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Phthalate Esters in Agricultural Soils of Udu, Delta State, Nigeria; Spatial Distribution and Potential Risks Assessment

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Abstract: Phthalate esters (PAEs) are widely used plasticizers that can leach into agricultural soils through plastic mulching films, irrigation pipes, and agrochemical residues, posing potential ecological and human health risks. This study assessed the spatial distribution and potential risks assessment of six PAEs in agricultural soils from Udu, Delta State, Nigeria. Soil samples were collected from twenty locations and analyzed using gas chromatography–mass spectrometry detector (GC–MSD) after extraction by ultrasonication. Total PAE concentrations (Σ6 PAEs) ranged from 8.46 to 40.3 ng g-1. On average, Diethyl Phthalate (DEP), Di(2-ethylhexyl) phthalate (DEHP) and Butyl benzyl phthalate (BBP) were the dominant congeners. Analysis of variance (ANOVA) indicated no significant variations ($p > 0.05$) in PAEs concentrations in among the locations. The potential risks assessed using hazard index and total cancer risk indicated that the risks for both children and adults were generally within acceptable limits. Although the overall risk levels were low, the persistence and bioaccumulative nature of DEHP and related congeners indicate potential long-term impacts on soil quality and food safety. The findings highlight the need for continuous monitoring, regulation of agricultural plastic usage, and adoption of biodegradable alternatives to mitigate phthalate contamination in farmlands and safeguard public health.

Keywords: Phthalate esters, Agricultural soils, Udu, GC–MS, Carcinogenic risk, Plasticizers

INTRODUCTION

Plasticizers known as phthalate esters (PAEs) represent a class of synthetic organic compounds that have become a pervasive component of modern polymer products. Commonly used to increase the flexibility, durability and process-ability of polyvinyl chloride (PVC) and other plastic materials (Okpara *et al.*, 2022). Because they are not chemically bound within the polymer backbone, they are susceptible to leaching, volatilization, migration and biodegradation once in the environment (Xu *et al.*, 2022; Okpara and Tesi *et al.*, 2025a). Over the last several decades, the proliferation of plastic materials in packaging, consumer goods, agricultural films, irrigation tubing and other applications has created a continuous source of PAE emissions to multiple environmental media including soils (Wang *et al.*, 2021). As plastic use intensifies in agriculture, the recognition of agricultural soils as important sinks and potential exposure media for PAEs has grown accordingly (Yesildagli *et al.*, 2024; Li *et al.*, 2023).

Agricultural soils, by virtue of their role as the interface between chemical inputs (fertilizers, herbicides and plastic-related residues), cropping systems, and sometimes waste-derived amendments or irrigation water, are particularly vulnerable to the accumulation of PAEs (Han *et al.*, 2025; Yesildagli *et al.*, 2024). Several pathways may lead to PAE inputs: direct contact between soils and plastic mulches, greenhouse films, drip-irrigation tubing and pesticide/fertilizer containers; reuse of wastewater or sludge as amendments; atmospheric deposition of volatile or particle-bound phthalates; and surface runoff of plastic-rich debris. For instance, Li *et al*. (2016) have reported that in irrigated agricultural soils, plastic film and mulching practices can significantly enhance PAE burdens in the soil matrix. A study conducted on a tropical island covering 106 agricultural sites found an average Σ16 PAE concentration of 451.87 ± 284.08 μg/kg, with land-use type (vegetable fields > orchards > paddy fields) and urbanization level strongly influencing PAE levels (Tian *et al.*, 2024). These findings confirm that agricultural soils are not passive media, but dynamic environments where human-driven materials may accumulate and pose risks to soil health and food safety.

Once in the soil environment, the behaviour of PAEs is complex and influenced by both intrinsic chemical properties (molecular weight, hydrophobicity, vapour pressure, water solubility) and soil parameters (organic carbon content, clay/sand texture, moisture, pH, microbial activity) (Ahmed *et al.*, 2014). Typically, longer-chain phthalates such as di-(2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DnBP) are more hydrophobic, less water-soluble and more prone to adsorption to organic matter or soil particles, leading to their accumulation in the topsoil layer. Shorter-chain congeners may migrate more readily downward or volatilize, depending on conditions (Taiwo *et al.*, 2025). Soil organic matter and clay minerals can act as sorption sites, thereby reducing the mobility of some PAEs; however, these same factors can protect PAEs from biodegradation, thereby prolonging their residence time in soil (Li *et al.*, 2023). The interplay of these processes means that agricultural soils in tropical environments characterized by high rainfall, warm temperatures, and intensive cropping may exhibit distinct PAE dynamics compared to temperate regions, especially when plastic material usage and waste-handling practices differ. From a human-health and ecological perspective, the presence of PAEs in soils raises multiple concerns. Many phthalate congeners are classified as endocrine-disrupting chemicals (EDCs); they have been linked to reproductive, developmental, hormonal and carcinogenic effects under chronic exposure scenarios (Okpara and Tesi, 2025b; Kingsley and Witthayawirasak, 2020a; Kingsley and Witthayawirasak, 2020b). In the context of agriculture, two primary exposure pathways are relevant: (1) the soil matrix itself, via incidental ingestion (children playing in fields), dermal contact or inhalation of soil dust; and (2) the food chain, when crops grown on contaminated soils uptake PAEs and transfer them to humans (Li *et al.*, 2018). While crop uptake of PAEs is less studied than that of heavy metals, evidence indicates that PAE accumulation in edible plant tissues is possible and may be especially noteworthy under high soil concentrations or when plastic mulch residues are in contact with the root zone (Tian *et al.*, 2024).

