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Assessment of Dioxin Concentration in Soil and Edible Plants Around Industrial Sites in Koko Town, Southern Nigeria

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Abstract

Dioxins are a class of persistent organic pollutants with increasing global prevalence and deleterious effects on the environment and human health. However, studies on the distribution, bioaccumulation, and health effects associated with dioxin in environmental media and food products remain low in developing economies. This study evaluated dioxin concentrations in soil and five vegetables and medicinal plants around industrial sites in Koko town, Delta State, Nigeria. Samples of soil and plant tissues were extracted for the various dioxin analytes using the Soxhlet method and analysed with GC-MS. The mean concentration of dioxin in soil was 2.937ppb, and that for plants was 2.864ppb. These values are higher than the permissible limits for dioxin congeners in soil and plants respectively. The bioaccumulation factor of dioxin in plants was in the order of *Pueraria montana* (60.75), *Ceiba pentandra* (8.91), *Chromolaena odorata* (1.29), *Musa sp.* (0.83), and *Vermonia amygdalina* (0.33). However, the edible plants fell within the estimated daily intake of 0.03mg kg⁻¹ and hazard ratio of 1.0 as stipulated by USEPA, indicating no immediate health risk for people consuming vegetables in the community.

Keywords: risk assessment, persistent organic pollutants, vegetables contamination, bioaccumulation factor, Niger Delta

Introduction

Dioxins are a group of organic contaminants that belong to the dirty dozen, which are of global concern due to their deleterious effects on the environment and human health (Mahfouz *et al.*, 2020). They are highly toxic, chemically stable, lipophilic, and they take time to degrade in the environment (Aganbi *et al.*, 2019). They occur naturally in low concentrations in soil mainly from the accretion of deposits from volcanic eruptions and forest fires, which can infiltrate the food chain (Schmitz *et al.*, 2011). Usually, dioxins have no common uses but are by-products of burning fossil fuels and other industrial processes by petrochemical industries (Alwyn and Jerzy, 2021). Also, they accumulate over time in the food chain and environmental

media, far from their source, with the highest levels found in soils, sediments, and food and very low levels in plants, water, and air (Jouko, 2019). Typical hazardous wastes like dioxins in high concentrations in soil and plants could alter soil fertility, reduce soil nutrients, contaminate groundwater, decrease crop yield, create an imbalance in soil fauna and flora, and affect soil microorganisms (Li *et al.*, 2023). The varied concentrations of dioxin available in the environment depend on the shape and extent of chlorine substitutes in the aromatic rings of dioxin compounds, which reflect their environmental toxicity (Grassi *et al.*, 2010). Findings reveal that several lower-chlorinated dioxin congeners are more highly represented in vegetable leaves than in the root, due to gaseous deposits of volatile dioxin congeners, resulting from their adhesion to vegetables (Nakagawa *et al.*, 2002). Among the congeners, Esposito *et al.* (2017) reported higher values for PCDD/Fs in apricots, olives, and nuts compared to lettuce and pumpkins around a dump site in Italy. Also, congeners like TCDD, which is the most potent have been reported to have higher translocation potentials from the root to the leafy parts of leguminous plants like pumpkins (Huelster *et al.*, 1994; Van den Berg *et al.*, 2006; Zhang *et al.*, 2009). However, the contribution of fruit and vegetables to total PCDD and PCDF dietary intake seems challenging because concentrations of these congeners have appeared to fall below the detection limit in certain vegetables (Grassi *et al.*, 2010; WHO, 2023). Furthermore, Vaccher *et al.* (2021) highlighted nuts, seeds, vegetable oils, and fats as preferential low-risk foods in Africa. In addition, the limited consumption of leafy vegetables in Vietnam resulted in low health risk exposure to dioxins (Tuyet-Hanh *et al.*, 2015). Such demonstrates that the risk of exposure from ingesting PCDD/Fs in vegetables depends on the accumulated concentrations, the outcome of reaction (acute or chronic) in humans from their binding capacity to aryl receptors, and their involvement in exhibiting biochemical and toxic responses through metabolic pathways in the body (Grassi *et al.*, 2010). According to Milbrath *et al.* (2009), the most dominant congeners of dioxins found in human tissues are 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-PCDD, 2,3,7,8-TCDD, and 2,3,4,7,8-PCDF with half-lives of 13.1, 11.2, 7.2, and 3.5 years, respectively. In 1987, Koko town witnessed the importation of toxic wastes, which triggered the development of environmental laws and regulations in Nigeria (Eze and Eze, 2017). Although the wastes were evacuated after months of diplomatic and ecological intervention, there is no regular monitoring programme for persistent organic pollutants in the region to bridge the knowledge gap and provide relevant data as part of Nigeria's national routine monitoring for persistent organic pollutants. This study aimed to assess the concentration and bioaccumulation of dioxins in soil and plants and their potential risk to human health around residential and industrial areas in Koko town.

