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Abstract

The increasing development of petroleum and petrochemical infrastructure in coastal Lagos raises concerns about the introduction and accumulation of emerging organic contaminants in surrounding environmental media. This study investigated the occurrence, distribution and contamination status of phthalate esters in soil and water around the new oil refinery area in Ibeju-Lekki, Lagos, Nigeria. Soil and water samples were collected systematically from selected locations within the study area during the rainy and dry seasons, with Olorogbo community used as a control/reference location. Samples were extracted using appropriate organic solvents and analysed by gas chromatography–mass spectrometry (GC-MS). The study evaluated spatial variations in phthalate concentrations using descriptive statistics, Pearson correlation, proximity analysis and hierarchical clustering, while contamination factor (CF), contamination factor index (CFI) and pollution load index (PLI) were used to assess the degree of contamination relative to selected background values. The results revealed considerable spatial heterogeneity in phthalate concentrations in soil. Dibutyl phthalate (DBP) was particularly prominent, with a concentration of 19.31 mg/kg at SS9A and a corresponding contamination factor of 521.89, making SS9A a major soil contamination hotspot. The soil PLI at SS9A was 29.65, while SW52A and SS13B also exhibited elevated contamination loads. Water samples generally showed near-zero concentrations at several locations; however, SW9A and particularly UW17A exhibited markedly elevated concentrations. UW17A recorded the highest CFI (14,959.80) and PLI (455.31), largely driven by bis(2-ethylhexyl) phthalate and benzyl butyl phthalate. Strong correlations between selected surface- and underground-water locations suggest possible common sources or hydrological connectivity. Overall, the findings demonstrate localized but substantial phthalate contamination in parts of the study area and emphasize the need for continued environmental monitoring, source identification and appropriate pollution-control measures around rapidly developing industrial zones.

Keywords: Phthalate esters; Environmental contamination; Ibeju-Lekki; GC-MS

INTRODUCTION

Industrialization, urban expansion and the increasing demand for energy and manufactured products have resulted in the release of numerous chemical substances into the environment. These substances may originate from industrial processing, transportation, commercial activities, waste disposal and other anthropogenic sources. Once released, contaminants can occur in different environmental compartments, including air, soil and water, and may be redistributed through atmospheric transport, surface runoff, precipitation, leaching and other environmental processes. The presence of potentially harmful contaminants in these media makes environmental monitoring important, particularly in areas experiencing rapid industrial development.

Organic pollutants represent an important group of environmental contaminants because they comprise chemicals with widely varying physical and chemical properties. They include volatile organic compounds (VOCs), semi-volatile organic compounds and compounds with persistent characteristics. Hydrocarbon compounds constitute an important component of the VOC group and include alkanes, alkenes, alkynes and aromatic hydrocarbons. Persistent organic pollutants (POPs), in contrast, are of particular environmental concern because some members can remain in environmental systems for prolonged periods, undergo long-range transport, accumulate in organisms and produce adverse effects on ecological systems and human health. Their ability to move beyond the locations where they were originally released provides an important justification for continued environmental surveillance and control measures (UNEP, 2009).

The environmental importance of persistent organic contaminants has led to international initiatives aimed at reducing their production, use and release. The Stockholm Convention, adopted in 2001, established an international framework to control persistent organic pollutants and reduce their adverse effects on human health and the environment (Garban et al., 2002). Monitoring programmes addressing long-range atmospheric transport and environmental contamination have consequently become important components of efforts to understand the movement and distribution of persistent contaminants. Polycyclic aromatic hydrocarbons (PAHs), for example, are environmentally important petroleum- and combustion-associated contaminants, with benzo(a)pyrene recognized as one of the most toxic members of this group. The continuing monitoring of such contaminants is therefore necessary for evaluating environmental quality and identifying potential risks associated with industrial activities (Garban et al., 2002).

Petroleum refining is one industrial activity with considerable potential to influence environmental quality. Refineries transform crude petroleum into fuels and other products that serve as feedstocks for numerous industrial and commercial applications. Petroleum-derived materials are consequently present in a wide range of products and services used in modern society. However, the processes involved in crude-oil refining can also generate environmental emissions. Refinery operations have been identified as important contributors to air pollution, with potential effects extending beyond the immediate vicinity of the facility (Galvan, 2007).

Several stages of petroleum processing can contribute to atmospheric emissions. Refining activities may release carbon monoxide, sulphur dioxide, nitrogen oxides, volatile organic compounds and particulate matter. The magnitude and composition of these emissions depend on the nature of the crude oil, the processing technologies employed and the operational characteristics of the refinery. Refinery capacity has expanded considerably over the past decades in response to global petroleum demand, thereby increasing the importance of understanding the environmental consequences associated with petroleum-processing activities (Adebiyi, 2002).

The environmental implications of refinery development may extend beyond emissions generated during routine processing. The construction and expansion of refinery infrastructure require substantial movement of equipment and materials and may involve heavy machinery, transport vehicles, storage facilities, pipelines, roads and other supporting infrastructure. Construction activities can alter existing soil surfaces and drainage patterns, while storage, transportation and industrial operations may provide additional opportunities for contaminants to enter surrounding environmental media. These processes may create pathways for both organic and inorganic substances to reach soil and surface-water systems, particularly where industrial infrastructure is developed close to previously less industrialized environments (Kappel et al., 2013).

These issues are particularly relevant to the Ibeju-Lekki area of Lagos State, Nigeria, where major industrial development has occurred within the Lekki Free Trade Zone. The area is situated near the Lekki Lagoon and the Atlantic Ocean and contains a combination of coastal ecosystems, residential communities and rapidly expanding industrial infrastructure. The establishment of the new refinery represents a major change in the industrial profile of the area. The refinery occupies approximately 2,635 hectares and was designed as an integrated refinery and petrochemical complex with a processing capacity of approximately 650,000 barrels of crude oil per day. Its product portfolio includes petroleum fuels and petrochemical products such as polypropylene. Its coastal location also provides logistical advantages for the transportation of crude oil, equipment and refined products.

The scale of this industrial development makes environmental assessment of the surrounding area particularly important. Construction, transportation, storage and refinery-related activities can interact with existing environmental pathways and potentially introduce contaminants into nearby soils and water bodies. The development of oil and gas infrastructure may therefore increase opportunities for contaminants to enter surface-water systems and other environmental compartments (Kappel et al., 2013).

1.1 Phthalates

Among the synthetic organic chemicals of increasing environmental concern are **phthalate esters (PAEs), commonly referred to as phthalates**. Scientific interest in these compounds has increased because of their extensive application, widespread occurrence in environmental media and potential effects on wildlife and human health. Investigations of phthalate contamination have consequently expanded considerably over recent decades (Adewuyi, 2012).

Phthalates are primarily used as plasticizers, where they improve the flexibility and durability of polymeric materials, particularly polyvinyl chloride (PVC). Their applications extend beyond plastics and include a wide range of consumer and industrial products. They have been reported in products such as cosmetics, soaps, shampoos, paints, pharmaceutical coatings and pesticide formulations (Blount et al., 2000; David et al., 2001). Other applications include their use in adhesives, defoaming agents, solvents and lubricants, while specific phthalates such as di(2-ethylhexyl) phthalate (DEHP) have been used extensively in medical equipment and related materials (NTP, 1998).

The environmental occurrence of phthalates is closely associated with their extensive use and their tendency to migrate from materials into surrounding environmental media. Because many phthalates are not covalently incorporated into the polymer matrix, they can gradually diffuse or leach from products during use, storage and disposal (Rock et al., 1986). Consequently, phthalates may enter environmental systems through several pathways, including waste disposal, industrial discharges, wastewater, runoff and leaching. Their occurrence in aquatic environments has been associated with effluent discharges, waste-dump leachates and diffuse sources (Fatoki et al., 2002).

Phthalates also undergo transformation following environmental or biological exposure. The metabolism of phthalates can initially produce monoester metabolites, which may subsequently undergo further oxidative transformation (ATSDR, 2002). Their physicochemical properties and environmental behaviour vary among individual phthalate congeners. Some compounds have an affinity for organic matter and may be transferred between environmental compartments, while their biological transformation and degradation depend on environmental conditions (Thuren, 1986). These characteristics make it important to consider individual phthalate compounds rather than treating all members of the group as environmentally identical.

The widespread use of phthalates has resulted in numerous opportunities for human exposure. Members of the general population may encounter these compounds through consumer products, food, water, medical materials and other sources (Swan et al., 2003). Their metabolites have been detected in human populations, reflecting the widespread nature of exposure (Becker et al., 2004). In addition, occupational and medical circumstances can result in substantially greater exposure than that experienced by the general population. The Agency for Toxic Substances and Disease Registry has reported exposure estimates for DEHP in the general population, while medical procedures involving DEHP-containing materials can result in considerably higher exposures (ATSDR, 1993; CERHR, 2000).

The toxicological significance of phthalates differs among individual compounds and depends on their chemical structures and exposure characteristics. Phthalates are diesters of phthalic acid, with variations in their side-chain structures contributing to differences in their biological activity and toxicity (Woodward, 1988). Evidence from toxicological and epidemiological investigations has raised concerns about their potential reproductive, developmental, respiratory and endocrine-related effects. Some studies have reported associations between phthalate exposure and carcinogenic or teratogenic effects (Moore et al., 2001), while other investigations have examined possible relationships with premature puberty and reproductive abnormalities (Colon et al., 2000; Fisher, 2003).

Additional studies have reported associations between exposure to certain phthalates and adverse reproductive outcomes, including effects on sperm quality and reproductive function in males (Rozaty et al., 2002) and pregnancy-related outcomes in women (Duty et al., 2003). Respiratory effects have also been investigated, including relationships between exposure to phthalate-associated compounds and impaired pulmonary function, airway obstruction and asthma (Jaakkola et al., 1999; Joppin et al., 2004). Among the concerns that have received particular attention is the capacity of some phthalates to interfere with endocrine function, thereby potentially affecting reproductive and developmental processes (EEA, 2005).

Water represents an important potential pathway for environmental exposure to phthalates. Contaminants released from industrial and domestic sources can be transported through wastewater, surface runoff and leaching processes and subsequently enter rivers, streams and other aquatic systems. This pathway is particularly relevant in developing regions where communities may depend substantially on surface-water resources and where water-treatment infrastructure may be limited. Consequently, monitoring phthalates in water can provide important information about environmental contamination and potential human exposure.

The potential for phthalates to occur simultaneously in soil and water is also important because these environmental compartments are interconnected. Contaminants deposited on land may be transported through runoff or leaching, while contaminated water may contribute to the redistribution of pollutants within surrounding terrestrial environments. In an area experiencing substantial petroleum-related and industrial development, these processes warrant systematic investigation because changes in land use, infrastructure and industrial activity may modify the pathways through which organic contaminants enter and move through the environment.