Despite awareness of PAE contamination in soils, there remain significant gaps in research—particularly in tropical agricultural zones and developing countries. A recent review highlighted that although PAEs have been widely detected in agricultural soils, most published work stems from China or temperate zones; tropical regions and African countries remain under-represented (Li *et al.*, 2023). In Nigeria, for instance, studies on PAE

contamination have largely focused on sediments, urban soils/dust or water rather than agricultural soils. One study in central Nigeria reported phthalate esters in sediments from Ilorin (Okoro *et al.*, 2024) while PAEs was assessed in indoor dust of some microenvironments within Ikeja and Ota, Nigeria (Anake & Nnamani, 2023). Moreover, a study in Delta State evaluated the levels of PAE plasticizers in surface water of Ethiope River system (Edjere *et al.*, 2016) while Agbozu *et al.* (2024) investigated PAEs in dumpsite soils of Isoko areas of Delta State. Consequently, agricultural zones in Nigeria especially those in the oil-rich Niger Delta region with high plastic use in farm operations and complex waste streams represent important knowledge gaps.

Udu in Delta State exemplifies a region where these research gaps converge. Udu is situated within a tropical deltaic environment characterized by high rainfall, intensive crop cultivation and proximity to petrochemical activities. The agriculture in Udu often employs plastic scarecrow, and heavy use of packaging for agrochemicals and fertilizers. These practices, combined with potential atmospheric or surface deposition of industrial-derived PAEs, create a plausible scenario for elevated soil PAE burdens. Yet to date no study has systematically quantified PAE concentrations, spatial variations or risks in agricultural soils in Udu. Understanding the prevalence of PAEs in this region is essential not only for local food-safety and soil-health concerns but also for national agricultural policy, given Nigeria's growing emphasis on sustainable crop production and land-use intensification. Therefore, this study aimed to quantify the levels od PAEs, assess the spatial distribution and potential risks of PAEs in agricultural soils in Udu, Delta State, Nigeria. By accomplishing these aims, the study will provide baseline data for PAE soil contamination in a tropical Nigerian agricultural context, and will support recommendations for waste management, plastic-use practices and policy formulation aiming at sustainable and safe agricultural production.

MATERIAL AND METHODS

Description of the Study Area

Udu is one of the Local Government Area (LGA) of Delta State, Nigeria located in the western Niger Delta and traditionally part of the Urhobo ethnic territory. Udu has over 30 communities with the administrative headquarters being Otor-Udu. Udu lies between Warri River to the West and Okpare Creek to the East, occupying coastal plain and lowland terrain typical of the Niger Delta. The study area supports perennial vegetation and year-round farming. Udu has an intricate network of rivers, creeks, lagoons, and seasonal wetlands – typical of the southern Niger Delta. These hydrological features influence drainage, sediment deposition and agricultural suitability. The map of the study area showing the sampling points is shown in Figure 1.

Sample Collection and Preparation

Twenty agricultural soils were collected from farmlands in twenty communities in Udu LGA of Delta State. In each farmland, soil samples were collected with the aid of a soil auger at a depth of 0-20 cm from five different points. The soils were pooled together after foreign materials have been removed and a single representative or composite sample was obtained. All the collected samples were kept in amber glass bottles, labelled appropriately, stored in a cooler containing ice block, and taken to the laboratory. In the laboratory, soil

samples were air dried at ambient temperature. Air-dried soil samples were sieved through a 2 mm stainless steel mesh and kept in amber glass bottles prior to extraction.

