Original Article

Phthalates in marine sediment, water and the cockle *Anadara antiquata* on the coast of Tanzania

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Abstract

Phthalates are a group of chemicals used as plasticisers, and are easily released into the environment, where they degrade over time. We investigated the concentrations of phthalates in sediments, seawater, and the cockle *Anadara antiquata* from beaches at Dar es Salaam, Mtwara, Tanga and Zanzibar in Tanzania. A dispersive liquid-liquid microextraction method was used to extract analytes from samples, whereafter they were analysed with a gas chromatograph coupled to a mass spectrophotometer. Concentrations of diisobutyl phthalate (DiBP), dibutyl phthalate (DBP) and Bis(2-ethylhexyl) phthalate (DEHP) were determined. DiBP concentrations were highest at Dar es Salaam (11.5 - 12.4 ng/mL in seawater; 11.5 - 13.6 ng/g dry weight in sediments), compared to the other three sites, where minimum and maximum concentrations in sediments were 3.5 ng/g dw (Mtwara) and 10.7 ng/g dw (Tanga). DBP concentrations were also highest at Dar es Salaam (12.4 - 20.6 ng/mL in seawater; 12.1 - 18.7 ng/g dw in sediments) compared to 2.7 (minimum, Mtwara) and 11.2 ng/g dw (maximum, Tanga). DEHP at Dar es Salaam ranged from un-detected to 12.6 ng/mL in seawater and to 12.6 ng/g dw in sediments. It was further revealed that *A. antiquata* from Kawe Beach (Dar es Salaam) had higher concentrations of DiBP, DBP, and DEHP compared to other sites. Monitoring of phthalate concentrations will indicate pollution hotspots and trends in the region.

Keywords: dibutyl phthalate, Bis (2-ethylhexyl) phthalate, diisobutyl phthalate, seawater, sediment, cockles, Tanzania

Introduction

Marine ecosystems in the Western Indian Ocean (WIO) region, similar to other coastal areas in the world, are vulnerable to synthetic organic pollutants from anthropogenic sources (Vered *et al*., 2019). Among the most widely used synthesised chemicals, phthalates have many applications in industrial products, such as plastic-based packaging material, adhesives, printing inks, canned food containers, cosmetics, paints, medical products, ammunition, and pesticides (Paluselli *et al.,* 2018). They are used with polymer-making materials such as polyvinyl chloride, polyethene terephthalate, polyethene, and polyvinyl acetate, making up to 60 % of the weight of the product (Bi *et al.,* 2021). In 2019, it was estimated that the global phthalate output ranged between 6 and 8 million metric tonnes per annual (Seyoum and Pradhan, 2019). China has been identified as the largest consumer, accounting for about 45 % of global phthalate output, whereas, Europe and the United State together have been estimated to consume 25 % (Holland, 2018; Zhang *et al.,* 2021). Due to the low production costs and lack of ideal alternatives, the demand for phthalates is constantly growing at an estimated rate of 1.3 % per year, which raises environmental concerns (De-la-Torre *et al.,* 2022).

Phthalates unavoidably contaminate numerous environmental systems as they are likely to escape from

the plastic matrix by volatilization, leaching, or abrasion (Paluselli *et al.,* 2018). Phthalates can infiltrate marine systems through atmospheric deposition, direct discharge and river runoff (Arslan *et al.,* 2021; Cao *et al.,* 2022). Coastal sediment is a major pollutant sink, carrier, and potential secondary pollution source of phthalates since most, particularly those with a higher molecular weight, possess high octanol-water partition coefficients and are primarily carried and