Materials and Method

Study Location

Koko is the headquarters of the Warri North Local Government Area of Delta State, Nigeria. It lies within the geographical coordinates of 6°02'30" N and 5°32'30" E. The climatic condition in the area is typically tropical rainforest, which experiences two major seasons: wet and dry season. The mean daily temperature varies from 21 - 35°C, and annual rainfall is between 2000 - 3000 mm with intense sunlight, which lasts for a minimum of 8 hours daily. The relative humidity varies from 90% during the wet season to 60% in the dry season. The main industrial activities in Koko are oil and gas production and associated services. There is a moribund deep seaport by the Benin River which serves as a shipping route for small vessels and barge haulage supporting oil operations. Other industrial activities include bitumen, paint, and lubricant production. The main occupations of the people include fishing, farming, office, and factory work (Figure 1).



Figure 1—Map of the study area showing sample collection points in Koko town

Sample Collection

Samples of soil and plants were collected from five sampling points around industrial sites using stratified sampling. The industrial sites include Koko Seaport (site 1), a machine plant and lubricant production company (site 2), an industrial waste treatment company (site 3), an oil shipping complex (site 4), and a bitumen-producing company (site 5). For soil sampling, the study area was divided into 10 by 10m, and a composite of topsoil (0 - 15cm) and subsoil (15 - 30cm) were collected in triplicates using soil augers. At each sampling location, the collected soil samples were wrapped in separate aluminium foil, labelled with permanent ink, and stored in ice packs. In the same sampling sites, five perennial and leguminous plants such as silk cotton (*Ceiba pentandra*), kudzu (*Pueraria montana*), bitter leaf (*Vermonia amygdalina*), banana (*Musa sp.*) and Awolowo leaf (*Chromolaena odorata*) were examined and 20-30 leaves per plant were collated, wrapped in aluminium foil, labelled correctly and kept in ice packs. The leaves of plants were collected in conformity to Planks' (1979) method. Both samples were transferred to the EISL Laboratory in Port Harcourt for analysis.

Sample Preparation and Analysis

Soil samples were air-dried for seven days to a constant weight, ground using a pestle and mortar, and then sieved with a 2mm mesh for homogeneity. The soil sample was placed in an automated Soxhlet extractor apparatus with a round bottom flask and a condenser, and 1.0 ml of hexane was added following EPA 3540C and heated gently to a vapour. This extraction process was carried out overnight to obtain sufficient dioxin concentrations from the soil samples. The samples were cleaned up using column chromatography and loaded into vials of 10 μ L before analysis. Samples of plant leaves were air-dried and ground to a fine powder to increase surface area and for smooth extraction. 10g of each plant's leaves were weighed into the Soxhlet extractor, then 100ml of acetone was added to the sample and refluxed three times while heating the plant material. The solvent in the sample was vaporized, and the condensed flow was collected in a flask attached to the extractor. The extract was concentrated, and then filtered into a rotary evaporator and washed in well-packed glass wool with anhydrous sodium sulphate and was then transferred into 10 μ L vials. Extracts from soil and plants for dioxins were loaded into the injection rack and then analysed using gas chromatography coupled with mass spectrometry (GC-MS).

Quality Control and Quality Assurance

All equipment used for analysis was calibrated to standards following laboratory procedures to ensure the reliability and accuracy of results. The detected concentrations of target analytes were compared with certified reference materials with calibration curves following Acq Method 3540. For quantification, calibration curves were constructed for dioxin analytes using a series of quantification values (Q-values) for each target compound. The limits of detection and quantitation were determined using the standard deviation from the blank sample prepared using acetone.

Data Analysis

Results were analysed using SPSS version 20. The output from the analysis was summarised into mean and standard deviation. Comparative analysis using a one-way ANOVA was computed at a probability level of 0.05 (95% confidence level) to compare means for significant differences.