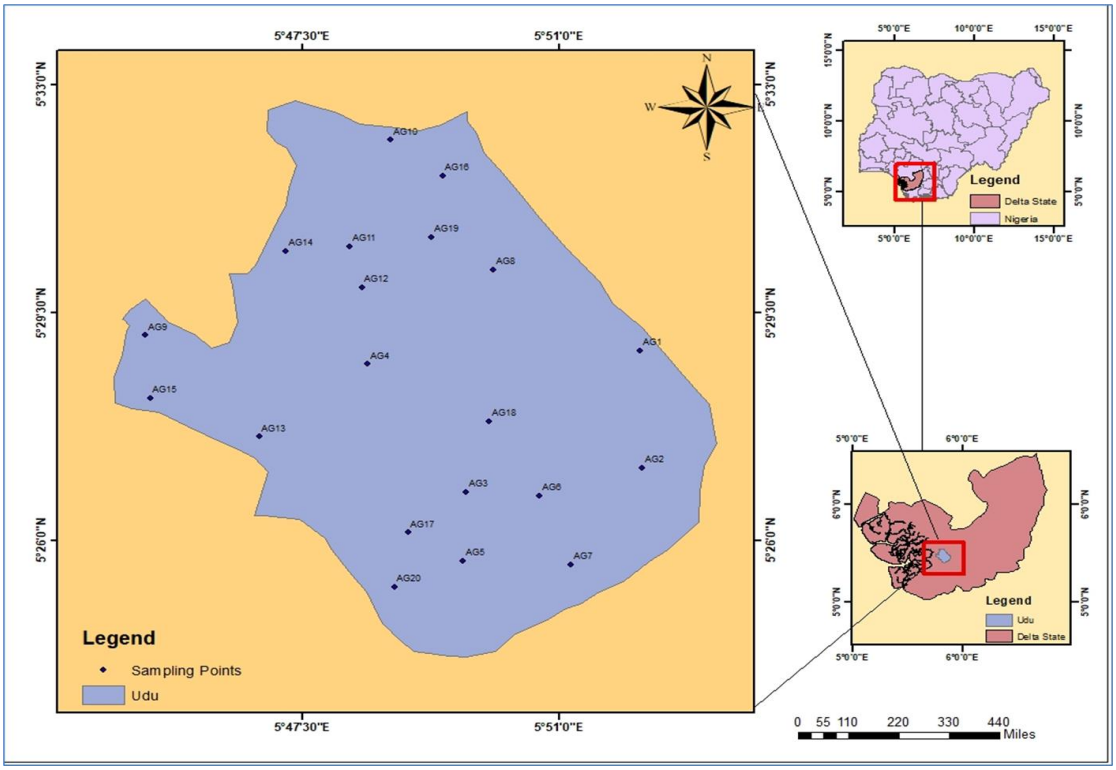

Figure 1: Map of study area

Standards and Reagents

A standard mixture of: 6 PAEs including, Dimethyl Phthalate (DMP), Diethyl Phthalate (DEP), Dibutyl Phthalate (DBP), Benzyl butyl Phthalate (BBP), Bis(2-Ethylhexyl) phthalate (DEHP) and Di-n-octyl phthalate (D*n*OP)) was obtained from Isotope Laboratories Inc., (Cambridge, MA, USA). Hexane, dichloromethane, ammonium hydroxide, copper powder, anhydrous sodium sulfate, florisil and silica gel were purchased from Merck (Darmstadt, Germany).

Extraction and Quantification of PAEs in Soil

The USEPA Method 3550C was used for the extraction. A mass of 10 g of the soil sample was mixed with 10 g of anhydrous Na_2SO_4. A 50 mL aliquot of n-hexane/dichloromethane (DCM) (1:1 v/v) was added. The mixture was extracted by ultrasonication for 30 minutes. The organic extract was filtered and the process was repeated two more times. The extracts were combined and reduced to 1 mL by using a rotary evaporator. The concentrated extract was cleaned-up in a multi-layer column containing anhydrous Na_2SO_4, alumina and silica gel packed from top to bottom. The elution of PAEs from the column was carried out with a 50 mL aliquot of a 1:1 n-hexane/DCM mixture. The eluate was concentrated to 2 mL under a slow flowing stream of pure nitrogen gas. The extracted samples were analyzed for PAEs by a gas chromatograph (GC) coupled to mass spectrometry detector (MSD) (Agilent Technologies, Santa Clara, USA). An HP-5 5% phenyl methyl Siloxane capillary column (30 m × 0.25 µm × 0.25 mm) was employed for separation. Pure helium gas of 1.8 mL/min flow rate was served as carrier gas. The GC column had a starting temperature of 150 °C, held

for 1.3 min, and then increased by 15 °C min^{-1} to 200 °C for 2 min and finally increased to 300 °C at 15 °C $min^{-1}$for 4 min. The transfer line, quadrupole, ion source and injection port temperatures were 280, 150, 230 and 250 °C respectively. The splitless mode was used in injecting 1 µL of the samples into the instrument. The MSD was run at an electron impact energy of 918 EmVolts and data were collected via ion monitoring mode. The PAEs were identified by comparing retention time of the PAEs in the samples to those from real PAEs standards.