Although considerable attention has been given internationally to phthalate contamination, information on the occurrence and distribution of these compounds in rapidly developing industrial areas of Nigeria remains comparatively limited. This is particularly important in Ibeju-Lekki, where the establishment and expansion of major petroleum and petrochemical infrastructure have introduced new industrial activities into an area containing residential communities and interconnected terrestrial and aquatic environments. Establishing the environmental status of phthalates in this setting is necessary to provide a reference against which subsequent changes in environmental quality can be evaluated.

Therefore, the present study was undertaken to investigate the occurrence and distribution of selected phthalate esters in soil and water within the Ibeju-Lekki area of Lagos State, Nigeria, with particular attention to the environment surrounding the new refinery. The study also assessed variations in phthalate concentrations among sampling locations and seasons and evaluated the degree of contamination in the investigated environmental media. The resulting information provides an environmental baseline that can support future monitoring, pollution-control measures and environmental management in this rapidly developing industrial area.

METHODOLOGY

2.0.1 Study Design

The study was conducted in Ibeju-lekki area of Lagos, Nigeria, specifically focusing on the areas surrounding the new Oil Refinery located in the Lekki Free Trade Zone. This region includes coastal areas, urban settlements, and the earmarked industrial zones. Samples were Collected during the rainy season (April – July) and dry season Dec. – Feb.), going for sampling on average of 2 - 3 times in a month (an average of once in every two weeks). Water samples were collected in two sets of different layers – surface layer and a depth of 15cm. Soil samples – subsoil depth varies depending on location. Typically, sampling starts around 15cm to 30cm below the surface. Area was mapped and sectionalized and one sampling carried out in each section systematically and randomly with each sampling point not being aligned. Control research at Olorogbo community to know the baseline geogenic contamination to ascertain if there is any known pollutant.

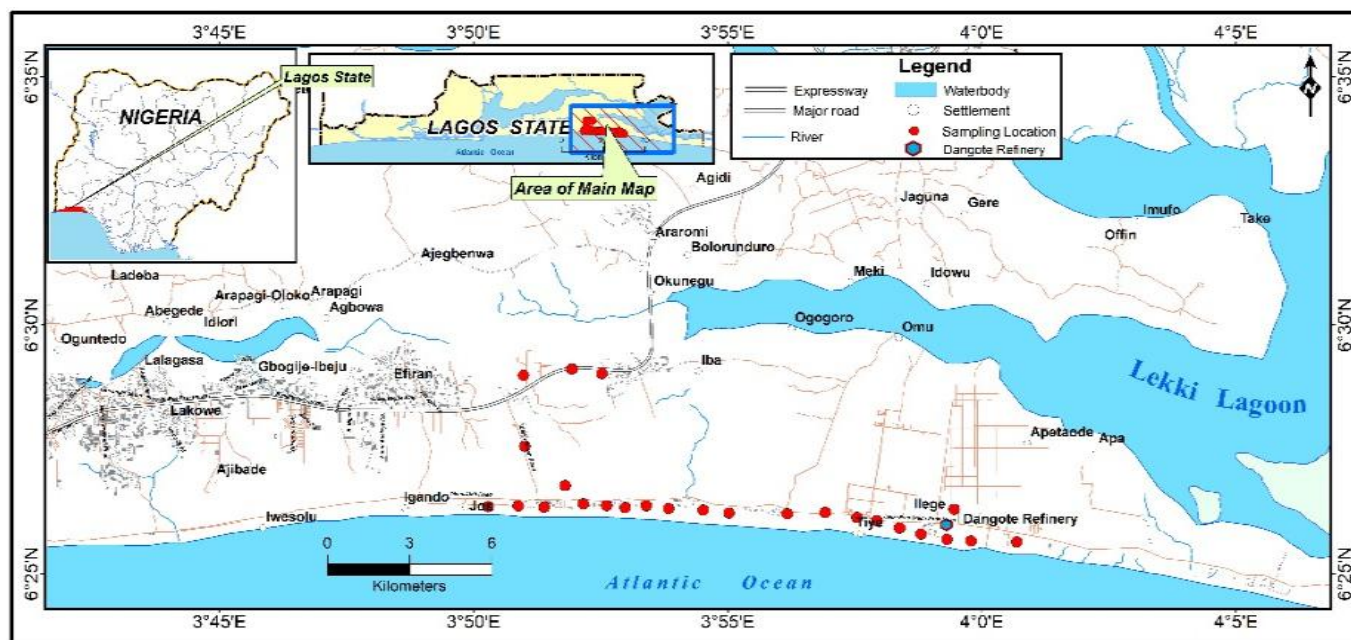


Fig. 2.1 Map Showing the Study Area, New Refinery and the Sampling Points

2.0.2 Study Area

The New Oil Refinery is located in the South-East of the Lekki Free Trade Zone (FTZ) in Ibeju-Lekki, Lagos, near the Lekki Lagoon, along the coast of Atlantic Ocean, covering a land area of approximately 2,635 hectares. It is Located on coordinates Latitude 6.45873° or 6° 27' 31" north; Longitude 4.01409 degrees or 4° 0' 51". Ibeju-Lekki (home of the New Oil Refinery), situated within the Lagos State town of Lekki, stands out for its exquisite charm, earning it the moniker “The New Lagos” and establishing itself as one of the most affluent neighborhoods in Lagos State. Bordered by Ogun State to the north, Eti-Osa LGA to the west, Epe LGA to the east, and the Atlantic Ocean to the south, with a population exceeding 100,000. Ibeju- Lekki is about 75km long and 20 km at its widest point and is spread over 646km² or a quarter of the total land mass of Lagos state. Located along the coastal plain of Nigeria, Ibeju-Lekki has

many creeks and Lagoons and it is mainly populated by Ijebu speaking people of the Yoruba tribe in Nigeria. Indigenes of Ibeju Lekki are mainly fishermen, who traverse the length and breadth of both Lagos Lagoon and Atlantic Ocean for different species of fishes, cray fish, prawn, lobsters and crabs. The resultant effect of this is that the women smoke/grill the catches from their husbands' nets. Smoked fish is a local delicacy which has been exported and is popularly eaten with sour garri, a local derivative of cassava, usually produced by Ijebu women. Indigenes of Ibeju Lekki also produce brooms, coconut oil and palm oil from the abundant coconut and palm trees that grow along the coastline (<https://nseenergybusiness.com/projects/dangote-refinery-lagos>).

2.1 CHEMICALS

Analytical grade n-hexane (99%), dichloromethane (99%) and acetone (99.5%) were purchased from Thermo Fisher Scientific, Waltham, Massachusetts, USA. Activated silica gel, anhydrous sodium sulphate and deionized water were obtained from Sigma-Aldrich, St. Louis, Missouri, USA.

2.2 SAMPLE COLLECTION

Water for the study were sampled according to the method of S. T. Grassloff, 1983. Water samples were collected directly from sample source using a properly pre-cleaned amber bottles. The bottles were first rinsed with the sample water before collection, and the collected samples were stored in an ice-packed cooler before being transported to the laboratory refrigerator for storage at a temperature of 4°C until the time for analysis. pH of water samples was determined and recorded at the point of collection. Soil samples were collected using soil auger, properly wrapped and stored in aluminum foil to prevent contact with plastic materials and kept in ice-packed cooler, thereafter transported to the laboratory refrigerator for storage at 4°C temperature until time of analysis. All collected samples were appropriately labelled. The use of plastics was strictly controlled to avoid contact with samples in order to prevent contamination during sample collection for phthalates. GPS location/coordinates of sample collection points were also taken and recorded. Samples were analysed within 24 hours of sample collection.

2.3 SAMPLE PREPARATION – SOIL SAMPLE

Apparatus used were Metal sieve, Analytical balance, Ultrasonic bath, Filter paper, Rotary evaporator, Beakers, Measuring cylinders and Spatula

2.3.1 Procedural steps

- i. Air dried pulverized soil samples were sieved to obtain a uniform particle size
- ii. 5 g of soil sample was weighed into a glass beaker
- iii. 50 ml solvent hexane:acetone (1:1) was added to the sample in an ultrasonic bath and sonicated for 20 minutes at 30°C
- iv. After the first extract, the beakers were swirled and sonication was repeated. This was done 3 to 4 times to ensure maximum recovery/extraction
- v. The extracts were combined, filtered and passed through activated silica gel and anhydrous sodium sulphate for clean-up

- vi. After clean-up, extract was concentrated using rotary evaporator at low temperature
- vii. Sample was then taken for GC-MS analysis (Andrianova & Quimby, 2019).

2.4 SAMPLE PREPARATION – WATER SAMPLE

Apparatus used were Retort stand, Separatory funnel, Measuring cylinder, beakers, flasks, Glass funnel and Rotary evaporator

2.4.1 Procedural Steps

- i. 50 ml water sample was measured into the separatory funnel
- ii. 5 ml dichloromethane was added into the sample in the separatory funnel as the solvent of extraction
- iii. The mixture was then shaken vigorously several times to allow the analytes to partition between the two liquid phases
- iv. After allowing the phases to separate, the extract was collected
- v. The extraction was repeated multiple times to ensure efficient recovery of the analytes
- vi. The extracts were then added together and passed through anhydrous sodium sulphate for clean-up
- vii. Afterwards, the volume was reduced using rotary evaporator (Anderson et al, 2015)

2.5 PREPARATION OF STANDARDS

PAE standard, 1000 ppm (Catalog Number M-8061-R1) containing 14 PEs components purchased from AccuStandard by Lagos State Environmental Protection Agency (LASEPA) was acquired and used to prepare a 5-point dilution calibration standards (0.1ppm, 0.05ppm, 0.025ppm, 0.06ppm and 0.03 ppm). A stock standard solution of the PEs was prepared by dissolving 10 ml of the reference standard (1000ppm) in 100 ml of deionized water to make 100 ppm stock solution from which the calibration standards were prepared using serial dilution. 20 µL of each working standard (in duplicates) was spiked into the GC-MS; the retention time and respective peak areas were created. The peak of the analyte was found by comparing the retention time of the ratio of analyte in the sample to that of the standard.

2.6 METHOD VALIDATION

Recovery Studies

20 uL of 0.1 ppm mixed standard was added to sample extracts and analysis was carried out. Percentage recovery was determined according to the following equation (Harris, 2001):

$$\% \text{ Recovery} = \frac{\text{Conc. of spiked Sample} - \text{Conc. of unspiked sample}}{\text{Concentration of added standard}} \times 100$$

Calibration Curves

The calibration plot of the heavy metals was achieved by plotting mean peak areas derived from replicate analysis of their standard solutions versus their respective concentrations.

The limit of detection (LOD) and limit of quantification (LOQ) are calculated using the equations below;

$$\text{LOD} = \frac{3 \times \text{standard deviation}}{\text{slope of calibration curve}}$$

$$\text{LOQ} = \frac{10 \times \text{standard deviation}}{\text{slope of calibration curve}}$$

2.7 INSTRUMENT DESCRIPTION

An Agilent 7890B GC with an Agilent 5977B MSD System equipped with a split/splitless inlet and an Agilent 7693 Automatic Liquid Sampler was used for this analysis. Analysis was run in duplicate. The table below shows the instrumental conditions used in the data acquisition.