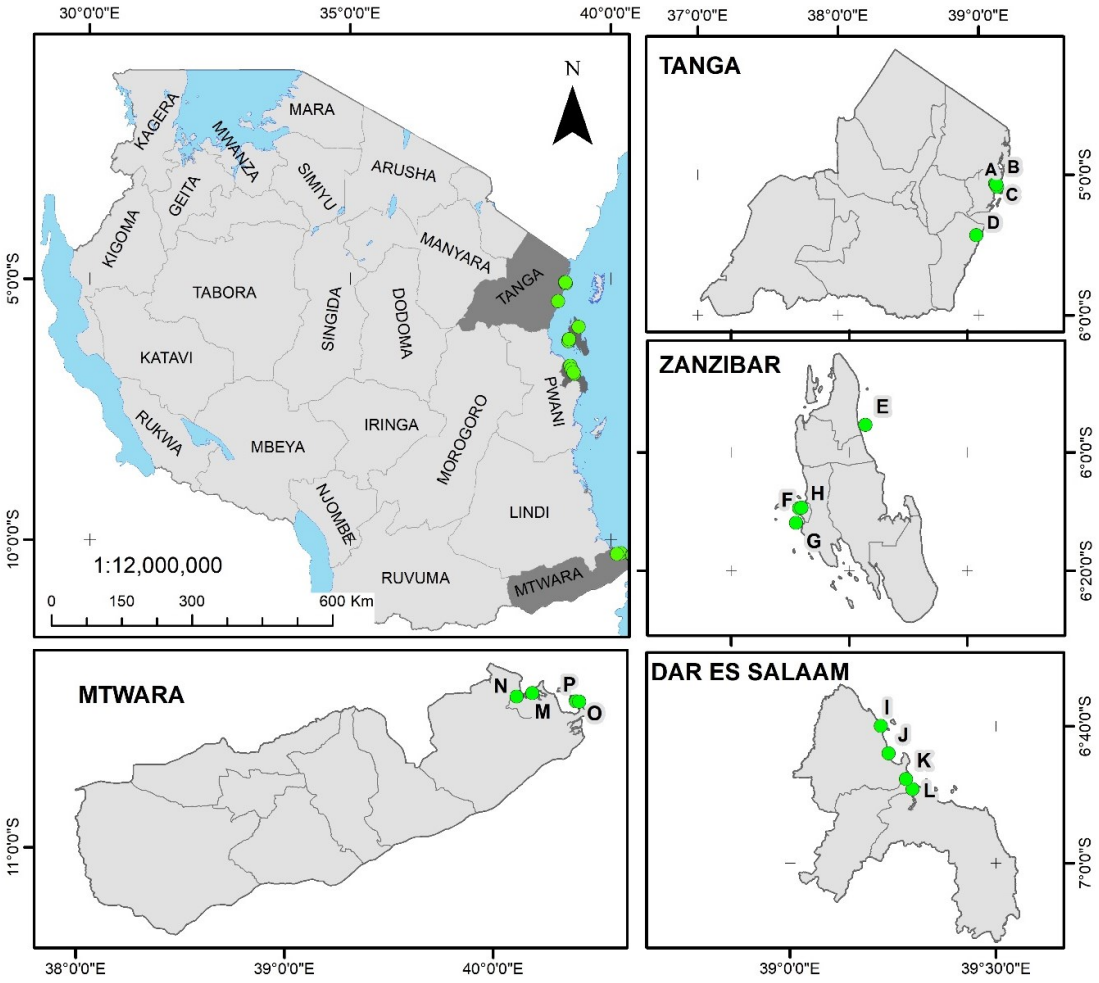

Figure 1. Map showing the locations of sampling sites. **A**: Tanga Sahare Fish Market Beach Beach, **B**: Tanga Raskazone Beach, **C**: Tanga Mkongeni Beach **D**: Pangani Fish Market Beach, E: Pwani Mchangani, **F**: Zanzibar Ferry Beach **G**: Zanzibar Mazizini Fish Market, **H**: Zanzibar Bwawani Komba, **I**: Kunduchi Beach, **J**: Kawe Beach, Selander Bridge, **L**: Posta Ferry Beach, **M**: Mtwara Ferry Fish Market Beach, **N**: Mikindani, **O**: Ruvula, **P**: Msimbati.

sequestered in solid-phase matrices in aquatic environments (Paluselli *et al.,* 2018; Jebara *et al.,* 2021).

Phthalates have long been considered pervasive and entrenched organic pollutants of major environmental concern (Zhang *et al*., 2018). These chemicals are well known for their adverse impact on organisms, including humans. Phthalates have endocrine-disrupting effects on marine organisms, impacting their development and the reproductive systems of amphibians, crabs, annelids, molluscs, fish, and insects (Godswill and Godspel, 2019). They have been linked to the development of genetic abnormalities in amphibians and crustaceans (Oehlmann *et al*., 2009). They have been associated with a reduction in the diversity and abundance of marine organisms in highly contaminated areas, by halting reproduction (Chaudhry, 2018).

Studies have revealed that swimming, fishing, and consuming marine biota contaminated by phthalates pose a risk to humans (Savoca *et al*., 2018; Cheng *et al*., 2018; Heo *et al.,* 2019; Kim *et al*., 2020). It has been reported that exposure to various types of phthalates can cause health issues, such as premature puberty and short anogenital distance, endocrine disruption, altered semen quality and quantity,

endometriosis, hyperactivity, mental impairment in children, metabolic syndrome, allergies, and breast cancer (Savoca *et al*., 2018; Cheng *et al*., 2018; Heo *et al*., 2019; Kim *et al*., 2020).

The presence of phthalates in the marine environment has been reported in various studies (Paluselli *et al.,* 2018; Mi *et al.,* 2019; He *et al.,* 2020; Ai *et al*., 2021; Jebara *et al.,* 2021). However, no study reported on the occurrence of phthalates in the marine environment along the Tanzanian coast. Furthermore, no study has been performed to assess the level of bioconcentration of plasticizers and their associated metabolites in biota along the Tanzanian coast. Effective environmental management and remediation need an understanding of the existing situation, pollutant sources, and ecological risk posed by phthalates along Tanzania's coast. The current study, therefore, investigated the levels of phthalates in beach sediment, seawater, and the cockle, *Anadara antiquata*.