Quality Control and Assurance

Strict quality control measures were adopted from the sampling to quantification stages in this study to reduce the possibility of PAEs contamination. No plastic material was used. All samples were collected using glassware. Every piece of glassware was thoroughly cleaned before used. The glassware was cleaned with a 10 % soap solution (Laboline, Fischer Scientific) and tap water. Then, it was rinsed with a 50 % HCl solution. These precautions were taken to preserve the samples' integrity and guard against any PAEs interference from outside sources. Before being used, the cleaned glassware was completely rinsed with HPLC-grade acetone after being immersed in diluted H_2SO_4 and dried in an oven at 105 °C for five hours. Blank samples were examined to determine the possible background contribution from instruments, glassware, solvents, and laboratory media. These blank samples, which included no target analytes, underwent the analytical and sample preparation processes as the real samples. By examining these blanks, any possible interference or contamination from the analytical procedure or the laboratory setting might be found and taken into consideration, guaranteeing precise evaluation of the target analytes in the samples. Ultrapure Milli-Q water, which is renowned for its exceptional purity, was used to prepare blanks. PAEs concentrations in blank samples were below their limit of quantifications. Moreover, *spiked recovery, the limit of detection (LOD), the limit of quantification (LOQ), precision and linearity were used for quality control and method validation in accordance to the European Commission (2019) guidelines.* For spiked recovery, a*lready analyzed soil samples were spiked with standard solutions* of the PAEs at three concentration levels (5, 10 and 20 ng L^{-1}) and the spiked samples were analyzed. Thereafter the percentage recoveries were computed. *The percentage of PAEs recovered ranged between* 82.3 % and 99.2 %. The linearity of the method was achieved with calibration curves of standard PAEs solutions at five concentration levels. The LOD (limit of detection) was calculated from the PAEs concentration that produced a signal : noise = 3, whereas the LOQ (limit of quantification) was calculated from the PAEs concentration that produced a signal : noise = 10. The LOD and LOQ of the PAEs congeners ranged from 0.003 to 0.03 ng g^{-1} and 0.01 to 0.09 ng g^{-1} respectively. The RSD for replicate analysis (n = 3) was < 6 % while the R^2 values obtained from the calibration curves ranged from 0.997 to 0.999.

Statistical Analysis

Statistical data analysis was done using the version 27 of IBM-SPSS software. Analysis of variance (ANOVA) was used to determine if there was a significant spatial variation in the concentrations of the PAEs in the soil samples after the Kolmogorov-Smirnov and Shapiro-Wilks normality tests indicated that the data were normally distributed.

Human Health Risks Assessment of PAEs in the Soil

The non-carcinogenic risk of PAEs in the soil was assessed using the hazard index via ingestion, inhalation and dermal contact whereas the carcinogenic risks was assessed using the total cancer risk. The risk assessment was obtained using equations (1) – (7) (USEPA, 1989; USEPA, 2009). Generally, HI value greater than 1 indicates that there is adverse non-carcinogenic risk while total cancer risk values greater than 1.0 x 10^{-6} indicate that there is carcinogenic risk (USEPA, 2022).

$$\text{Hazard index (HI)} = HQ_{Ing} + HQ_{Inh} + HQ_{Dermal} \quad (1)$$

$$HQ_{Ing} = \frac{CDI_{Ing}}{RfD_o}\ ;\ HQ_{Inh} = \frac{CDI_{Inh}}{RfD_i}\ ;\ HQ_{Derm} = \frac{CDI_{Derm}}{RfD_o \times GIABS} \quad (2)$$

$$CDI_{Ing} = \left[\frac{\text{C} \times \text{IngR x EF x ED}}{\text{BW x AT}_{nc}} \times 10^{-6}\right] \quad (3)$$

$$CDI_{Inh} = \frac{C \times Inh \times EF \times ED \times ET}{PEF \times ATnc} \quad (4)$$

$$CDI_{Dermal} = \left[\frac{\text{C x SA x AF x ABS x EF x ED}}{\text{BW x AT}_{nc}} \times 10^{-6}\right] \quad (5)$$

$$\text{Total cancer risk} = ILCR_{Ing} + ILCR_{Inh} + ILCR_{Dermal} \quad (6)$$

$$ILCR_{Ing} = CDI_{Ing} \times CSF\ ;\ ILCR_{Inh} = CDI_{Inh} \times IUR\ ;\ ILCR_{Dermal} = CDI_{Derm} \times (CSF \times GIABS) \quad (7)$$

Where $HQ_{Ing,}$ HQ_{Inh} and HQ_{Dermal} are hazard quotients for ingestion, inhalation and dermal contact respectively whereas the $ILCR_{Ing}$, $ILCR_{Inh}$ and $ILCR_{Dermal}$ are corresponding incremental lifetime risks. The definitions of other terms and values of variables used for evaluating the human health risk are shown in Table 1.

Table 1: Definitions and values of variables for human health risk assessment of PAEs in soil

Variables	Unit	Definition	Values		References
			Child	Adult	
C	ng g^{-1}	Concentration of PAEs in soils			
AF	mg/cm^2	Soil to skin adherences factor	0.2	0.07	USEPA, 2011
BW	Kg	Average body weight	15	60	Tesi *et al*. (2025)
ED	Year	Exposure duration	6	30	USEPA, 2001
EF	day/yr	Exposure frequency	350	350	USEPA, 2001
ET	hr/day	Exposure time	8	8	USEPA, 1989
ABS	-	Absorption factor	0.001	0.001	USEPA, 2011
IngR	mg/day	Ingestion rate	200	100	USDOE, 2011
InhR	m^3/day	Inhalation rate	12	50	USDOE, 2011
SA	cm^2/event	Skin surface area	2800	5700	USDOE, 2011
ATnc	D	Averaging time for non-carcinogenic	ED x 365		USDOE, 2011
ATca	d	Averaging time for carcinogenic	LT x 365		USDOE, 2011
LT	Year	Lifetime	63 years		WHO, 2026
PEF	m^3/kg	Soil to air particulate emission factor	1.36 x 10^9		USDOE, 2011