Table 2.1: Chromatographic Conditions

GC	Agilent 7890B coupled with 5977B Mass selective Detector
Sampler	Agilent 7693 Injector tower with 10µL syringe
Carrier	Helium [flow; 1.2mL/min]
Injection	1µL Splitless, 250 °C
Column	HP-5ms 30 m, 250 µm, 0.25 µm
Oven	50 °C (hold 1 min) to 270 °C at 20 °C/min (hold 4 min)
MSD	Transfer line temp [280] Quadrupole temp [150 °C] Ion source temp [230°C]

RESULTS AND DISCUSSION

Table 3.1: Phthalate Concentration in Soil Samples

Compound Name	UNIT	CSWE	CSWE	SS	SS	SS	SS	SS	SS	SW	SW	SWS	SS 15A
		2B	1B	9A	10B	13B	14A	15A	16B	5A	52A	3B	
Dimethyl phthalate	mg/Kg	0.02	0.03	0.11	0.01	0.01	0.00	0.02	0.01	0.00	0.02	0.01	0.10
Diethyl Phthalate	mg/Kg	0.07	0.17	0.85	0.03	0.06	0.00	0.23	0.09	0.02	0.21	0.07	0.01
Diisobutyl phthalate	mg/Kg	0.45	0.92	10.13	0.17	0.17	0.00	1.40	0.32	0.10	0.86	0.24	0.10
Dibutyl phthalate	mg/Kg	1.29	1.26	19.31	0.36	0.47	0.01	1.09	1.16	0.11	3.09	0.25	0.20
Bis(2-methoxyethyl) phthalate	mg/Kg	0.06	0.04	1.61	0.02	0.02	0.02	0.01	0.04	1.66	0.06	0.01	0.01

bis(4-Methoxyethyl)phthalate	mg/Kg	0.07	0.03	3.16	0.04	0.01	0.00	0.02	0.05	0.15	0.01	0.00	0.04
bis(2-Ethoxyethyl)phthalate	mg/Kg	1.03	0.58	1.20	0.26	0.12	0.00	1.17	0.09	0.15	0.13	0.07	0.20
Dipentyl phthalate	mg/Kg	0.00	0.08	0.19	0.00	0.03	0.00	0.01	0.01	0.02	0.00	0.00	0.40
Dihexyl phthalate	mg/Kg	0.01	0.01	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.56	0.00	0.30
Benzyl butyl phthalate	mg/Kg	0.06	0.03	0.21	0.00	0.01	0.00	0.02	0.02	0.01	2.12	0.01	0.20
bis(2-Ethylhexyl)phthalate	mg/Kg	29.84	0.70	0.55	1.98	13.30	1.07	0.34	1.86	1.51	9.38	1.60	0.10
Di-n-octyl phthalate	mg/Kg	6.50	1.55	3.19	7.23	2.87	0.17	0.22	2.46	0.55	5.41	2.33	0.70
Dinonyl phthalate	mg/Kg	2.39	0.05	1.79	1.14	0.43	0.05	0.02	3.38	0.79	0.94	0.19	0.50

Table 3.2: Descriptive Statistics of Phthalates Concentration in Soil Samples

	Minimum	Maximum	Mean		Std.
	Statistic	Statistic	Statistic	Std. Error	Deviation
					Statistic
SS 9A	0.02	19.31	3.2541	1.53227	5.52466
SS 10B	0.00	7.23	0.8679	0.55450	1.99927
SS 13B	0.00	13.30	1.3452	1.01955	3.67605
SS 14A	0.00	1.07	0.1012	0.08189	0.29527
SS 15A	0.00	1.40	0.3510	0.14199	0.51195
SS 16B	0.00	3.38	0.7301	0.31493	1.13551
SW 5A	0.00	1.66	0.3902	0.16132	0.58165
SW 52A	0.00	9.38	1.7527	0.77388	2.79025
SWS 3B	0.00	2.33	0.3682	0.20225	0.72921
SS15A	0.01	0.70	0.2200	0.05732	0.20668

3.0.1 Descriptive Analysis

The results showed high value for SS 9A (0.02 - 19.31) and SW 52A (0 - 9.38) which indicates substantial heterogeneity, possibly due to localized contamination “hotspots” (e.g., dumping or runoff areas). SS 14A (0 - 1.07) and SS 15A (0.01 - 0.70) suggest more uniform or low-level concentrations, possibly background or control samples. A wide range generally indicates heterogeneous soil contamination or elemental distribution, which is common in field sites affected by differential deposition or leaching.

SS 9A (Mean = 3.25) and SW 52A (Mean = 1.75) are the highest, implying that these sites might have the greatest contaminant load or nutrient concentration while SS 14A (Mean = 0.10) is the lowest, suggesting a relatively clean or unimpacted site. This pattern may reflect spatial variation in anthropogenic input (industrial, agricultural, or domestic sources).

The highest SD: SS 9A (5.52) and SW 52A (2.79) indicate high data dispersion which is possible non-uniform contamination or inconsistent soil matrix.

The lowest SD: SS 14A (0.30) and SS 15A (0.21) indicate more stable concentrations and homogeneity.

These statistics suggest the soil system is spatially heterogeneous and certain sites (SS 9A, SW 52A) may be environmental “hotspots”. The Data variability implies the influence of site-specific activities, soil type, or hydrological differences.

3.0.2 Correlation Analysis

Two matrices presented were one two-tailed and another one-tailed where both reflects Pearson’s correlation coefficients (r) among all 10 sample variables.

The Strong Positive Correlations (Highly Significant at 0.01 level)

SS13B ↔ SS14A ($r = 0.998$, $p < 0.01$). Almost perfect correlation from both sites behave almost identically. Possibly same source or soil matrix condition.

SS10B ↔ SWS3B ($r = 0.927$, $p < 0.01$). This indicates shared influence, maybe from similar contamination or hydrological connection.

SW52A ↔ SS13B ($r = 0.908$, $p < 0.01$) and SW52A ↔ SS14A ($r = 0.883$, $p < 0.01$)

Suggests that SW52A ↔ SS13B contamination correlates strongly with SS13B and SS14A, implying possible leaching or runoff transfer.

SS10B ↔ SS15A ($r = 0.706$, $p < 0.01$). This demonstrates that spiked and natural concentrations follow a similar pattern, confirming consistency or controlled spiking behavior.

Significant Positive Correlations (at 0.05 level)

SS9A ↔ SS15A ($r = 0.677$, $p = 0.011$). Indicates that the contaminant or property measured is spatially consistent between these locations.

SS16B ↔ SW52A ($r = 0.559$, $p = 0.047$) and SS16B ↔ SWS3B ($r = 0.627$, $p = 0.022$). Implies strong environmental coupling between subsurface and surface layers.

Some pairs like SS9A ↔ SS14A (-0.148) and SS15A ↔ SW5A (-0.187) show negative or weak associations, meaning their behavior is independent or inversely related which perhaps may be due to differing soil types or localized anthropogenic activities.

Table 3.3: Correlation Matrix (2-Tailed) of Phthalate Concentration in Soil Samples

		SS 9A	SS 10B	SS 13B	SS 14A	SS 15A	SS 16B	SW 5A	SW 52A	SWS 3B	SS 15A
SS 9A	Pearson Correlation	1	-0.009	-0.117	-0.148	.677*	0.133	-0.156	0.104	0.011	-0.053
	Sig. (2-tailed)		0.976	0.703	0.631	0.011	0.664	0.611	0.736	0.971	0.863
	N	13	13	13	13	13	13	13	13	13	13
SS 10B	Pearson Correlation	- 0.00 9	1	0.370	0.316	-0.060	.646*	0.260	.603*	.927**	.706**
	Sig. (2-tailed)	0.97 6		0.214	0.293	0.845	0.017	0.391	0.029	0.000	0.007
	N	13	13	13	13	13	13	13	13	13	13
SS 13B	Pearson Correlation	- 0.11 7	0.370	1	.998**	-0.001	0.422	.597*	.908**	.677*	-0.016
	Sig. (2-tailed)	0.70 3	0.214		0.000	0.997	0.151	0.031	0.000	0.011	0.959
	N	13	13	13	13	13	13	13	13	13	13
SS 14A	Pearson Correlation	- 0.14 8	0.316	.998**	1	-0.025	0.401	.612*	.883**	.630*	-0.055
	Sig. (2-tailed)	0.63 1	0.293	0.000		0.936	0.174	0.026	0.000	0.021	0.859

[illegible]

SS 15A	Pearson Correlation	-0.053	.706**	-0.016	-0.055	-0.158	.641*	-0.061	0.218	0.511	1
	Sig. (2-tailed)	0.863	0.007	0.959	0.859	0.605	0.018	0.843	0.474	0.074	
	N	13	13	13	13	13	13	13	13	13	13

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 3.4: Correlation Matrix (1-Tailed) of Phthalate Concentration in Soil Samples

		SS 9A	SS 10B	SS 13B	SS 14A	SS 15A	SS 16B	SW 5A	SW 52A	SWS 3B	SS 15A
SS 9A	Pearson Correlation	1	-0.009	-0.117	-0.148	.677**	0.133	-0.156	0.104	0.011	-0.053
	Sig. (1-tailed)		0.488	0.351	0.315	0.005	0.332	0.306	0.368	0.486	0.432
	N	13	13	13	13	13	13	13	13	13	13
SS 10B	Pearson Correlation	-0.009	1	0.370	0.316	-0.060	.646**	0.260	.603*	.927**	.706**
	Sig. (1-tailed)	0.488		0.107	0.146	0.422	0.009	0.196	0.015	0.000	0.003
	N	13	13	13	13	13	13	13	13	13	13
SS 13B	Pearson Correlation	-0.117	0.370	1	.998**	-0.001	0.422	.597*	.908**	.677**	-0.016

	Sig. (1-tailed)	0.351	0.107		0.000	0.498	0.076	0.016	0.000	0.006	0.479
	N	13	13	13	13	13	13	13	13	13	13
SS 14A	Pearson Correlation	-.148	0.316	.998**	1	-0.025	0.401	.612*	.883**	.630*	-0.055
	Sig. (1-tailed)	0.315	0.146	0.000		0.468	0.087	0.013	0.000	0.010	0.429
	N	13	13	13	13	13	13	13	13	13	13
SS 15A	Pearson Correlation	.677*	-.060	-0.001	-0.025	1	-0.038	-0.187	0.072	0.018	-0.158
	Sig. (1-tailed)	0.005	0.422	0.498	0.468		0.451	0.271	0.408	0.476	0.303
	N	13	13	13	13	13	13	13	13	13	13
SS 16B	Pearson Correlation	0.133	.646*	0.422	0.401	-0.038	1	0.429	.559*	.627*	.641**
	Sig. (1-tailed)	0.332	0.009	0.076	0.087	0.451		0.072	0.023	0.011	0.009
	N	13	13	13	13	13	13	13	13	13	13
SW 5A	Pearson Correlation	-.156	0.260	.597*	.612*	-0.187	0.429	1	.493*	0.407	-0.061

	Sig. (1-tailed)	0.306	0.196	0.016	0.013	0.271	0.072		0.043	0.084	0.421
	N	13	13	13	13	13	13	13	13	13	13
SW 52A	Pearson Correlation	0.104	.603*	.908**	.883**	0.072	.559*	.493*	1	.836**	0.218
	Sig. (1-tailed)	0.368	0.015	0.000	0.000	0.408	0.023	0.043		0.000	0.237
	N	13	13	13	13	13	13	13	13	13	13
SWS 3B	Pearson Correlation	0.011	.927*	.677**	.630*	0.018	.627*	0.407	.836**	1	.511*
	Sig. (1-tailed)	0.486	0.000	0.006	0.010	0.476	0.011	0.084	0.000		0.037
	N	13	13	13	13	13	13	13	13	13	13
SS 15A SPIKE D	Pearson Correlation	-0.053	.706*	-0.016	-0.055	-0.158	.641**	-0.061	0.218	.511*	1
	Sig. (1-tailed)	0.432	0.003	0.479	0.429	0.303	0.009	0.421	0.237	0.037	
	N	13	13	13	13	13	13	13	13	13	13

** . Correlation is significant at the 0.01 level (1-tailed).

* . Correlation is significant at the 0.05 level (1-tailed).