Materials and methods

Study area and sample collection

The sampling locations were chosen to reflect a spectrum of anthropogenic activities, from marine protected areas and park reserves (Ruvula and Msimbati in Tanga) to heavily industrialized areas (Kunduchi Beach, Kawe Beach, Selander Bridge and Posta Ferry Beach in Dar es Salaam) (Table 1 and Fig. 1). Most of the sampling sites were characterized by fishing and/or recreational activities. Sampling was performed during the Northern Monsoon period, between November 2020 and February 2021. This period corresponds to summer in temperate regions of the southern hemisphere, and to the transition from the dry to wet season. At each site a hand-held metal shovel was used to collect triplicate sediment samples of about 500 g by scraping about 5 cm off the surface at three designated points spaced about 300 m apart. The sediment samples were placed into aluminium bags, which were sealed tightly and stored in a cooler box containing ice

Table 1. The locations and descriptions of anthropogenic activities at the sampling sites.

S/NO	Sampling site	Coastal Region	Location sample corrected	Main Anthropogenic Activities
1	Tanga Sahare Fish Market Beach (TSB)	**Tanga**	(-5.087628, 39.130000)	The sandy beach is mostly used for recreational and fishing activities.
2	Pangani Fish Market Beach (PFM)		(-5.430754, 38.982405)	Recreational activities and fishing are predominant along the sandy beach.
3	Tanga Mkongeni Beach (TMB)		(-5.061770, 39.115607)	Recreational activities and fishing are predominant along the sandy beach.
4	Tanga Raskazone Beach (TRB)		(-5.068851, 39.125562)	The sandy beach is mostly used for recreational activities.
5	Mtwara Ferry Fish Market Beach (MTF)	**Mtwara**	-10.262807, 40.187560	Sandy beach that is primarily dominated with ferry transportation landings and fish commerce.
6	Mikindani (MK)		-10.278588, 40.112321	A beach dominated mostly by ferry transportation, fishing, small-scale trade, and boat building.
7	Ruvula (RU)		-10.301849, 40.396824	A sandy beach situated within a marine park reserve, with restricted fishing and recreational pursuits.
8	Msimbati (MS)		-10.304109, 40.411538	A sandy beach situated within a marine park reserve, with restricted fishing and recreational pursuits.
9	Zanzibar Ferry Beach (ZF)	**Unguja (Zanzibar)**	-6.157824, 39.191915	Marine transportation and small businesses.
10	Zanzibar Mazizini Fish Market (ZMF)		-6.199110, 39.182703	Dominated by fishing activities and small businesses.
11	Pwani Mchangani (PM)		-5.922915, 39.378741	Recreational activities.
12	Zanzibar Bwawani Komba (ZBK)		-6.155921, 39.197996	Recreational activities.
13	Kunduchi Beach (KU)	**Dar es Salaam**	-6.666713, 39.220493	Fishing, and small businesses.
14	Kawe Beach (K)		-6.733608, 39.239545	Recreational activities, fishing and small businesses.
15	Selander Bridge (S)		-6.733785, 39.239609	Mouth of Msimbazi river receiving water from industries and domestic wastes.
16	Posta Ferry Beach (PF)		-6.820087, 39.297296	Transportation, fishing and small businesses.

bags. For seawater sampling, a boat was used to collect samples (1 L each) offshore using a Niskin bottle and transferred to amber bottles precleaned with absolute acetone and dichloromethane. The samples were collected from three sampling points situated about 100 m from the shore and about 300 m apart at each site. The cockle, *A. antiquata*, was purchased from fishermen at each site. Three different fishermen were randomly chosen at each site to obtain different *A. antiquata*. When only one or two fishermen were available at a site, the *A. antiquata* specimens were randomly separated by eye. A total of 48 seawater, 48 sediments, and 15 *A. antiquata* samples were collected. Physical parameters including temperature, pH, total dissolved solids (TDS) and electrical conductivity (EC) were measured using a low-range Combo® pH/EC/TDS meter (Model HI 98129, HANNA Instruments Inc., USA).

Sample preparation

In the laboratory, sediment samples were sieved to remove organic shells, plants, and any other non-sediment material. They were dried at room temperature (25 °C) overnight in a laminar flow cabinet (Model: EC6VF) using an airflow of 0.5 m/s to facilitate the drying process. The samples were subsequently crushed using a mortar and pestle to ensure homogeneity and reduce particle size. This step was crucial for increasing the surface area to volume ratio of the sediments to enhance the efficiency of the extracting solvent. After homogenization, 10 mL of analytical-grade ethanol (99.9 %) was added to 1 g of sediment and sonicated for 30 minutes at 30 ± 3 °C. The mixture was centrifuged for 5 min at 1500 X g (Hettich Zetrifugen Model: Universal 320R, Andreas Hettich GmbH & Co. KG, 78532 Tuttlingen, Germany). The supernatant was transferred to screw-capped test tubes.

The tissue of *A. antiquata* was dissected from the shell and homogenised using a blender. After homogenization, 10 mL of analytical-grade ethanol (99.9) was added to 1 g of tissue sample, and the mixture was sonicated for 60 minutes at 30 ± 3 °C. The sample was then centrifuged (Hettich Zetrifugen Model: Universal 320R, Andreas Hettich GmbH & Co. KG, 78532 Tuttlingen, Germany) for 5 min at 1500 X g, and the supernatant transferred to screw-capped test tubes. Seawater was filtered using clean and sterilised cloth gauze.

