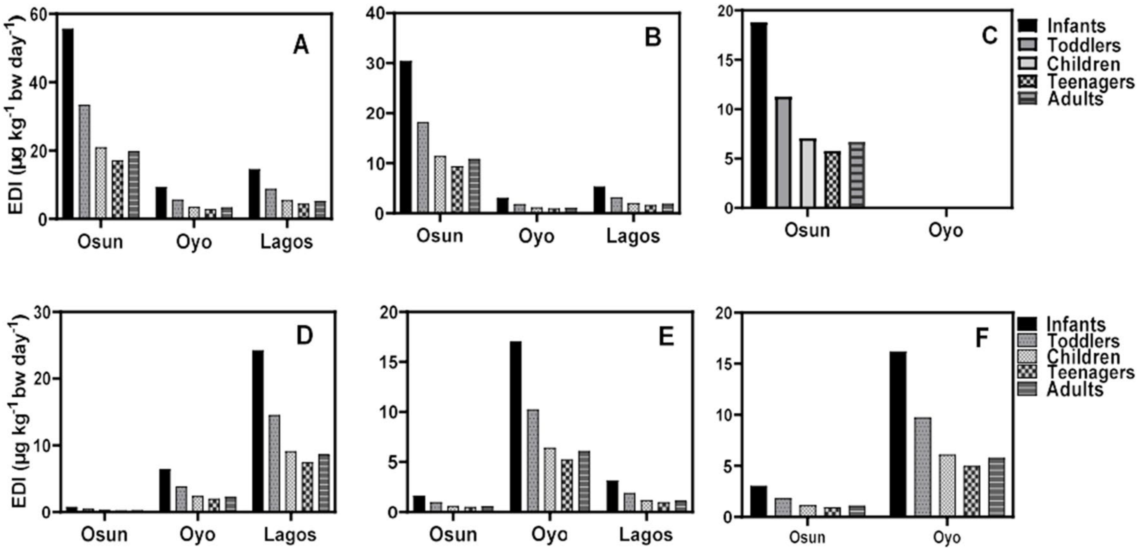

Fig. 12 Estimated daily intake (EDI) calculated with the median concentration values of (**A**) 2,4-Dinitrophenol, (**B**) Phenol, (**C**) 2,4,6-Trichlorophenol in surface water during rainy season, (**D**) 2,4-Dinitrophenol, (**E**) Phenol, and (**F**) 2,4,6-Trichlorophenol in surface water during the dry season for various exposure groups in Osun, Oyo, and Lagos States, Nigeria

increased for Oyo State. This is likely because of the unusual event earlier mentioned that highlights the impact of climate change on seasonal variation.

Nevertheless, from this study, it is observed that 2,4-DNP in groundwater is most toxic to all exposure groups (infants, toddlers, children, teenagers, and adults) from the three States (Osun, Oyo, Lagos) than other phenolic compounds studied, judging from its higher EDI values in comparison with the other phenolic compounds (Figs. 9 and 10).

Human risk assessment

To measure human risks from ingesting these phenolic compounds from water, the hazard quotient is used as described in "Health risk assessment".

The hazard quotient (HQ) and human exposure assessment results (Tables 3 and 4) showed that human exposure to these phenolic compounds needs to be further controlled by regular monitoring and assessment of the surface and groundwater quality in these areas.

The results in Tables 3 and 4 show that with the highest concentrations of the phenolic compounds in groundwater and surface water samples, 2,4-DNP and 2,4,6-TCP show high NCR (HQ_{NCR} >> 1.0) for the adult population in all three States and in both seasons with 2,4,6-TCP providing the highest NCR in most cases (Tables 3 and 4). In groundwater, the NCR of 2,4-DNP is generally higher during the dry season than in the rainy season (Table 3). When median concentrations of the phenolic compounds were used for HQ calculations, the results show no significant NCR for both children and adult population across the three states, in both ground and surface water samples, and in both dry and rainy seasons (Table S7). HQ_{CR} values for 2,4,6-TCP are greater than $>10^{-6}$ in water samples for all three states in both groundwater and surface water (Table 3).