3.0.3 Proximity Matrix (Squared Euclidean Distances)

This matrix shows pairwise dissimilarities among the 13 cases (samples).

Most Similar Pairs (Low Distance) are;

Case 1 & 8 (0.098)

Case 8 & 9 (0.350)

Case 1 & 9 (0.339)

Case 2 & 7 (1.120)

These sites have nearly identical chemical signatures, likely belonging to the same pollution cluster.

Most Dissimilar Pairs (High Distance) are;

Case 4 with others (e.g., 4–1 = 380.97; 4–11 = 564.67)

Case 11 - 4 and 11 - 10 show extremely high dissimilarity.

Case 4 and Case 11 appear as outliers or unique sites, possibly due to extreme contamination or different soil composition.

The low Euclidean distances among 1–2–7–8–9 indicate homogeneity while high distances with 4, 11, and 12 suggest spatial segregation with different zones, pollution sources, or land use types.

Table 3.5: Proximity Matrix of Sample Sites

Squared Euclidean Distance													
Case	1	2	3	4	5	6	7	8	9	10	11	12	13
1	0.000	0.652	103.392	380.972	5.011	9.338	2.639	0.098	0.339	4.440	278.009	111.058	17.302
2	0.652	0.000	88.158	351.250	3.341	5.443	1.120	0.690	0.960	4.152	272.361	103.759	14.523
3	103.392	88.158	0.000	90.041	77.872	51.486	80.593	101.861	104.627	102.199	348.769	137.047	82.645
4	380.972	351.250	90.041	0.000	327.603	273.058	338.080	377.899	381.361	368.447	564.667	325.355	318.805
5	5.011	3.341	77.872	327.603	0.000	4.695	3.918	4.875	5.610	8.950	275.526	104.248	14.421

6	9.338	5.443	51.48 6	273.0 58	4.695	0.000	5.283	8.956	10.23 9	13.17 8	284.2 13	100.9 28	15.913
7	2.639	1.120	80.59 3	338.0 80	3.918	5.283	0.000	2.519	3.043	6.360	272.1 09	100.1 37	14.557
8	0.098	0.690	101.8 61	377.8 99	4.875	8.956	2.519	0.000	0.350	4.536	277.8 67	110.4 18	16.878
9	0.339	0.960	104.6 27	381.3 61	5.610	10.23 9	3.043	0.350	0.000	2.493	268.5 52	105.7 88	16.806
10	4.440	4.152	102.1 99	368.4 47	8.950	13.17 8	6.360	4.536	2.493	0.000	243.0 56	92.09 5	17.367
11	278.0 09	272.3 61	348.7 69	564.6 67	275.5 26	284.2 13	272.1 09	277.8 67	268.5 52	243.0 56	0.000	162.2 22	245.49 8
12	111.0 58	103.7 59	137.0 47	325.3 55	104.2 48	100.9 28	100.1 37	110.4 18	105.7 88	92.09 5	162.2 22	0.000	70.578
13	17.30 2	14.52 3	82.64 7	318.8 05	14.42 1	15.91 3	14.55 7	16.87 8	16.80 6	17.36 7	245.4 98	70.57 8	0.000

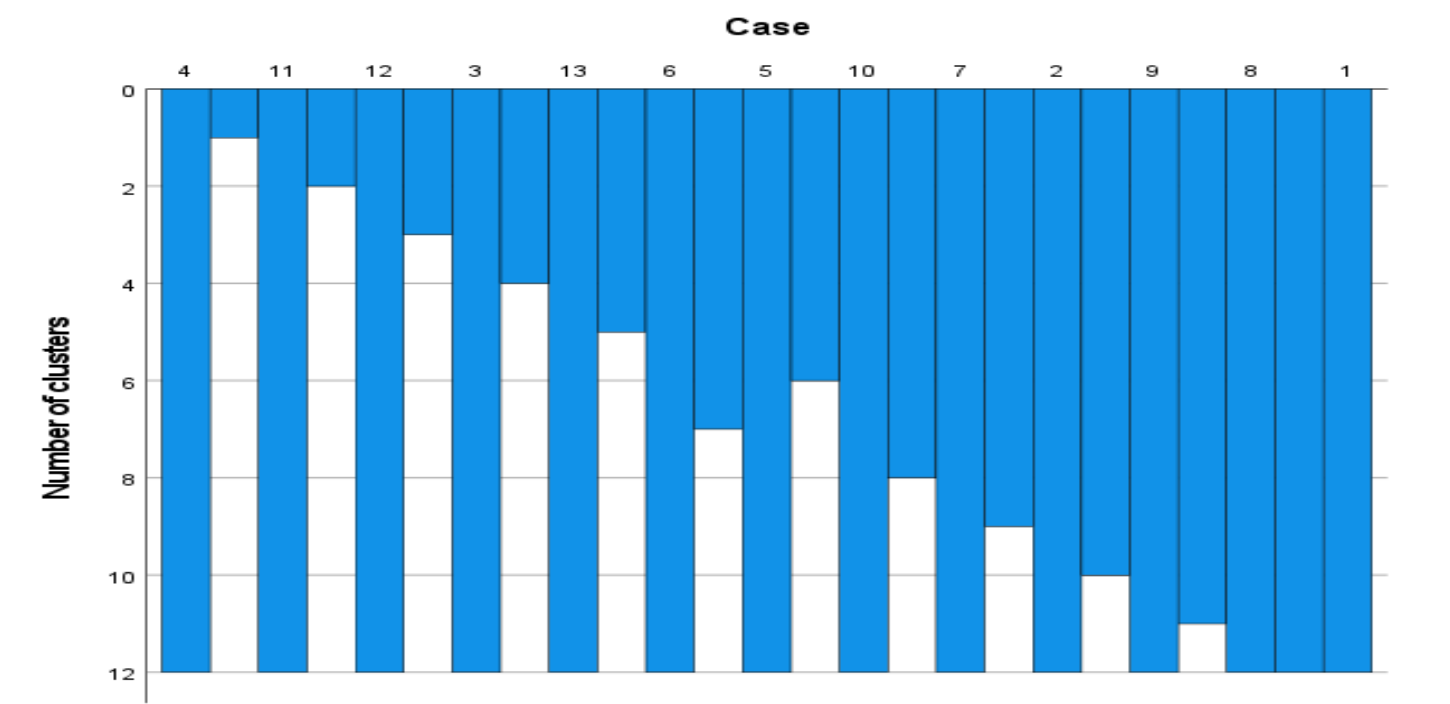


Fig. 3.1: Hierarchical Clustering of Soil Sample Sites

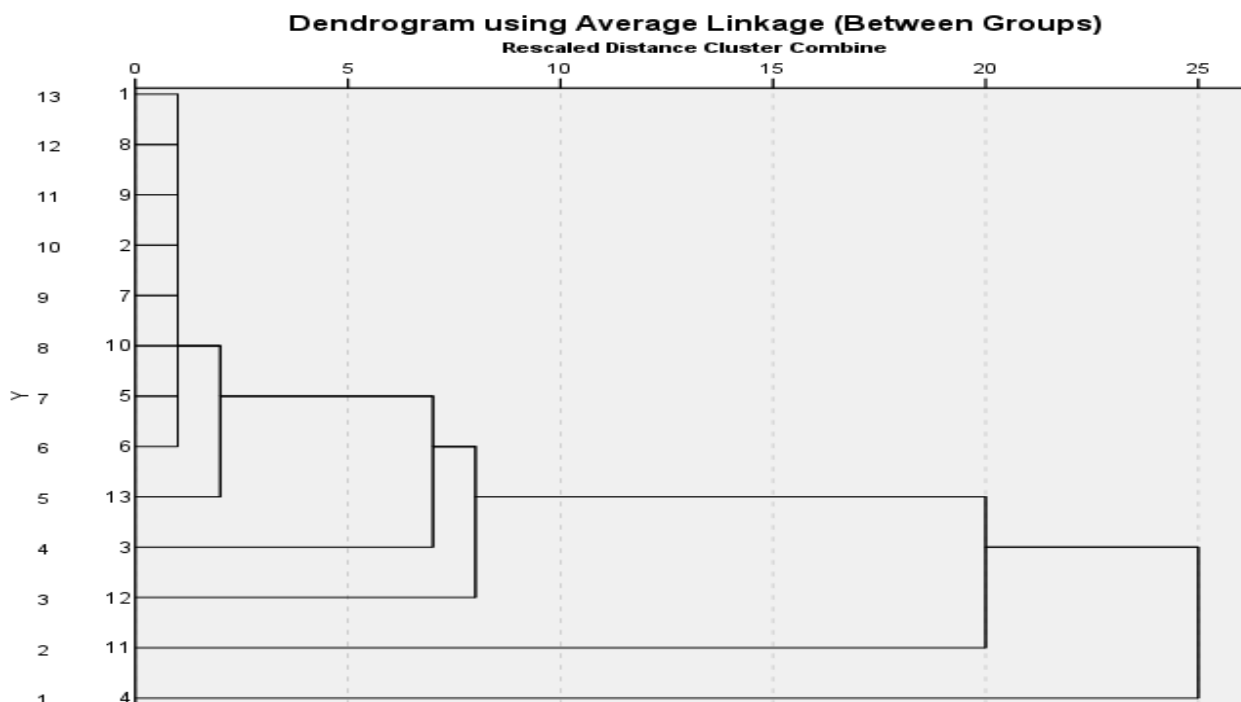


Fig. 3.2: Hierarchical Clustering Dendrogram of Soil Sample Sites

3.0.1 Summary

The descriptive summary reveals substantial variability across the sites. SS9A and SW52A show the widest ranges and highest mean values, suggesting localized hotspots of contamination or nutrient enrichment. Conversely, SS14A and SS15A have low mean and narrow ranges, indicating background or controlled conditions.