Extraction of analytes

Phthalates were extracted using a dispersive liquid-liquid microextraction method, adapted from Liang *et al.* (2008). Twenty aliquots, each containing 5 mL of the sample solution, were added to separate conical-bottomed glass test tubes from each sample. A 1 mL glass syringe (Pressure-Lok, VICI Precision Sampling Inc., Baton Rouge, LA, USA) was used to inject 1 mL of acetonitrile (CAS No. 75-05-8, Sigma Aldrich Japan KK) into the sample solution as the dispersive solvent, followed by 100 µL of carbon tetrachloride (CCl_4) (CAS No. 56-23-5, VWR International BVBA, Leuven, UK) as the extraction solvent. The mixture was vortexed using a Scientific Vortex-2 Genie (Model: G-560E, Scientific Industries, Inc., Bohemia, NY, 11716, USA) for 5 minutes and then centrifuged (see model above) for 5 minutes at 3000 X g to create a cloudy solution of very small droplets of CCL_4. Due to its high density, sedimented CCl_4 was collected using a 100 µL glass syringe into a single vial and allowed to dry overnight, before being dissolved in 1 mL dichloromethane (99.5%, AR/ACS, CAS: 75-092 ADR/PG, LOBA Chemie., Jehangir Villa, 107 Wonderhouse, Mumbai, India).

Determination of phthalates

An analytical standard phthalate mixture of 1000 µg/mL was diluted by methanol (Brand: Supelco: CRM48805, Sigma-Aldrich Chemie GmbH) and used for the preparation of external calibration curves for quantification of analytes in the samples. The standard mixture contained Dimethyl phthalate, Diethyl phthalate, Diisobutyl phthalate, Dibutyl phthalate, Methyl glycol phthalate, Phthalic acid, di(2-methylpent-3-yl) ester, Dimethoxyethyl phthalate, Di-n-pentyl phthalate, di-n-Hexyl phthalate, Benzyl butyl phthalate, Bis (2-butoxy ethyl) phthalate, Diisooctyl phthalate, Dicyclohexyl phthalate, 1,2-Benzenedicarboxylic acid, diphenyl ester, Di-n-octyl phthalate, Phthalic acid, and Nonyl pentadecyl ester.

Determination of phthalates was performed using Gas Chromatography-Mass Spectrometry (GC-MS) using a Shimadzu GC-MS-2010 instrument operated in Electron Ionization (EI) mode (MS) at 70 eV and Flame Ionization Detector (FID) for GC (Lo Brutto *et al.*, 2021). A Restek-5MS column (30 m x 0.25 mm x 0.25 µm) was used. The oven temperature programming was 90 °C to 280 °C, held at 90 °C for two minutes. The temperature was increased to 280 °C for 10 minutes (hold time), at a rate of 15 °C per minute. The injection temperature was 250 °C with splitless injection mode. The flow rate of carrier gas Helium was 1.21 mL min^{-1}. The ion source temperature and interface temperature in MS were 230 °C and 300 °C, respectively. The final instrumental runtime per sample was 26.48 minutes.

Phthalate bioaccumulation in *Anadara antiquata*

Bioconcentration of plasticizers in *A. antiquata* was calculated as:

$$BCF = {}^{C_B}/_{C_w} \quad \text{Equation (1)}$$

Where BCF is the bioconcentration factor, C_B is the concentration in the organism, and Cw is the concentration in seawater.

Biota sediment accumulation factor was calculated as:

$$BSAF = {}^{C_B}/_{C_S} \quad \text{Equation (2)}$$

Where BSAF is the bioconcentration factor in sediment, C_B is the concentration in the organism, and Cs is the concentration in sediment.

Quality control and assurance

All solvents were measured for phthalates before analysis. Plastic experimental tools were avoided whenever deemed necessary. Sampling and procedural blanks were used to check for background contamination of target contaminants. Trace levels of phthalates detected in procedural blanks were subtracted from the real samples. Percentage recovery was determined by spiking a known concentration of the analytical standard solution into sediment, seawater, and *A. antiquata* tissue. The spiked samples were subsequently subjected to liquid-liquid microextraction and the percentage recovery was determined using Equation 3. The limit of detection (LOD) and limit of quantification (LOQ) were determined by applying Equations 4 and 5, respectively (Table 2). Samples that fell below the detection limit were statistically treated as half of the detection limit. Triplicate samples were taken and treated as separate samples; the average concentration of the triplicate samples was determined, and the results are presented as the mean and standard deviation.

$$\%\text{Recovery} = \frac{C_o - C_e}{C_s} x100 \quad \text{Equation (3)}$$

Where C_o is the observed Concentration, C_e is the endogenous concentration, Cs is the spiked concentration of the standard (Burns *et al.,* 2002).

$$\text{LOD} = \text{mean of limit of blank} + 3\ \text{SD} \quad \text{Equation (4)}$$

$$\text{LOQ} = \text{Limit of blank (mean value)} + 10\ \text{SD} \quad \text{Equation (5)}$$

Where, LOD is the limit of detection, LOQ is the limit of quantification, SD is the standard deviation of the low-concentration sample (Taleuzzaman 2018).