RfDo	(mg/kg/d)	Oral reference dose	Contaminant specific	USEPA (2022)
CSF	(mg/kg/d)	Oral slope factor	Contaminant specific	USEPA (2022)
IUR	($\mu g/m^3$)	Inhalation unit risk	Contaminant specific	USEPA (2022)

RESULTS AND DISCUSSIONS

Concentrations and Distribution of Phthalate Esters in the Agricultural Soils

The concentrations of the six phthalate esters (PAEs) detected in agricultural soils from Udu are presented in Table 2. PAEs occurred consistently in all samples indicating their widespread and diffuse sources. The widespread detection of multiple PAEs demonstrates the pervasive influence of human activities on the agricultural soils of Udu. There was wide spatial variation across the twenty sampling sites. Total PAE concentrations (Σ6 PAEs) ranged from 8.46 ng g^{-1} (AG5) to 40.3 ng g^{-1} (AG18), with an overall mean of 17.2 ng g^{-1} suggesting moderate but heterogeneous contamination within the study area. On average, the occurrence pattern of the PAEs was in the order of DEP (8.08 ng g^{-1}) > DEHP (4.69 ng g^{-1}) > BBP (3.30 ng g^{-1}) > DBP (0.67 ng g^{-1}) > DMP (0.28 ng g^{-1}) > DnOP (0.22 ng g^{-1}) (Figure 2). The predominance of DEP, DEHP and BBP mirrors patterns reported in other tropical and temperate agricultural environments, where these congeners are widely used as plasticizers in irrigation hoses, polyethylene films, pesticide containers, and fertilizer packaging (Staples *et al.*, 1997; Ahmed *et al.*, 2014). Sites AG7 (25.3 ng g^{-1}), AG12 (29.5 ng g^{-1}), AG16 (25.8 ng g^{-1}), AG17 (25.8 ng g^{-1}), AG18 (40.3 ng g^{-1}) and AG20 (30.4 ng g^{-1}) recorded the highest Σ6 PAEs. The elevated Σ6 PAEs concentrations in these sites correspond to intensive crop production zones which might facilitate the leaching of PAEs through photo-oxidation and mechanical weathering (Li *et al.*, 2023).

Table 2: Phthalate esters concentrations (ng g^{-1}) in the agricultural soils

Samples	DMP	DEP	DBP	BBP	DEHP	DnOP	Σ6 PAEs
AG1	0.40	8.24	0.04	0.04	0.02	0.35	9.09
AG2	1.03	8.37	0.03	0.05	0.02	0.02	9.52
AG3	0.09	8.23	0.05	0.07	0.37	0.04	8.85
AG4	0.27	4.32	0.20	0.35	4.24	0.07	9.45
AG5	0.05	8.23	0.05	0.06	0.05	0.02	8.46
AG6	0.12	8.25	0.08	1.14	2.33	0.03	12.0
AG7	0.08	8.26	0.06	0.15	16.7	0.03	25.3
AG8	1.33	8.51	0.03	0.01	0.01	0.02	9.91
AG9	0.17	8.27	0.07	1.06	0.02	0.02	9.61
AG10	0.26	8.21	0.54	0.52	0.45	0.05	10.0
AG11	0.18	8.23	0.12	4.09	0.55	0.34	13.5
AG12	0.29	8.24	2.15	6.09	12.4	0.33	29.5
AG13	0.28	8.23	0.12	0.21	0.31	0.42	9.57
AG14	0.04	8.20	3.04	4.02	3.03	0.02	18.4
AG15	0.25	8.38	0.13	6.32	2.19	2.13	19.4
AG16	0.16	8.27	6.27	4.16	6.66	0.23	25.8
AG17	0.09	8.23	0.05	5.07	12.3	0.04	25.8
AG18	0.08	8.26	0.06	16.2	15.7	0.03	40.3
AG19	0.12	8.25	0.08	5.14	6.33	0.03	20.0
AG20	0.25	8.38	0.13	11.3	10.2	0.10	30.4

Conversely, relatively lower concentrations reported in other sites may reflect less intensive cultivation, improved soil aeration, or higher microbial degradation rates factors known to influence PAE dissipation in tropical soils (Edjere *et al.*, 2016). The one-way ANOVA revealed no statistically significant difference in PAE concentrations among the 20 agricultural sites (F-cal = 0.844656, p = 0.649742 > 0.05) (Table 3). The F-value was lower than the F-critical (1.691496), indicating that variations in PAE levels across sites were not significant at the 95% confidence level.