Strong positive correlations were observed between SS13B and SS14A ($r = 0.998$, $p < 0.01$), and between SS10B and SWS3B ($r = 0.927$, $p < 0.01$), indicating strong environmental or source similarities. Soil–water interactions were evident from high correlations between SW52A and SS13B ($r = 0.908$) and between SW52A and SS14A ($r = 0.883$). Weak or negative correlations such as between SS9A and SS14A ($r = -0.148$) suggest independent behaviors likely due to differences in soil texture or pollution exposure.

Cases 1, 8, and 9 displayed the smallest distances (<0.4), indicating similar soil composition or contamination profiles. In contrast, Cases 4 and 11 exhibited very high distances (>380), marking them as outliers likely influenced by distinct environmental conditions or pollutant sources.

3.1 POLLUTION LOAD INDEX (PLI) AND CONTAMINATION FACTOR INDEX (CFI) FOR SOIL SAMPLE PHTHALATES RESULTS

Table 3.6: Background Values for Phthalates in Soil (mg/Kg)

Compound Name	Background Value (mg/Kg)
Dimethyl phthalate	0.01

Diethyl Phthalate	0.02
Diethyl Phthalate	0.02
Diisobutyl phthalate	0.10
Dibutyl phthalate	0.20
Bis(2-methoxyethyl) phthalate	0.01
bis(4-Methoxyethyl)phthalate	0.01
bis(2-Ethoxyethyl)phthalate	0.05
Dipentyl phthalate	0.01
Dihexyl phthalate	0.01
Benzyl butyl phthalate	0.01
bis(2-Ethylhexyl)phthalate	0.10
Di-n-octyl phthalate	0.10

Table 3.6: The PLI Values for Each Sample Site

Sample	PLI
SS 9A	31.33
SS 10B	0.00
SS 13B	0.00
SS 14A	0.00
SS 15A	0.00
SS 16B	0.00
SW 5A	0.00
SW 52A	0.00
SWS 3B	0.00
SS 15A	4.22

The high PLI in sample SS 9A indicates significant contamination compared to background levels, while other samples show no significant contamination based on the background values chosen.

The Contamination Factor Index (CFI), calculated as the sum of contamination factors for each sample, is as follows:

Table 3.7: The CFI Values for Each Sample Site

Sample	CFI
SS 9A	867.55
SS 10B	134.10
SS 13B	187.75
SS 14A	15.45
SS 15A	68.35
SS 16B	139.10
SW 5A	225.95
SW 52A	480.85
SWS 3B	54.65
SS 15A	129.50

These values provide an overall contamination load based on phthalate concentrations relative to background values for each sample. Higher CFIs indicate greater contamination levels. SS 9A shows the highest contamination among the listed samples. The PLI and CFI together give a good assessment of pollution and contamination load for the collected soil samples.

Results of CF (CFi) per Compound and PLI per Sample are tabulated below. All concentrations are in mg/kg. Values rounded to 2 decimal places.

Table 3.8: The CF (CFi) And PLI Values for Each Sample Site

Sample	CF_DEP	CF_DBP	CF_DEHP	PLI	CF_sum
SS 9A	21.79	521.89	2.29	29.65	545.98
SS 10B	0.77	9.73	8.25	3.95	18.75
SS 13B	1.54	12.70	55.42	10.27	69.66
SS 14A	0.00	0.27	4.46	0.99	4.73
SS 15A	5.90	29.46	1.42	7.04	36.78
SS 16B	2.31	31.35	7.75	6.12	41.41

SW 5A	0.51	2.97	6.29	2.44	9.77
SW 52A	5.38	83.51	39.08	26.00	127.98
SWS 3B	1.79	6.76	6.67	4.32	15.22
SS 15A	0.26	5.41	0.42	0.83	6.08

SS 9A, SS 13B, and SW 52A exhibit exceptionally high DBP CFs, driving the highest PLI values. Most samples have $PLI > 1$, showing contamination relative to background levels. SS 9A ($PLI \approx 29.6$) and SW 52A ($PLI \approx 26.0$) show the strongest.

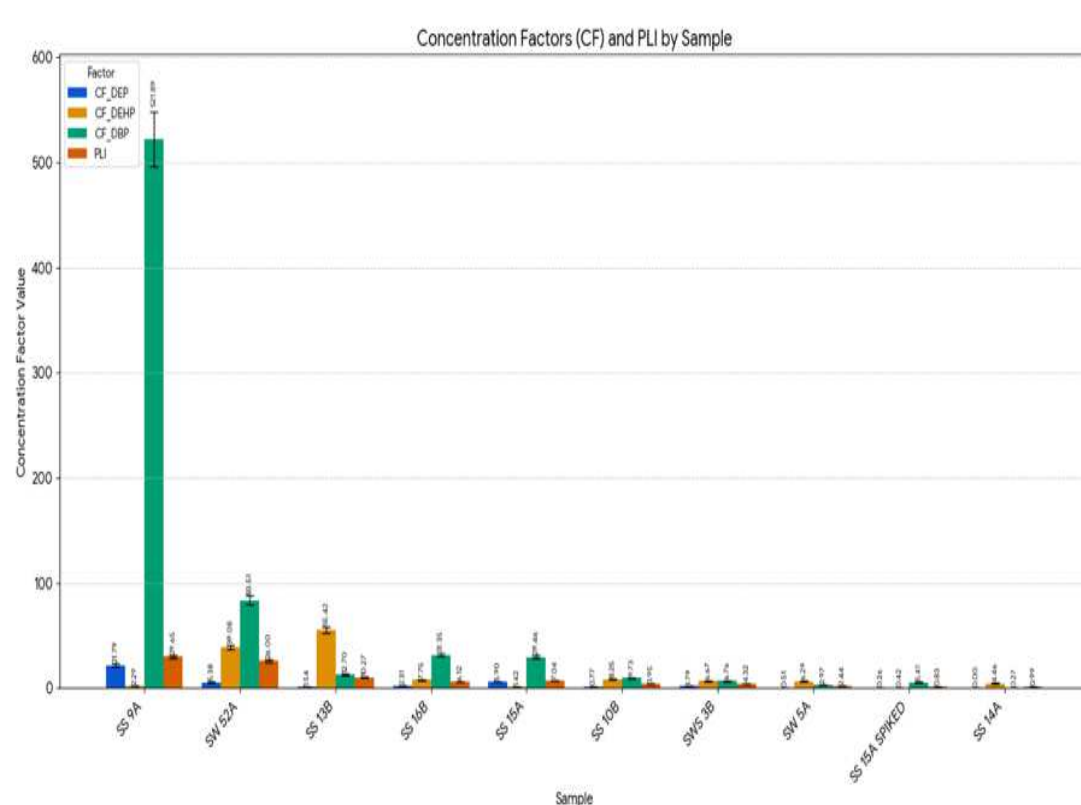


Fig: 3.3: CF and PLI by sample site

The grouped bar chart (Fig. 3.3) provides a detailed, sample-by-sample breakdown of the four analyzed factors (CF_DEP, CF_DBP, CF_DEHP, and PLI), revealing the composition and intensity of contamination at each site.

The grouped bar chart shows an overwhelming dominance of CF_DBP (Di-n-butyl phthalate Contamination Factor) at sample SS 9A (521.89). This single factor is responsible for approximately 95% of the site's total CF (sum), indicating a highly specific and massive point source of DBP contamination.

The CF_DEHP (Di-ethylhexyl phthalate Contamination Factor) is the primary driver at SS 13B (55.42), making that site a significant hotspot for this specific contaminant. However, CF_DBP is the largest factor in most of the high-to-moderate contamination samples (SS 9A, SW 52A, SS 16B, SS 15A) while

CF_DEHP is the second major contributor in several sites (SS 13B, SW 52A, SS 10B, SW 5A, SWS 3B), this indicates its major presence, though at lower absolute values than the DBP.

CF_DEP (Diethyl phthalate Contamination Factor) values are low across the sites, only reaching a notable level at SS 9A (21.79) compared to other sites.

The highest PLI is at SS 9A (29.65), followed by SW 52A (26.00). The high PLI at SS 9A is entirely driven by the high CF_DBP value, confirming that the overall ecological risk is concentrated at this site due to the single DBP contaminant.

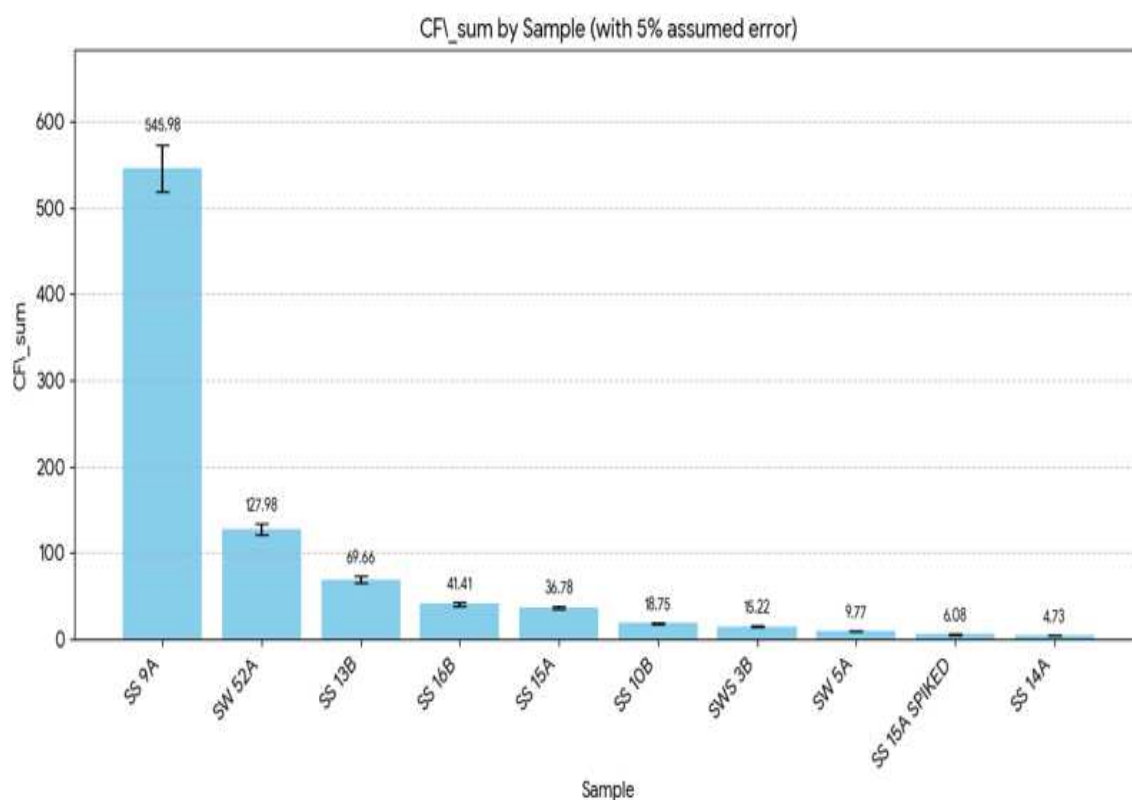


Fig: 3.4: CF Sum by Sample Site

The bar chart (Fig. 3.4) visualizes the CF_sum (Contamination Factor Sum) for ten different environmental samples, providing a clear comparison of the total contamination levels across the sites. Sample SS 9A stands out significantly with the highest CF_sum of 545.98. This value is over four times greater than the next highest sample, indicating that SS 9A is a severe contamination hotspot compared to all other sampling locations. The second tier of samples shows a moderate level of contamination. SW 52A (127.98) and SS 13B (69.66) represent the highest values in this group, suggesting substantial but less extreme contamination relative to SS 9A. Samples SS 16B (41.41) and SS 15A (36.78) form a cluster with similar, moderate CF_sum values.