Overall, the hazard quotients shown in Tables 3 and 4 show that ingesting high concentrations of 2,4-DNP (≥400 mg/L) and 2,4,6-TCP (≥70 mg/L) from either groundwater and surface water over a long period of time (30 years) has the potential to cause non-carcinogenic health issues including breakdown of the central nervous system, negative impact on the cardiovascular system, cataracts, and increased metabolism resulting in fever, headache, profuse sweating, thirst, fatigue, etc. The maximum EDI values for 2,4-DNP, Phenol, and 2,4,6-TCP in groundwater water for all exposure groups were higher than the prescribed acceptable daily intake (ADI) of 2.0, 1.0, and 1.5 µg kg^{-1} bw day^{-1}, respectively, for drinking water (EPA and Technology 2015). The same is true for 2,4-DNP in water samples (including groundwater) from all the States which also posed high carcinogenic risk to the humans because their concentrations currently exceed the USEPA recommended limit of 10 mg/L in drinking water (Rani et al. 2020).

Furthermore, the high carcinogenic risk from the concentrations of 2,4,6-TCP in groundwater samples across all sampling sites in all three States supports the HQ results shown in Tables 3 and 4. This is supported by the fact that some of the concentrations of 2,4,6-TCP found in water samples were far beyond the current recommended limits suggested as 18 mg/L by Australia and 5 mg/L by Canada (https://www.dcceew.gov.au/environment/protection/npi/substances/fact-sheets/chlorophenols-di-tri-tetra sourced online 8th April 2023) (Warrington 2021).

Conclusion

Following the thorough 1-year monitoring of water sources in three South-Western States in Nigeria, the three phenolic compounds (2,4-DNP, Phenol, and 2,4,6-TCP) were present in most of the sampling sites both in surface water and groundwater, with the latter being the major source of drinking water in Osun, Oyo, and Lagos States, Nigeria. From the mean concentrations of these phenolic compounds in water samples reported in this study, it is evident that these are among the highest reported in recent times. The most frequently detected phenolic compound was phenol, while 2,4-DNP was reported as having the highest mean concentration (>90% of samples) in water samples.

Generally, the concentrations of these phenolic compounds decreased during the dry season compared with the rainy season except for samples collected from Oyo State, which showed a reversed trend because samples were collected from the State a day after heavy rainfall during a season (dry season) expected to be devoid of rain. This underscores the impact of climate change on the environment. However, there was no significant difference between concentrations of 2,4-DNP, Phenol, and 2,4,6-TCP found in water samples from urban and rural sites. Ecological risk assessment suggests that of the three aquatic lives (Algae, *Daphnia*, and Fish), *Daphnia* and Algae are more susceptible to toxicities from 2,4-DNP, respectively, in the surface water and groundwater environment from the different States. Results from the PCA indicate, generally, that groundwater samples had multiple sources of contamination unlike with surface water samples.

This study show that infants are highly vulnerable to these phenolic compounds in water, hence families may require point-of-use treatment facilities since boiling (commonly used in treating water used for babies) might not be sufficient.

The most detected compounds were 2,4-DNP and Phenol in both surface water and the groundwater. There is clear indication that the presence of these phenolic compounds in aquatic systems vary with seasons.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-023-27622-w.

Author contribution All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Oluwaferanmi Otitoju, Moses Alfred, and Chidinma Olorunnisola. The first draft of the manuscript was written by Oluwaferanmi Otitoju, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Funding Authors EIU, OBO, ODO, AO, and OOO were funded by The World Academy of Sciences-Islamic Development Bank (TWAS-IsDB) collaborative research grant (grant number: 4500420197) for this study. The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Data availability Yes

Materials availability Yes

Declarations

Ethics approval Not applicable

Consent to participate All the authors approved of participating in this publication.

Consent for publication All the authors approved the manuscript for publication.

Competing interests The authors declare no competing interests.

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