Statistical analysis

Statistical tests were performed using nonparametric or parametric tests, chosen based on the data distribution determined using the F-test. ANOVA was used for parametric data, while Mann-Whitney and Kruskal-Wallis tests were used for non-parametric data. In all cases, a p-value of < 0.05 was used to identify statistically significant differences between phthalate concentrations amongst groups. Pearson's correlation test was used to evaluate the correlation among and between phthalates and physico-chemical parameters (temperature, pH, EC, TDS). The Paleontological Statistics Software Package for Education and Data

Table 2. Analytical recovery, limit of detection (LOD), and limit of quantification (LOQ).

Analyte Name	%Recovery			LOD	LOQ
	Sediment	Seawater	A. antiquata	ng/mL	
Dimethyl phthalate	92.81	97.23	86.68	0.03	0.11
Diethyl phthalate	87.02	96.06	81.42	0.04	0.13
Diisobutyl phthalate	100.75	91.32	78.44	0.05	0.13
Dibutyl phthalate	103.04	118.04	81.60	0.06	0.21
Methyl glycol phthalate	86.97	93.25	75.02	0.08	0.29
Phthalic acid, di(2-methylpent-3-yl) ester	94.01	94.76	80.76	0.07	0.23
Diethoxyethyl phthalate	86.78	90.50	83.50	0.04	0.15
Di-n-pentyl phthalate	86.92	89.02	76.02	0.07	0.24
di-n-Hexyl phthalate	87.07	90.25	90.25	0.06	0.20
Benzyl butyl phthalate	78.70	80.44	74.06	0.05	0.16
Bis(2-butoxyethyl) phthalate	86.24	91.22	81.00	0.05	0.18
Bis(2-ethyhexyl) phthalate	89.48	78.20	78.20	0.17	0.58
Dicyclohexyl phthalate	79.02	86.10	77.78	0.06	0.22
1,2-Benzenedicarboxylic acid, diphenyl ester	86.23	93.09	76.44	0.09	0.33
Di-n-octyl phthalate	87.61	89.73	79.06	0.08	0.27
Phthalic acid, nonyl pentadecyl ester	80.56	86.00	73.56	0.22	0.72

Analysis (PAST), version 4.09 (Hammer *et al.*, 2001), was used to conduct the statistical analyses. Graphs were generated using Microsoft® Excel Version 16.52.

Results

Quality control and assurance

The percentage recovery, LOD, and LOQ are provided in Table 2. Recovery ranged from 73.56 to 118.04 %, which is within the acceptable range of 70 to 120 % (Shabeer *et al.*, 2018). A test for instrument sensitivity under the set of machine measurement acquisition revealed that the LOD ranged from 0.03 to 0.22 ng/mL, while the LOQ was from 0.11 to 0.72 ng/mL.

Phthalates in Dar es Salaam samples

Figure 2 presents the presence of three phthalates (DBP, DiBP, and DEHP) in sediment, seawater, and *A. antiquata* samples from four sampling sites in Dar es Salaam. The levels of DiBP varied from 11.53 ± 0.41 ng/mL to 13.35 ± 1.41 ng/g dw in seawater and sediment samples, respectively, meanwhile, the concentration in *A. antiquata* was 11.82 ± 4.21 ng/g fw. DBP levels ranged from 12.09 ± 0.28 ng/g dw to 20.63 ± 0.99 ng/g dw in sediments and seawater, respectively, whereas in *A. antiquata* samples it was 12.19 ± 1.81 ng/g fw. DEHP was detected at Kawe Beach and Selander Bridge, which levels ranged from 6.04 ± 2.52 ng/mL to 12.57±2.52 ng/mL in seawater and 7.57 ± 1.02 ng/g dw to 12.52 ng/g dw in sediments, and 5.87 ± 2.47 ng/g fw in *A. antiquata*. One-Way ANOVA revealed no significant differences in phthalate levels between seawater and sediment amongst the sampling locations ($p > 0.05$) (Table 3). However, the distribution of phthalates in sediment showed significant differences, with DBP having the highest mean concentration, followed by DiBP and DEHP ($p > 0.05$) (Table 3).