However, the remaining five samples (SS 10B, SWS 3B, SW 5A, SS 15A, SS 14A) all have very low CF_sum values, ranging from 18.75 down to the lowest value of 4.73 for SS 14A. These locations suggest minimal cumulative contamination by the analyzed compounds.

Dibutyl Phthalate, DBP

In the PAE soil samples, Dibutyl Phthalate (DBP) was identified as the compound with the highest contamination factor (CF_1), with a concentration of 19.31 ppm at location SS 9A. This indicates that SS 9A is a significant hotspot for phthalate pollution that is potentially influenced by improper waste disposal, soil leaching from plastic residues, or agricultural inputs containing phthalate esters. The high concentration of DBP, alongside other phthalates such as Diisobutyl Phthalate and bis(4-Methoxyethyl) phthalate, thereby contributes substantially to the overall contamination load of the sample location. Consequently, SS 9A likely exhibits the highest Contamination Factor Index (CFI) and Pollution Load Index (PLI), as both indices are influenced by the magnitude of the calculated individual CF_1 values. The elevated PLI reflects the cumulative pollution intensity, while the high CFI indicates multiple phthalates contributing to the contamination, posing potential threats to soil microorganisms and plant growth which might be due to phthalate-induced toxicity.

3.2 PHTHALATES (WATER SAMPLE)

Table 3.9: Phthalate Concentration in Water Sample

Compound Name	UNIT	CSW 4A	CUW 3A	CUW 5A	SW 6A	SW 8A	SW 9A	UW 17A	UW 18A	UW 19A	UW 20A	UW 21A	UW 22A	CUW 5B
Dimethyl phthalate	Mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
Diethyl Phthalate	Mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04
Diisobutyl phthalate	Mg/L	0.00	0.00	0.01	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.10
Dibutyl phthalate	Mg/L	0.00	0.00	0.01	0.00	0.00	0.01	0.08	0.00	0.00	0.00	0.00	0.00	0.10
Bis(2-methoxyethyl) phthalate	Mg/L	0.00	0.00	0.01	0.00	0.00	0.36	1.32	0.00	0.00	0.00	0.00	0.00	0.06
bis(4-Methoxyethyl)phthalate	Mg/L	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.00	0.00	0.00	0.00	0.00	0.04
bis(2-Ethoxyethyl)phthalate	Mg/L	0.00	0.00	0.03	0.00	0.00	0.01	0.05	0.00	0.00	0.00	0.00	0.00	0.12
Dipentyl phthalate	Mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06
Dihexyl phthalate	Mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06
Benzyl butyl phthalate	Mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10
bis(2-Ethylhexyl)phthalate	Mg/L	0.00	0.00	0.00	0.00	0.02	0.25	1.96	0.00	0.00	0.05	0.00	0.01	0.07

Di-n-octyl phthalate	Mg/L	0.01	0.01	0.01	0.00	0.00	0.05	0.41	0.00	0.00	0.01	0.00	0.00	0.41
Dinonyl phthalate	Mg/L	0.00	0.00	0.00	0.00	0.00	0.07	0.34	0.00	0.00	0.00	0.00	0.00	0.08

Table 3.10: Descriptive Statistics of Phthalates Concentration in Soil Samples

	Minimum	Maximum	Mean		Std.	
	Statistic	Statistic	Statistic	Std. Error	Deviation	Variance
	Statistic	Statistic	Statistic	Statistic	Statistic	Statistic
SW 6A	0.00	0.00	0.0009	0.00041	0.00149	0.000
SW 8A	0.00	0.02	0.0017	0.00116	0.00418	0.000
SW 9A	0.00	0.36	0.0587	0.03143	0.11333	0.013
UW 17A	0.00	1.96	0.3257	0.16966	0.61174	0.374
UW 18A	0.00	0.00	0.0004	0.00016	0.00056	0.000
UW 19A	0.00	0.00	0.0017	0.00043	0.00155	0.000
UW 20A	0.00	0.05	0.0057	0.00415	0.01495	0.000
UW 21A	0.00	0.00	0.0008	0.00028	0.00100	0.000
UW 22A	0.00	0.01	0.0015	0.00096	0.00345	0.000

3.2.1 Descriptive Statistics

SW 6A Minimum $\approx$ -0.00, Maximum 0.00, Mean $\approx$ 0.0009, Std Dev $\approx$ 0.00149, Variance $\approx$ ~0.000. This is essentially zero with negligible spread. No evidence of elevated values at SW6A. SW 8A Mean $\approx$ 0.0017, Std Dev $\approx$ 0.0042 (small). Max 0.02. A very low concentration; a little more variability than SW6A, but still near-zero. SW 9A Mean $\approx$ 0.0587, Std Dev $\approx$ 0.1133, Max 0.36. It is substantially higher than other SW sites. SW9A is a notable surface site with measurable values and higher variability. Could indicate local input or episodic contamination. UW 17A Mean $\approx$ 0.3257, Std Dev $\approx$ 0.6117, Max 1.96. This is clearly the most elevated site with high mean and a large max indicate either a persistent elevated concentration. UW 18A Mean $\approx$ 0.0004, Std Dev $\approx$ 0.00056. This is essentially zero. UW 19A Mean $\approx$ 0.0017, Std Dev $\approx$ 0.00155. This near-zero with a little variability. UW 20A Mean $\approx$ 0.0057, Std Dev $\approx$ 0.01495, Max 0.05. This is slightly larger than some UW sites but still small compared to UW17A or SW9A. UW 21A Mean $\approx$ 0.0008, Std Dev $\approx$ 0.0010. UW 22A Mean $\approx$ 0.0015, Std Dev $\approx$ 0.00345 it is near-zero with small variability.

From the result, it can be deduced that two sites stand out (UW17A (largest) and SW9A with moderately elevated). The rest are effectively background/near-zero.

3.2.2 Correlation Matrices

SW8A ↔ UW20A $r \approx 0.994$ (very near perfect), $p \approx 6.5e-12$. This identical patterns between these two sites across the 13 samples could mean the same measurement values (perhaps same instrument artifact), the same source influencing both sites simultaneously, or one dataset copied / very strongly coupled hydrologically.

SW8A ↔ UW22A $r \approx 0.984$, $p \approx 7.6e-10$ is also extremely strong showing that SW8A, UW20A, and UW22A form a tight trio with almost identical behavior.

SW9A ↔ UW17A $r \approx 0.911$, $p \approx 0.000-0.002$ indicate a strong positive association that the higher readings at UW17A tend to occur when SW9A is higher. This suggests either shared source/process or cross-contamination between these particular surface and underground points.

UW17A ↔ UW20A $r \approx 0.810$, $p \approx 0.001$ (significant).

UW20A (small mean though) co-varies with UW17A. Given UW20A is otherwise low magnitude, the high correlation likely results from the few samples where UW17A spikes coinciding with slight increases at UW20A.

UW20A ↔ UW22A $r \approx 0.968$, $p \approx 0.000$. This also shows an identical series between UW20A and UW22A.

UW19A ↔ UW21A $r \approx 0.682$, $p \approx 0.010$ (2-tailed flagged) indicates a moderate strong positive relationship between these two underground sites.

Some moderate correlations such as the SW6A ↔ UW19A ($r \approx 0.527$, $p \approx 0.064$ two-tailed — borderline), UW18A ↔ UW19A ($r \approx 0.536$, $p \approx 0.059$) are weaker and borderline significant.

However, negative values appear (e.g., SW6A with SW9A $r = -0.238$) but none are strong and significant. No major inverse relationships detected.

The correlation structure is dominated by two clusters of highly co-varying sites (SW8A, UW20A, UW22A that are extremely tightly correlated) and (SW9A, UW17A that are strongly correlated, also linking to UW20A somewhat). The rest mostly show low/insignificant correlations because their values are near zero and show little variation. Thereby, the extremely high correlations ($r > 0.98$) suggest either the sites are measuring essentially the same physical signal (very strong hydrological connection or same source), or a shared episodic event affecting those monitoring points identically

Table 3.11 Correlation Matrix (1-Tailed) of Phthalates in Water Samples

		SW 6A	SW 8A	SW 9A	UW 17A	UW 18A	UW 19A	UW 20A	UW 21A	UW 22A
SW 6A	Pearson Correlation	1	-0.056	-0.238	-0.207	0.428	.527*	-0.121	0.117	0.014
	Sig. (1-tailed)		0.428	0.217	0.249	0.072	0.032	0.346	0.352	0.482
	N	13	13	13	13	13	13	13	13	13
SW 8A	Pearson Correlation	-0.056	1	.478*	.794**	0.016	0.001	.994**	0.093	.984**
	Sig. (1-tailed)	0.428		0.049	0.001	0.479	0.499	0.000	0.382	0.000
	N	13	13	13	13	13	13	13	13	13
SW 9A	Pearson Correlation	-0.238	.478*	1	.911**	-0.154	-0.240	.497*	0.023	0.453
	Sig. (1-tailed)	0.217	0.049		0.000	0.308	0.215	0.042	0.471	0.060
	N	13	13	13	13	13	13	13	13	13
UW 17A	Pearson Correlation	-0.207	.794**	.911**	1	-0.109	-0.150	.810**	0.093	.764**
	Sig. (1-tailed)	0.249	0.001	0.000		0.361	0.313	0.000	0.382	0.001
	N	13	13	13	13	13	13	13	13	13
UW 18A	Pearson Correlation	0.428	0.016	-0.154	-0.109	1	.536*	-0.016	.481*	0.131
	Sig. (1-tailed)	0.072	0.479	0.308	0.361		0.030	0.479	0.048	0.335
	N	13	13	13	13	13	13	13	13	13
UW 19A	Pearson Correlation	.527*	0.001	-0.240	-0.150	.536*	1	0.005	.682**	-0.017

[illegible]

UW 21A	Pearson Correlation	0.117	0.093	0.023	0.093	0.481	.682*	0.148	1	0.071
	Sig. (2-tailed)	0.704	0.763	0.942	0.763	0.096	0.010	0.631		0.818
	N	13	13	13	13	13	13	13	13	13
UW 22A	Pearson Correlation	0.014	.984**	0.453	.764**	0.131	-0.017	.968**	0.071	1
	Sig. (2-tailed)	0.963	0.000	0.120	0.002	0.669	0.957	0.000	0.818	
	N	13	13	13	13	13	13	13	13	13

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

3.2.3 Proximity Matrix

The proximity (distance) matrix shows pairwise distances used for hierarchical clustering. Small numbers indicate similarity; large numbers indicate dissimilarity. The unit depends on whatever distance metric (likely Euclidean) was used.