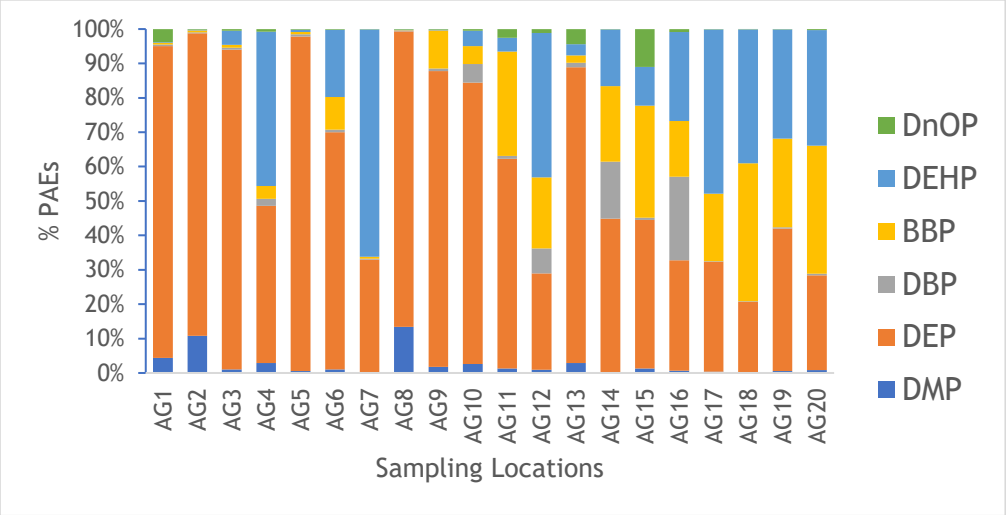

Figure 2: Percentage composition of PAEs in the agricultural soils

Table 3: ANOVA results of PAEs in the agricultural soils

Source of Variation	SS	df	MS	F-cal	P-value	F-crit
Between Groups	279.6109	19	14.71636	0.844656	0.649742	1.691496
Within Groups	1742.291	100	17.42291			
Total	2021.902	119				

Most of the total variance (SS = 2021.902) was attributed to within-group differences, suggesting similar agricultural practices across Udu. This agrees with findings from other agroecosystems where diffuse plastic-related pollution leads to even distribution of phthalates in soils (Lu *et al.*, 2022; Okoro *et al.*, 2024).

The consistent detection of DEHP in all samples can be attributed to its hydrophobicity (log $K_oW \approx 7.5$), low volatility, and strong sorption affinity for organic matter and clay fractions, which enhance persistence and hinder degradation (Staples *et al.*, 1997). These characteristics make DEHP a recalcitrant contaminant capable of bioaccumulation in soil organisms and transfer to crops. Short-chain congeners such as DMP and DEP, though more soluble, may volatilize or leach deeper, creating multiple exposure routes (Ahmed *et al.*, 2014). Although the present levels are not extreme, they are environmentally significant considering the persistence and cumulative nature of PAEs. These compounds can inhibit soil enzyme activity, disrupt microbial community structure, and interfere with nutrient cycling (Ahmed *et al.*, 2014), thereby impairing soil fertility and resilience over time. The presence of DEHP and BBP both prioritized endocrine-disrupting chemicals (EDCs) under the

EU REACH regulation further elevates ecological concern due to potential effects on soil biota and trophic dynamics. From a human-health perspective, PAE contamination in agricultural soils poses both direct and indirect risks. Direct exposure occurs through dermal contact, inhalation of contaminated dust, or incidental ingestion of soil particles by farmers and children. Indirect exposure arises from crop uptake, as PAEs are translocated from roots into edible tissues (Kingsley and Witthayawirasak *et al.*, 2020a). Chronic dietary exposure to DEHP, DBP, and BBP has been associated with reproductive toxicity, hormonal imbalance, and developmental disorders (Okoro *et al.*, 2024). While the current concentrations remain below most international soil quality thresholds, ongoing plastic use in agriculture could lead to cumulative buildup. Under tropical conditions that accelerate plastic degradation, additive release may intensify, increasing ecological and health risks.

Table 4: Comparison of PAEs in agricultural soils of Udu with others in literature

Location	No. of samples	No. of PAEs	Total PAEs Concentration (ng g^{-1})	References
Udu, Nigeria	20	6	8.46-40.3	This study
Turkey	40	13	212-484	Yesildagli *et al.* (2024)
Turkey	5	13	240-1248	Yesildagli *et al.*, 2024
Turkey	5	13	35-585	Yesildagli *et al.*, (2024)
China (Fujian, Guandong etc)	123	15	75.0 - 6369	Niu *et al.* (2014)
Mainland China	109	16	23.5-903	Chen *et al.* (2024)
Ningxia, China	-	5	156-566	Zhang *et al.* (2023)
Czech Republic	12	2	0.21-3.47	Daňková *et al.* (2015)
Eastern China (Shangai & Jiagstu)	26	5	109-5560	Sun *et al.* (2018)
Jilin Province, China	8	19	0.69-3.30	Lu *et al.* (2022)
China (Guangdong & Guangzhou)	37	17	0.445-4.437	Xing *et al.* (2022)
Xinjiang, China	249	16	7.29-1064	Li *et al.* (2025)
Yinchuan, Northwest China	89	16	0.391-11.924	Tao *et al.* (2020)
A tropical island in China	106	16	451.87±284.08	Tian *et al.* (2024)
Shandong Pennisula, East China	36	16	1.374-18.810	Li *et al.* (2016)
Nanjing, China	44	6	0.40-6.20	Wang *et al.* (2015)
Nanjing, China	27	6	0.15-9.68	Wang *et al.* (2013)
Nanjing, China	4	6	930±840	Ma *et al.* (2015)
Huang-Huai-Hai region of China	136	16	51.7-3569	Zhou *et al.* (2020)
Xinjiang Oasis, China	58	5	0.6280 - 515	Liu *et al.* (2025)
Chongqing, China	10	11	0.12-0.46	Li *et al.* (2020)
Nanjing, China	111	5	0.26-2.53	Chen *et al.* (2017)
Yellow River Delta, China	100	6	1.087-14.391	Sun *et al.* (2023)
Yangtze River Delta of China	4	6	5.42-1580	Wei *et al.* (2020)
Tianjin, China	-	6	0.05-10.4	Kong *et al.* (2012)