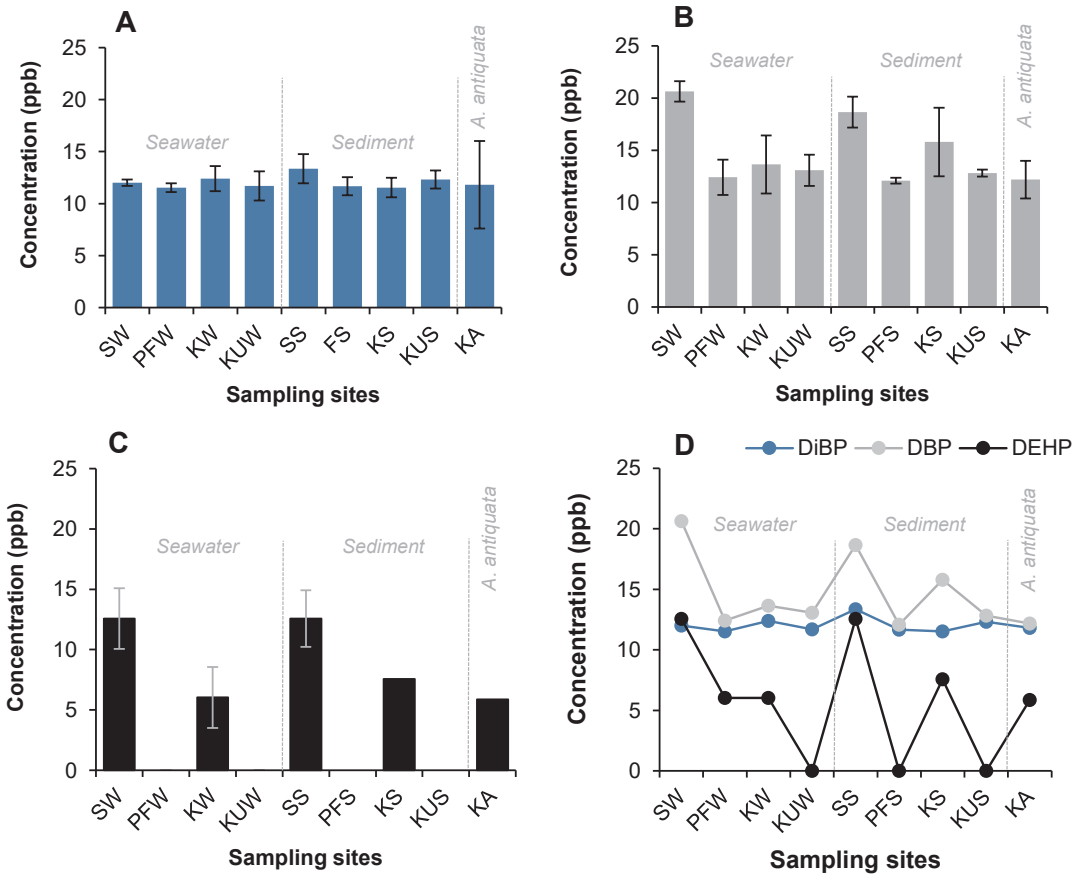

Figure 2. Concentrations of phthalates along the coast of Dar es Salaam. **A**: Diisobutyl phthalate (DiBP) **B**: Dibutyl phthalate (DBP), **C**: Bis(2-ethyhexyl) phthalate (DEHP), **D**: DiBP, DBP and DEHP concentration comparison. SW: Selander Bridge-Seawater, SS: Selander Bridge-Sediment sample, PFW: Posta Ferry Beach-Seawater, FS: Posta Ferry-Sediment sample, KW: Kawe Beach-Seawater, KS: Kawe Beach-Sediment, KUW: Kunduchi Beach-Seawater and KUS: Kunduchi Beach-Sediment. Error Bar= Standard deviation (SD, n=3). Part per billion (ppb)= ng/mL for seawater, ng/g dw (dry weight) for sediment), ng/g fw (fresh weight) for *A. antiquata*.

Table 3. Concentration of DiBP, DBP and DEHP along the coast of Tanzania.