The distances among many sites (SW6A, SW8A, SW9A, UW18A, UW19A, UW20A, UW21A, UW22A) are extremely small (0.000 - 0.199). This reflects very small absolute differences among their series (but note SW9A had higher variance at the 0.199 entries involving SW9A represent slightly larger distances).

However, the distances between UW17A and essentially every other site are very large (~4.055 to 5.867). That mirrors descriptive stats that UW17A is an outlier with much higher magnitude values.

For instance, UW17A ↔ SW6A = 5.867 (very large), UW17A ↔ SW9A = 4.055 (largest among those but still large), UW20A ↔ SW8A = 0.002 (tiny). These distances confirm clustering: UW17A stands apart; several other sites are extremely similar to each other.

Table 3.13: Proximity Matrix Water Sample Sites

	SW 6A	SW 8A	SW 9A	UW 17A	UW 18A	UW 19A	UW 20A	UW 21A	UW 22A
SW 6A	0.000	0.000	0.199	5.867	0.000	0.000	0.003	0.000	0.000
SW 8A	0.000	0.000	0.191	5.807	0.000	0.000	0.002	0.000	0.000
SW 9A	0.199	0.191	0.000	4.055	0.199	0.197	0.173	0.198	0.193
UW 17A	5.867	5.807	4.055	0.000	5.867	5.859	5.647	5.862	5.818
UW 18A	0.000	0.000	0.199	5.867	0.000	0.000	0.003	0.000	0.000

UW 19A	0.000	0.000	0.197	5.859	0.000	0.000	0.003	0.000	0.000
UW 20A	0.003	0.002	0.173	5.647	0.003	0.003	0.000	0.003	0.002
UW 21A	0.000	0.000	0.198	5.862	0.000	0.000	0.003	0.000	0.000
UW 22A	0.000	0.000	0.193	5.818	0.000	0.000	0.002	0.000	0.000

3.2.4 Agglomeration Schedule (Hierarchical Clustering)

Early stages (1 - 6) combine pairs of very similar sites in which coefficients at those stages are 0.000 - 0.003 (i.e., negligible distance). That means those sites are almost identical and merge immediately in the clustering process.

Stage 7 merges a cluster with coefficient ≈ 0.193 (this likely brings SW9A or similar into a slightly larger cluster).

Final stage (stage 8) merges the two big clusters at coefficient 5.598 — a very large jump compared with earlier merges. That is the classic sign of a distinct outlier cluster: everything else is very similar, and UW17A (or analogous cluster containing it) merges only at a high distance.

Hierarchical clustering shows essentially two groups:

A large tight cluster of near-zero/background sites (many SW and UW sites).

A separate cluster containing UW17A (and perhaps SW9A ties), which joins the main cluster only at a high dissimilarity level. This again points to UW17A as the major anomaly.

Table 3.13: Agglomeration Schedule Water Sample Sites

Stage	Cluster Combined		Coefficients	Stage Cluster First Appears		Next Stage
	Cluster 1	Cluster 2		Cluster 1	Cluster 2	
1	5	8	0.000	0	0	3
2	2	9	0.000	0	0	5
3	1	5	0.000	0	1	4
4	1	6	0.000	3	0	5
5	1	2	0.000	4	2	6
6	1	7	0.003	5	0	7
7	1	3	0.193	6	0	8
8	1	4	5.598	7	0	0

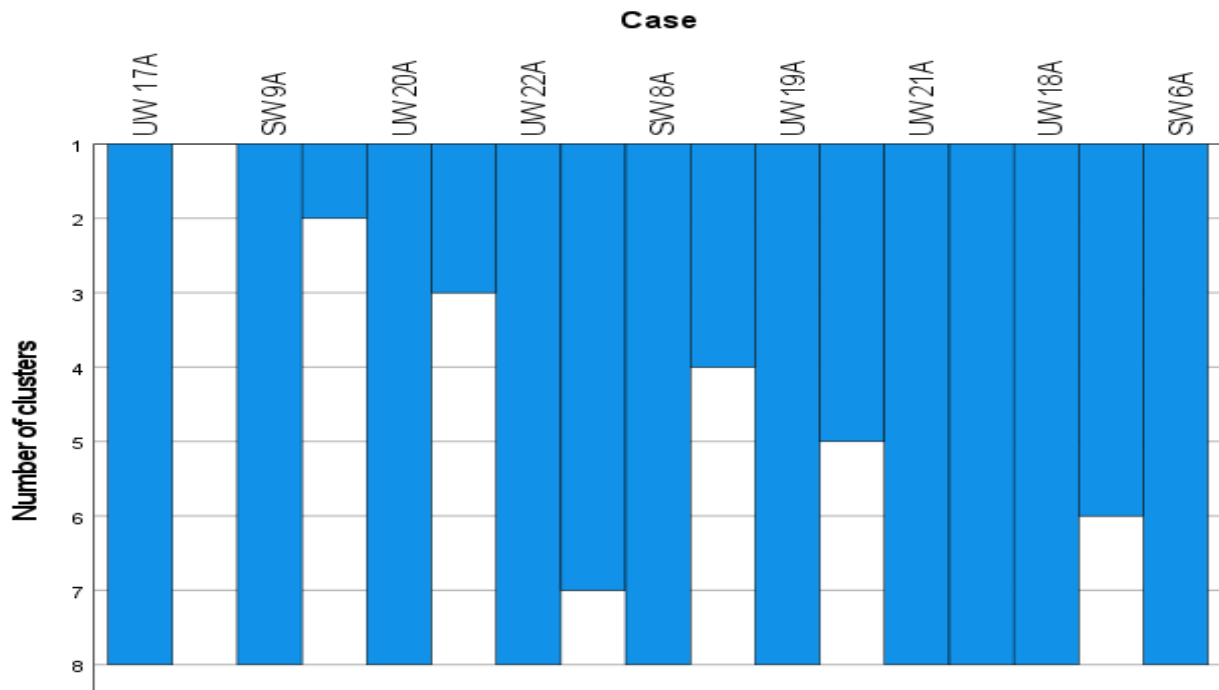


Fig. 3.5: Hierarchical Clustering of Water Sample Sites

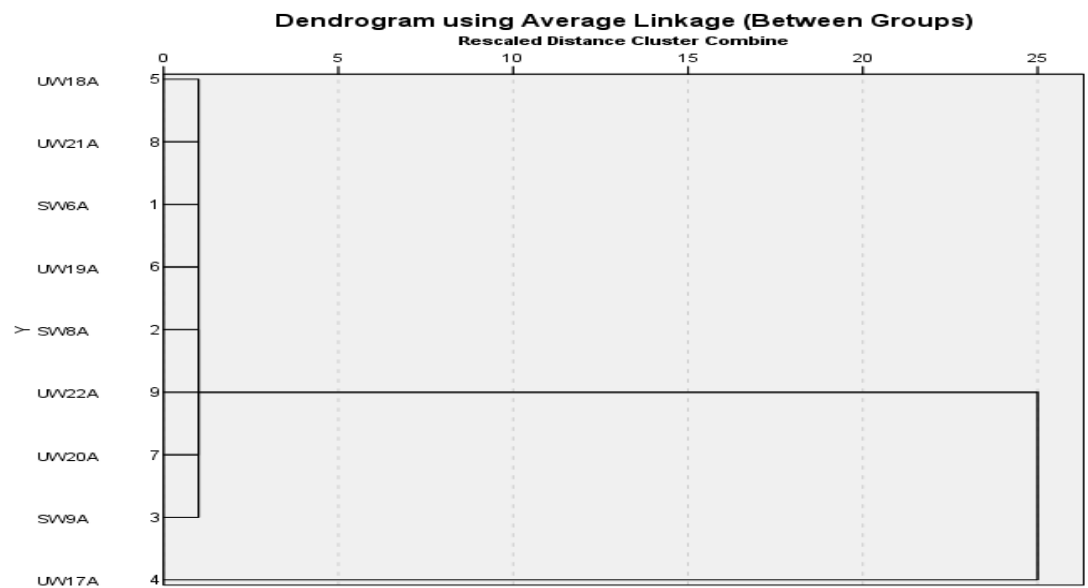


Fig. 3.6: Hierarchical Clustering Dendrogram of Water Sample Sites

3.2.5 Summary

Sample size is small but equal across variables: $N = 13$ for every site/variable.

Most sites have values extremely close to zero (many means ≈ 0.000 – 0.006) except UW 17A (mean ≈ 0.326 , max 1.96) and SW 9A (mean ≈ 0.059 , max 0.36). These two stand out as having substantially larger magnitudes and variance than the others.

Several very strong positive correlations ($r > 0.8$) occur between specific surface (SW) and underground (UW) sites (e.g., SW8A ↔ UW20A, SW8A ↔ UW22A, SW9A ↔ UW17A, UW20A ↔ UW22A).

The proximity matrix and agglomeration schedule show almost all low-value sites clustering tightly together (very small distances ≈ 0.000 – 0.003), while UW17A is distant from those and merges last (large linkage about 5.6), indicating it is an outlier / distinct cluster.

Finally, most sites behave the same (near-zero values); a small subset (especially UW17A, SW9A, and to a lesser extent UW20A/UW22A/SW8A) are differentiated — likely different source or contamination event, measurement issue, or natural variation.

3.3 POLLUTION LOAD INDEX (PLI) AND CONTAMINATION FACTOR INDEX (CFI) FOR WATER SAMPLE PHTHALATES RESULTS

The table below shows the calculated CFI (Contamination Factor Index) and PLI (Pollution Load Index) for the collected samples. The CFI (sum) indicates the total potential impact, while the PLI (geometric mean) provides a generalized measure of the overall pollution status.