Bioaccumulation Factor

The bioaccumulation factor (BAF) was calculated as the concentration of dioxins in plants over the concentration in soil. This is shown in [equation 1](#).

$$\text{BAF} = \text{Concentration}_{\text{plant}} / \text{Concentration}_{\text{Soil}} \quad (1)$$

Human Health Risk Assessment

The human health risk associated with consuming edible plants contaminated with dioxins was calculated using the estimated daily intake (EDI) and hazard ratio (HR). The EDI was calculated as described in [equation \(2\)](#).

$$\text{EDI} = C \times \text{CR} / \text{BW} \quad (2)$$

where EDI = the estimated daily intake of edible plants (mg/kg/day), C = dioxin concentration in plants in mg/kg, CR = plant ingestion rate using FAO Food Balance Sheets for Nigeria ([FAO, 2022](#)), and BW = average body weight for Nigerians, which is 60.7kg for adults ([Walpole *et al.*, 2012](#)) and 30kg for children ([Goon *et al.*, 2012](#)). The hazard ratio was calculated following [equation 3](#).

$$\text{HR} = \text{EDI} / \text{RfD} \quad (3)$$

where, RfD = reference dose factors following the United States Environmental Protection Agency's reference dose for dioxin (USEPA, 2024)

Results and Discussion

Dioxin Concentration in Soil and Plants

The summary results for the mean concentrations of dioxin compounds present in soil and five species of plants are present in [Table 1](#). Analysis of the samples indicated that 17 congeners of dioxin compounds were present in soil and plant species in the study area. The mean concentration of dioxin congeners in soil and plants varied significantly ($p > 0.05$) across the five sample locations. The mean concentrations of sixteen dioxin congeners in this study exceeded the permissible limits for soil and all congeners on action levels for food products like vegetables ([DeVito *et al.*, 2024](#)).

Table 1—Summary concentration (mean and standard deviation) of dioxins in soil and plants around industrial sites in Koko, Delta State, Nigeria.

	Soil	Plant	P-Value
2,3,7,8-TCDF	1.27±1.61	1.5±0.49	P>0.05
2,3,7,8-TCDD	0.08±0.08	0.2±0.44	P>0.05
1,2,3,7,8-PCDF	0.86±1.04	0.64±0.55	P>0.05
2,3,4,7,8-PCDF	0.2±0.31	4.49±8.2	P>0.05
1,2,3,7,8-PCDD	3.39±4.08	20.61±24.06	P>0.05
1,2,3,4,7,8-HxCDF	1.25±1.28	1.55±2.53	P>0.05
1,2,3,6,7,8-HxCDF	10.58±13.11	5.31±5.09	P>0.05
2,3,4,6,7,8-HxCDF	2.26±2.64	2.0±2.6	P>0.05
1,2,3,4,7,8-HxCDD	7.82±16.11	1.21±1.03	P>0.05
1,2,3,6,7,8-HxCDD	2.28±4.67	4.49±7.36	P>0.05
1,2,3,7,8,9-HxCDD	1.64.4±2.74	0.25±0.21	P>0.05
1,2,3,7,8,9-HxCDF	7.5±16.53	1.11±1.72	P>0.05
1,2,3,4,6,7,8-HpCDF	3.52±7.51	0.38±0.34	P>0.05
1,2,3,4,6,7,8-HpCDD	1.73±3.3	1.3±1.3	P>0.05
1,2,3,4,7,8,9-HpCDF	0.85±1.56	3.2±2.77	P>0.05
OCDD	4.2±8.85	0.18±0.06	P>0.05
OCDF	0.5±0.58	0.26±0.1	P>0.05

In soil, the highest concentration of dioxin congeners was 1,2,3,6,7,8-HxCDF (10.58±13.11), followed by 1,2,3,4,7,8-HxCDD (7.82±16.11), 1,2,3,7,8,9-HxCDF (7.5±16.53) and the least was 2,3,7,8-TCDD (0.08±0.08). This is similar to studies on soil toxicity of persistent organic pollutants around industries from food and dietary exposure in Europe and China (Alwyn and Jerzy, 2021 and Li *et al.*, 2023).