Statistical comparison	Sample type	Sampling sites	Phthalates (Concentration Mean ± SD)		
Dar es Salaam (D)			**D_DiBP**	**D_DBP**	**D_DEHP**
(W_DiBP Vs W_DBP VsW_DEHP)** (S_DiBP Vs S_DBP Vs S_DEHP)* (W_DiBP Vs S_DiBP) * (W_DBP Vs S_DBP)* (W_DEHP Vs S_DEHP)*	Seawater (W) (ng/mL)	SW	12.00 ± 0.31	20.63 ± 0.99	12.57 ± 2.52
		FW	11.53 ± 0.41	12.41 ± 1.69	nd
		KW	12.4 ± 1.20	13.64 ± 2.78	6.04 ± 2.52
		KUW	11.70 ± 1.40	13.08 ± 1.49	nd
	Sediment (S) (ng/g dw)	SS	13.35 ± 1.41	18.65± 1.49	12.57 ± 2.35
		FS	11.67 ± 0.86	12.09 ± 0.28	nd
		KS	11.54 ± 0.94	15.83 ± 3.28	7.57 ± 1.02
		KUS	12.32 ± 0.86	12.82 ± 0.33	nd
	A. antiquata (A) (ng/g fw)	KA	11.82 ± 4.21	12.19±1.81	5.87 ± 2.47
Mtwara (M)			**M_DiBP**	**M_DBP**	**M_DEHP**
(M_DiBPVs M_DBP Vs M_DEHP)* *(W_DiBP Vs W_DBP Vs W_DEHP)** *(S_DiBP Vs S_DBP Vs S_DEHP)** *(W_DiBP Vs S_DiBP)** (W_DBP Vs S_DBP)* (W_DEHP Vs S_DEHP)*	Seawater (W) (ng/mL)	MTFW	14.35 ±1.12	11.15 ± 0.76	nd
		MKW	6.17 ± 1.34	7.07 ± 1.04	nd
		RUW	3.71 ± 0.58	5.82 ±1.02	nd
		MSW	5.54 ± 1.43	6.31 ± 1.61	nd
	Sediment (S) (ng/g dw)	MTFS	10.42 ± 0.89	9.71 ± 0.14	nd
		MKS	7.81 ± 1.43	8.40 ± 0.09	nd
		RUS	6.30 ± 1.04	4.3 ± 0.60	nd
		MSS	4.56 ± 1.21	5.26 ± 0.37	nd
	A. antiquata (A) (ng/g fw)	MTFA	2.60 ± 1.12	4.43 ± 0.95	nd
		MKA	2.72 ± 0.66	3.53 ± 0.62	nd
Tanga (T)			**T_DiBP**	**T_DBP**	**T_DEHP**
(T_DiBP Vs T_DBP Vs T_DEHP)*** (W_DiBP Vs W_DBP Vs W_DEHP)* (S_DiBP Vs S_DBP Vs S_DEHP)* (W_DiBP Vs S_DiBP)* (W_DBP Vs S_DBP)* (W_DEHP Vs S_DEHP)*	Seawater (W) (ng/mL)	TSBW	8.23 ± 0.94	9.32 ± 1.16	nd
		PFMW	9.23 ± 0.94	4.86 ± 0.71	nd
		TRZBW	9.56 ± 1.65	5.36 ± 1.34	nd
		MBW	4.56 ± 1.71	5.96 ± 1.60	nd
	Sediment (S) (ng/g dw)	TSBS	10.16 ± 0.82	11.23 ± 0.93	3.14 ± 1.32
		PFMS	10.72 ± 1.27	7.87 ± 1.37	4.61 ± 1.17
		TRZBS	7.91 ± 2.13	5.67 ± 0.98	0.57± 0.64
		MBS	5.12 ± 2.05	6.97 ± 2.13	nd
	A. antiquata (A) (ng/g fw)	TSBA	2.61 ± 0.56	3.17 ± 0.97	1.37 ± 0.65
		PFMA	1.69 ± 0.65	1.48 ± 0.67	0.87 ± 0.56
Zanzibar(Z)			Z_DiBP	**Z_DBP**	**Z_DEHP**
(Z_DiBP^{+++} Vs Z_DBP^{++} Vs Z_DEHP^{+})*** ((W_DiBP Vs W_DBP VsW_DEHP)* (S_DiBP Vs S_DBP Vs S_DEHP)* (W_DiBP Vs S_DiBP)* (W_DBP Vs S_DBP)* (W_DEHP Vs S_DEHP)*	Seawater (W) (ng/mL)	PMW	3.67 ± 0.93	5.23 ± 0.93	nd
		ZFAW	9.87 ± 2.02	6.78 ± 1.13	3.31 ± 1.24
		ZBKW	3.07 ± 0.32	6.67 ± 0.56	nd
		ZFMW	8.48 ± 0.27	5.56 ± 1.46	nd
	Sediment (S) (ng/g dw)	PMS	4.81 ± 2.54	4.44 ± 2.54	nd
		ZFAS	12.87 ± 1.56	9.54 ± 2.45	4.67 ± 0.84
		ZBKS	5.78 ± 1.04	5.32 ± 0.63	1.04 ± 0.21
		ZFMS	4.72 ± 0.21	5.72 ± 0.51	2.17 ± 0.32
	A. antiquata (A) (ng/g fw)	ZFMA	2.97 ± 0.93	3.31 ± 1.09	0.86 ± 0.27

(xxi)(D_DiBP vs. M_ DiBP)***, (xxii) (D_DiBP vs. T DiBP***, (xxiii)(Da_DiBP vs. Z_DiBP)***, (xxiv)(M_DiBP vs. T_DiBP)*, (xxv) (M_DiBP vs. Z_DiBP)*, (xxvi)(T_DiBP vs. Z_DiBP)*. (xxvii)(D_DBP vs. M_DBP)*,(xxviii)(D_DBP vs. T_DBP)***, (xxix)(D_DBP vs. Z_DBP)***, (xxx)(M_DBP vs. T_DBP)*, (xxxi)(M_DBP vs. Z_DBP)*, (xxxii)(T_DBP vs. Z_DBP)*.

Key:

***p < 0.01 (highly significant difference)

** p < 0.05 (significant difference)

*p (no significant difference)

Post Hoc

$^{+++}$p<0.01

$^{++}$p<0.05

$^{-}$p (no significant difference)