Table 2 compares our results with others previously reported for agricultural soils from other parts of the world without taking into account the number of congeners examined, the analytical technique employed, variations in the physicochemical characteristics of these matrices, or the environmental conditions of the various regions. Such a comparison identifies hotspot areas for PAEs and offers information on global PAE concentrations trends. The concentrations of PAEs found in this study were higher than those reported in Czech Republic (Dankova *et al.*, 2015) and China (Liu *et al.*, 2022; Li *et al.*, 2020; Chen *et al.*, 2017; Wang *et al.*, 2015; Wang *et al.*, 2013). However, the PAEs in

agricultural soils from Udu were lower than the those reported in Turkey (Yesildagli *et al.*, 2024) and China (Niu *et al.*, 2014; Zhang *et al.*, 2023; Sun *et al.*, 2018; Tian *et al.*, 2024; Ma *et al.*, 2015; Zhou *et al.*, 2020).

Hazard Index (HI) of Phthalate Esters (PAEs) in Agricultural Soils

The calculated hazard index (HI) values for phthalate esters (PAEs) in agricultural soils are presented in Figure 3. The HI values for both children and adults were below the critical threshold of 1 across all sampling sites, implying an overall absence of immediate non-carcinogenic risk from soil exposure. However, children exhibited significantly higher HI values than adults, a trend consistent across all sampling points. The highest HI values were recorded at AG7, AG12, AG16, and AG19, ranging between 1.20×10^{-2} and 1.75×10^{-2}, while adult HI values in the same sites were generally below 3.00×10^{-3}. The elevated HI values in these specific locations correspond with areas where higher concentrations of DEHP, DBP, and BBP were previously observed, suggesting that spatial variations in HI are driven by differences in the abundance and mobility of dominant PAEs in the soils. Although the HI values for both population groups were < 1, indicating that the current non-carcinogenic risks are within acceptable limits, the comparatively higher values observed for children signify potential susceptibility to long-term or cumulative effects. Children are more vulnerable to soil contaminants due to their lower body weight, higher ingestion rate of soil particles, and frequent hand-to-mouth activities (Niu *et al.*, 2014). Chronic exposure to low levels of PAEs such as DEHP and DBP, even below the regulatory threshold, may contribute to endocrine disruption, reproductive toxicity, and developmental abnormalities (Zeng *et al.*, 2009). The detection of higher HI values in several sampling sites may therefore be an early indicator of potential public health concern if the continuous accumulation of PAEs in the soil persists.

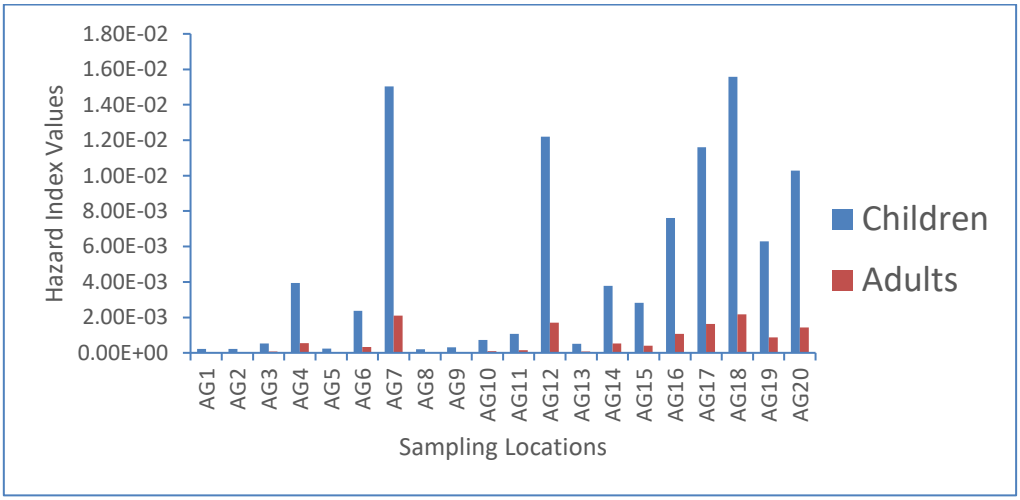

Figure 3: Hazard index of PAEs in the agricultural soils

Total Cancer Risk Assessment of Phthalate Esters in Agricultural Soils

Figure 4 shows the estimated total cancer risk values of PAEs in the agricultural soils. For children, the risk values ranged from 2.22×10^{-9} to 3.50×10^{-6}, whereas for adults the total

cancer risk values ranged from 1.50 ×10^{-9} to 2.38 × 10^{-6}. The consistent pattern of children having higher risk estimates than adults reflect age-dependent exposure factors. From an environmental and health standpoint, these risk levels carry meaningful implications. Although most estimated risks lie on the low end of the usual carcinogenic risk spectrum (commonly referenced thresholds: CR <10^{-6} = very low, 10^{-6} < CR<10^{-4} = low) — consistent with other agricultural soil and crop studies where PAE carcinogenic risks fell into the "very low" category (Xing *et al.*, 2022). Nevertheless, the highest values (3.5×10^{-6} for children) slightly exceed the commonly used "very low" boundary (10^{-6}), suggesting a need for caution and further monitoring.