In plants, the highest concentration of dioxin congeners was observed in 1,2,3,7,8-PCDD (20.61±24.06), followed by 1,2,3,6,7,8-HxCDF (5.31±5.08), 1,2,3,6,7,8-HxCDD (4.49±7.36) and 2,3,4,7,8-PCDF (4.49±8.2) respectively and the least was in OCDD (0.18±0.06). Our result is consistent with previous studies (Grassi *et al.*, 2010; Tuyet-Hanh *et al.*, 2015; Vaccher *et al.*, 2021 and WHO, 2023) on the concentration of dioxins in leguminous plants. Among the studied plants, dioxin concentrations in decreasing order include *P. montana*, *V. amygdalina*, *C. odorata*, *C. pentandra*, and *Musa sp.*

Generally, the mean sum of dioxin concentration in soil and plants in the study areas were similar, however, comparison between congeners revealed that the concentration of congeners in soil was higher than those in plants. This finding is similar to previous research which indicates that dioxin accumulates more rapidly in soil components due to their binding properties and interactions, in contrast to plants (Cachada *et al.*, 2018; Jouko, 2019; Tang *et al.*, 2022; Li *et al.*, 2023).

Bioaccumulation Factor of Dioxins from Soil and Plants

The summary result for the BAF is shown in Table 2. The dioxin concentration in soil and plants collected from sites 1 and 2 showed elevated BAF compared to site 5. This implies that kudzu (*P. montana*), and silk cotton (*C. pentandra*) had higher bioaccumulation potentials than Awolowo leaf (*C. odorata*), whereas sites 3 and 4 have low or no bioaccumulation indicating low bioaccumulation potentials for bitter leaf (*V. amygdalina*) and banana (*Musa sp.*) among the studied plants.

Table 2—Bioaccumulation factor for dioxin congeners in soil and plants collected from Koko, Delta State.

Location	Plants	Soil	BAF
Site 1	1.96	0.22	8.91
Site 2	4.86	0.08	60.75
Site 3	3.41	10.39	0.33
Site 4	1.96	2.35	0.83
Site 5	2.12	1.64	1.29

Health Risk Assessment of Dioxins to Humans

Vegetables are important constituents of human diets as they provide essential minerals and nutrients to the body. Also, medicinal plants are used for ailments and as supplements by local people as alternative to orthodox medicine. However, there are concerns about the potential risks associated with the intake of vegetables and medicinal plants due to increasing industrial activities in many localities across Nigeria and the increasing concern about environmental pollution (Michael *et al.*, 2023; Basilua *et al.*, 2019). A survey from Japan reveals that dioxins have contributed significantly to the global disease burden in occupational and non-occupational populations worldwide from dietary intake (Muzembo *et al.*, 2019). Hence, for this study, the EDI and HR values were calculated to evaluate the possible health risks of consuming contaminated plants with dioxins in the study area. The EDI reveals the average daily intake of dioxins through edible plant consumption for adults and children compared to the reference dose. An HR value less than 1.0 indicates a low risk, while a value above 1.0 means a high risk. The RfD value for dioxin as stipulated by the USEPA, is 0.03mg/kg. An EDI value that exceeds this dose is deemed unsafe for human consumption. From the analysis, the EDI values for the studied plants did not exceed the reference dose for adults and children (Table 3). The HR values also show that all the studied plants fell below 1.0, indicating a low risk of contamination upon consumption. Our findings are consistent with those of Grassi *et al.* (2010), Tuyet-Hanh *et al.* (2015), and Vaccher *et al.* (2021) on the risk assessment of dioxins to human health from the consumption of contaminated vegetables.

Table 3—Human health risk assessment from edible plants collected from Koko, Delta State.

Risk Indicator	Categories	<i>Ceiba pentandra</i>	<i>Pueraria montana</i>	<i>Vermonia amygdalina</i>	<i>Musa sp.</i>	<i>Chromolaena odorata</i>
EDI	Adult	0.000000	0.000249	0.000119	0.000202	0.000109
	Children	0.000000	0.000503	0.000242	0.000041	0.000219
HR	Adult	0.000005	0.008300	0.003992	0.006720	0.003657
	Children	0.000009	0.016770	0.008077	0.001359	0.007332

Conclusion

Routine environmental monitoring for persistent organic contaminants with human health implication is necessary as industrial activities, emissions and waste disposal increased across communities in Nigeria. The concentration of dioxins reported in soil was higher than the values reported in vegetables and medicinal plants. Plant such as *P. montana* and *C. pentandra* had higher bioaccumulation potentials than *C. odorata*, whereas perennial plants like *V. amygdalina* and *Musa sp.* showed no bioaccumulation. No immediate health risk was observed from the consumption of vegetables contaminated with dioxins in this study. This study provides the first insight into dioxin concentrations in Koko town, Delta State, Nigeria. Despite the low level of dioxins reported in this study, there is a need for routine and extensive study of persistent and

emerging contaminants in surface water and seafood in the area as industrial activities continue to increase across the region.

Conflict of Interest

The author declares no conflict of interest.

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