Table 3.14: CFI of Water Sample Points

Sample	CFI (Sum of CFs)
SW6A	365.7650
SW8A	222.5880
SW9A	1692.0000
UW17A	14959.8000
UW18A	323.1760
UW19A	1814.4700
UW20A	462.0000
UW21A	176.1180
UW22A	312.1180

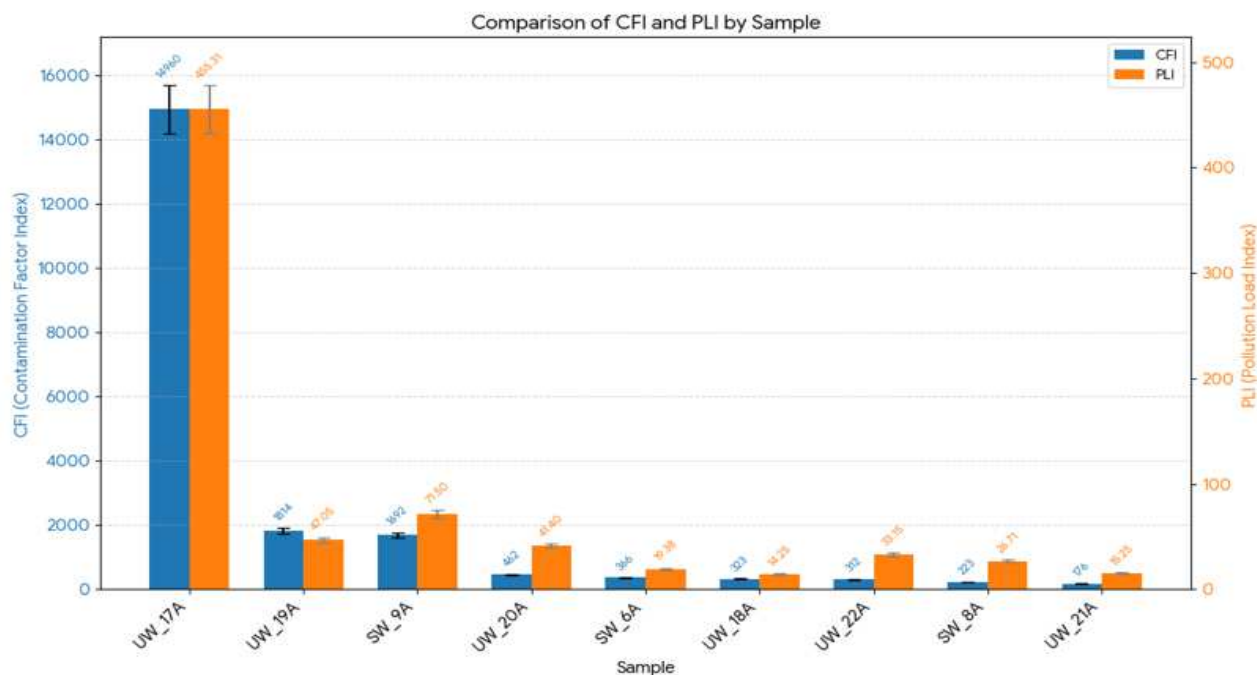


Fig. 3.7: Comparison of PLI and CFI by sample

UW 17A shows by far the highest contamination, with a CFI of 14,959.8 and a PLI of 455.31 (Fig. 4.22), indicating extremely severe pollution relative to the background values. SW 9A and UW 19A also show high contamination, with CFI values over 1,500. In addition, all the calculated samples have a PLI significantly greater than 1, confirming a high pollution load for the analyzed phthalates at all these sites.

Table 3.15: CFI (sum) of phthalates per sample

Sample	Dimethyl_ phthalate	Diethyl_ Phthalate	Dibutyl_ phthalate	Benzyl_butyl_phthalate	bis(2- Ethylhexyl)phthalate	CFI (Sum)
SW6A	50.00	2.00	62.00	250.00	1.76	365.76
SW8A	50.00	2.00	30.00	50.00	90.59	222.59
SW9A	50.00	4.00	128.00	50.00	1460.00	1692.00
UW17A	50.00	12.00	1616.00	1750.00	11531.80	14959.80
UW18A	50.00	2.00	20.00	250.00	1.18	323.18
UW19A	100.00	4.00	54.00	1650.00	6.47	1814.47
UW20A	50.00	4.00	38.00	50.00	320.00	462.00
UW21A	50.00	2.00	20.00	100.00	4.12	176.12
UW22A	50.00	2.00	36.00	150.00	74.12	312.12

The overall high CFI for UW 17A (14,959.80) is primarily driven by the massive CF values for bis(2-Ethylhexyl)phthalate (11531.80) and Benzyl_butyl_phthalate (1750.00). This indicates these two compounds are highly concentrated relative to their background values at this site. ALSO, the high value of CFI for UW 19A (1814.47) is overwhelmingly dominated by the CF for Benzyl_butyl_phthalate (1650.00). in addition, the elevated CFI for SW 9A (1692.00) is mainly due to the CF for bis(2-Ethylhexyl)phthalate (1460.00). The breakdown clearly shows which specific phthalates are contributing most significantly to the total pollution load at each sample site.

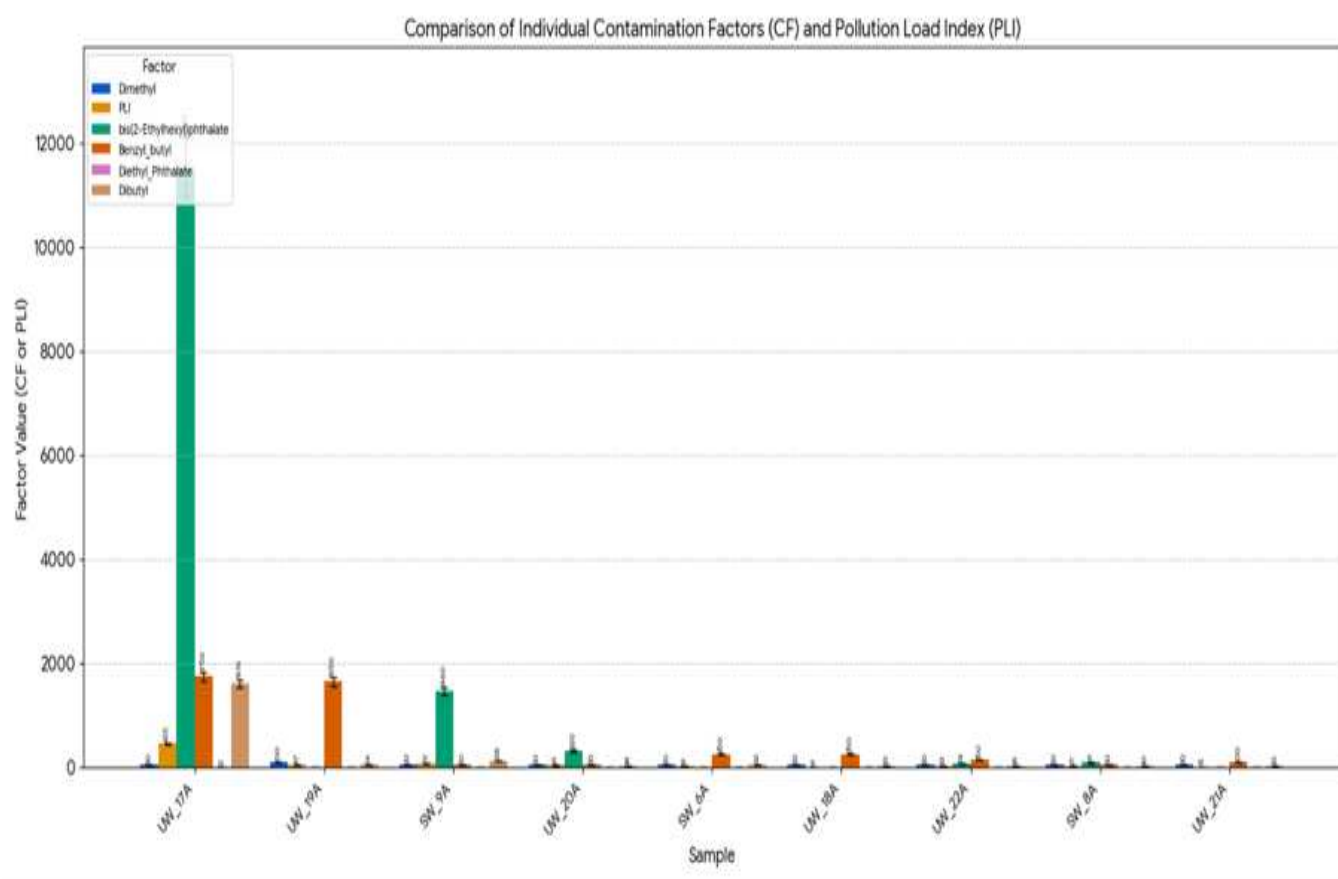


Fig. 3.8: Comparison of individual CF and PLI in Water Sample.

All factors, including the PLI, are presented with an assumed $\pm 5\%$ error bar.

The most significant feature is the CF_DEHP (bis(2-Ethylhexyl) phthalate) bar at sample UW 17A, which reaches a value of $\approx 11,532$. This compound is the primary driver of the extreme overall contamination at this site. SW 9A is dominated by CF_DEHP ($\approx 1,460$), UW 20A has a relatively high CF_DEHP (≈ 320). For most other samples, the CF_Benzyl butyl factor is the highest of the individual contaminants. This chart effectively highlights that phthalate contamination in these samples is driven by one or two major compounds, particularly bis(2-Ethylhexyl) phthalate and Benzyl butyl phthalate, relative to the chosen background levels. Benzyl butyl is the primary driver in UW 19A ($\approx 1,650$), making it the second most polluted site by CFI. This indicates a different type of source or usage pattern compared to the site dominated by DEHP. The Hotspots: Besides UW 17A, SW 9A also shows extreme contamination from

CF. Also, DEHP ($\approx 1,460$), which accounts for most of its high CFI ($\approx 1,692$). This suggests industrial or waste-related sources of DEHP are scattered across the sampled area. The factors CF Dimethyl and CF Diethyl contribute very little to the overall pollution load in any sample, generally staying below a CF of 100.

The PLI (Pollution Load Index, shown on the far right of each group) is a geometric mean, so its value is always much lower than the peak CF value, but it still clearly reflects the relative severity. UW 17A has the highest PLI (≈ 455), SW 9A (≈ 72) and UW 19A (≈ 47) follow, confirming the high risk at these sites. The PLI values (e.g., $\text{PLI} \approx 455$ for UW 17A) are much lower than the corresponding CFI (Sum of $\approx 15,000$). This difference is expected because PLI is a geometric mean.

Bis(2-Ethylhexyl)phthalate, DEHP

The contamination factor (CF_i) for bis(2-Ethylhexyl)phthalate (DEHP) in PE water samples was found to be exceptionally high, with the highest CF_i value reaching 11,531.80 at location UW 17A. This extraordinarily large value can be attributed to the raw concentration of DEHP in this location, which was measured at 1.9604 mg/L. This is the highest value recorded for any phthalate compound in the analysed samples. Furthermore, the background concentration (B_i) of DEHP used for normalization was 0.00017 mg/L, a very small value that amplifies the resulting CF_i when applied in the ratio ($\text{CF}_i = C_i / B_i$). This implies that UW 17A experiences extreme contamination from DEHP which is likely stemming from industrial or municipal effluent discharges, plastic waste degradation, or leaching from polymeric materials. The presence of DEHP at such concentrations poses significant ecological and human health risks, as DEHP is a well-known endocrine disruptor capable of bioaccumulation in aquatic organisms.

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