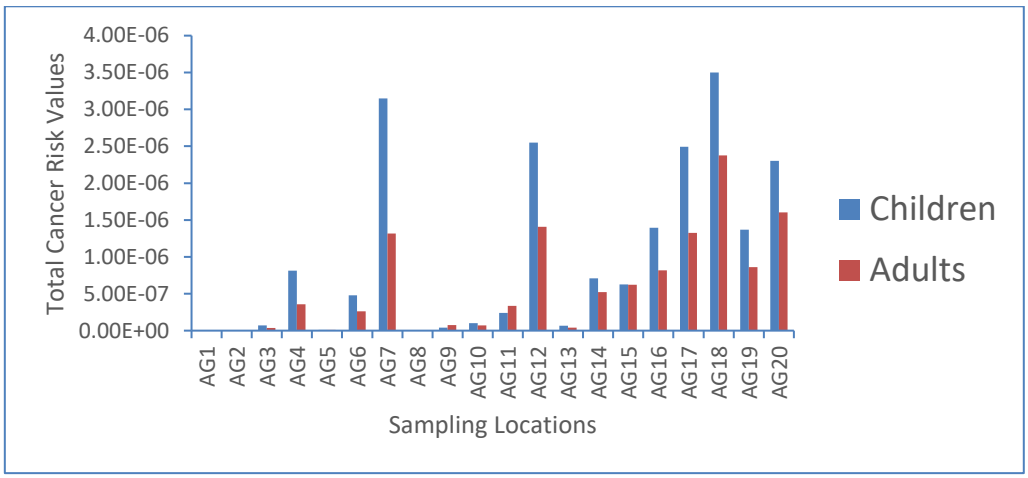

Figure 4: Total cancer risk of PAEs in the agricultural soils

The pattern of higher risk in children aligns with known vulnerability: children have lower body weights, higher intake rates (soil ingestion, hand-to-mouth activity) and longer lifetime exposure horizons (Xing *et al.*, 2022; Ma *et al.*, 2015). Environmentally, the elevated cancer-risk values at particular hotspots indicate that certain soils may have accumulated higher loads of carcinogenic or potentially carcinogenic phthalates (e.g., Di(2-ethylhexyl) phthalate (DEHP)). Once in soil, PAEs can migrate to plants, enter the food chain and re-expose humans with leafy crops known to bio-accumulate PAEs under certain conditions (Peijnenburg & Struijs, 2006). From a public-health perspective, even these low-magnitude risks warrant attention because: (1) They accrue over a lifetime, so small differences can compound; (2) They are non-uniform across sites, which means localized exposures may be disproportionately high; (3) The fact that children are more exposed and potentially more sensitive to endocrine-disrupting effects of PAEs (in addition to cancer-risk) raises the concern that risk assessments based only on cancer endpoints may underestimate vulnerability. For example, phthalates have been linked to endocrine disruption, alterations in thyroid and reproductive systems, and increased cancer incidence in pediatric populations (Li *et al.*, 2016). However, while the overall estimated cancer-risks from PAEs in these agricultural soils are mostly within accepted low-risk bounds, the presence of "hot-spots" and differential vulnerability (children vs adults) implies that site-specific management, further detailed exposure assessment (including dietary and non-dietary pathways), and source-control strategies are justified (Zhang *et al.*, 2023; Khishdost *et al.*, 2023).

CONCLUSION

This study revealed the widespread presence of multiple phthalate esters (PAEs) in agricultural soils of Udu. The dominant congeners were DEP, DEHP and BBP consistent with their extensive use as plasticizers in agricultural films, irrigation pipes, and fertilizer packaging. Statistical analyses demonstrated no spatial variability and shared pollution sources. Although the total concentrations of PAEs generally fell within ranges reported for other agricultural regions, their persistence and tendency for bioaccumulation raise ecological and human-health concerns. The cancer-risk assessment indicated low but notable risks, especially for children, underscoring potential long-term exposure through direct soil contact and indirect dietary uptake. Environmentally, these contaminants may impair soil microbial activity, enzyme function, and nutrient cycling, thereby reducing soil fertility and ecosystem resilience. The findings emphasize the need for proactive management of plastic use in agriculture. Strategies such as promoting biodegradable mulching materials, minimizing plastic waste accumulation, and establishing periodic monitoring programs are essential for preventing further buildup of phthalates in farmlands. Future research should integrate crop uptake studies and multi-pathway risk modeling to provide a more holistic evaluation of human and ecological health implications.

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