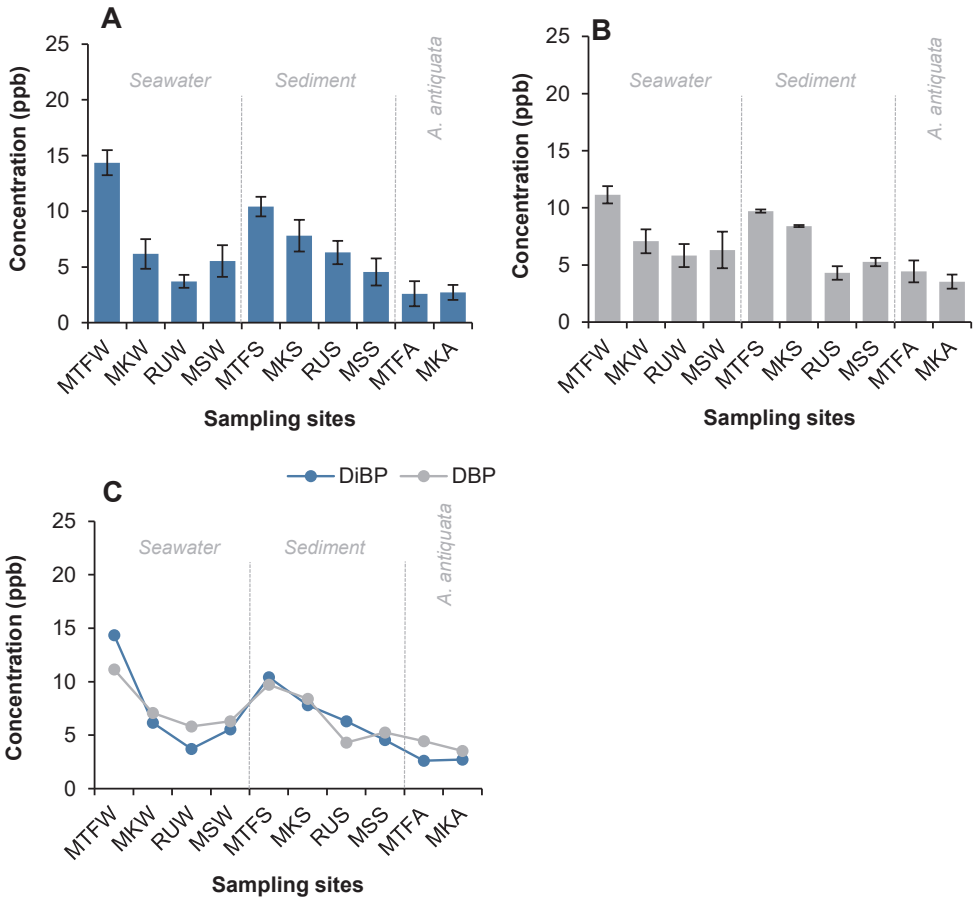

Figure 3. Concentrations of phthalates along the coast of Mtwara. **A**: Diisobutyl phthalate (DiBP) **B**: Dibutyl phthalate (DBP), **C**: DiBP, DBP and DEHP concentration comparison. MTFW (Mtwara Ferry Fish Market Beach Beach-Seawater), MTFS (Mtwara Ferry Fish Market Beach-Sediment), MTFA (Mtwara Ferry Fish Market Beach-A. antiquata), MKW (Mikindani-Seawater Sample), MKS (Mikindani-Sediment), MKA (Mikindani-A. antiquata), RUW (Ruvula-Seawater), RUS (Ruvula-Sediment), MSW (Msimbati-Seawater) and MSS (Msimbati-Sediment). Error Bar= Standard deviation (SD, n=3). Part per billion (ppb)= ng/mL for seawater, ng/g dw (dry weight) for sediment), ng/g fw (fresh weight) for *A. antiquata*.

Phthalates in Mtwara samples

Figure 3 compares the presence of DiBP and DBP in sediment, seawater, and *A. antiquata* samples collected at four Mtwara sites (Mtwara Ferry Fish Market Beach, Mikindani, Ruvula, and Msimbati). DiBP concentrations in sediments ranged from 4.30 ± 0.60 to 9.71 ± 0.14 ng/g dw, with the highest concentration observed at Mtwara Ferry Fish Market Beach. Seawater samples had DiBP concentrations from 5.82 ± 1.02 to 11.15 ± 0.76 ng/mL, with the highest concentration at Mtwara Ferry Fish Market Beach. *A. antiquata* from Mtwara Ferry Fish Market Beach had a higher DBP concentration (4.43 ± 0.95 ng/g fw) compared to Mikindani (3.53 ± 0.62 ng/g fw). DBP concentrations in sediments ranged from 4.56 ± 1.21 to 10.42 ± 0.89 ng/g dw, with the highest concentration observed at Mtwara Ferry Fish Market Beach. Seawater samples had DBP concentrations from 3.71 ± 0.58 to 14.35 ± 1.21 ng/mL. Statistical analysis revealed no significant differences in DiBP and DBP concentrations between seawater and sediments (Table 3).

Phthalates in Tanga samples

Figure 4 compares the results obtained from the Tanga coast, which indicated the presence of phthalates (DiBP, DBP, and DEHP) in sediment, seawater and *A. antiquata* samples. The concentration of DiBP in sediments varied between 5.12 ± 2.05 and 10.72 ± 1.27 ng/g dw, with the highest level observed at Pangani Fish Market. In seawater, DiBP concentrations ranged from 4.76 ± 1.71 to 9.56 ± 1.65 ng/mL, with the highest level found at Tanga Raskazone Beach. *A. antiquata* samples had DiBP levels of 2.61 ± 0.56 ng/g fw for Tanga Sahare Fish Market Beach and 1.69 ± 0.65 ng/g fw for Pangani Fish Market Beach. DBP concentrations in sediments ranged from 5.67 ± 0.98 to 11.23 ± 0.93 ng/g dw, with the highest concentration observed at Tanga Sahare

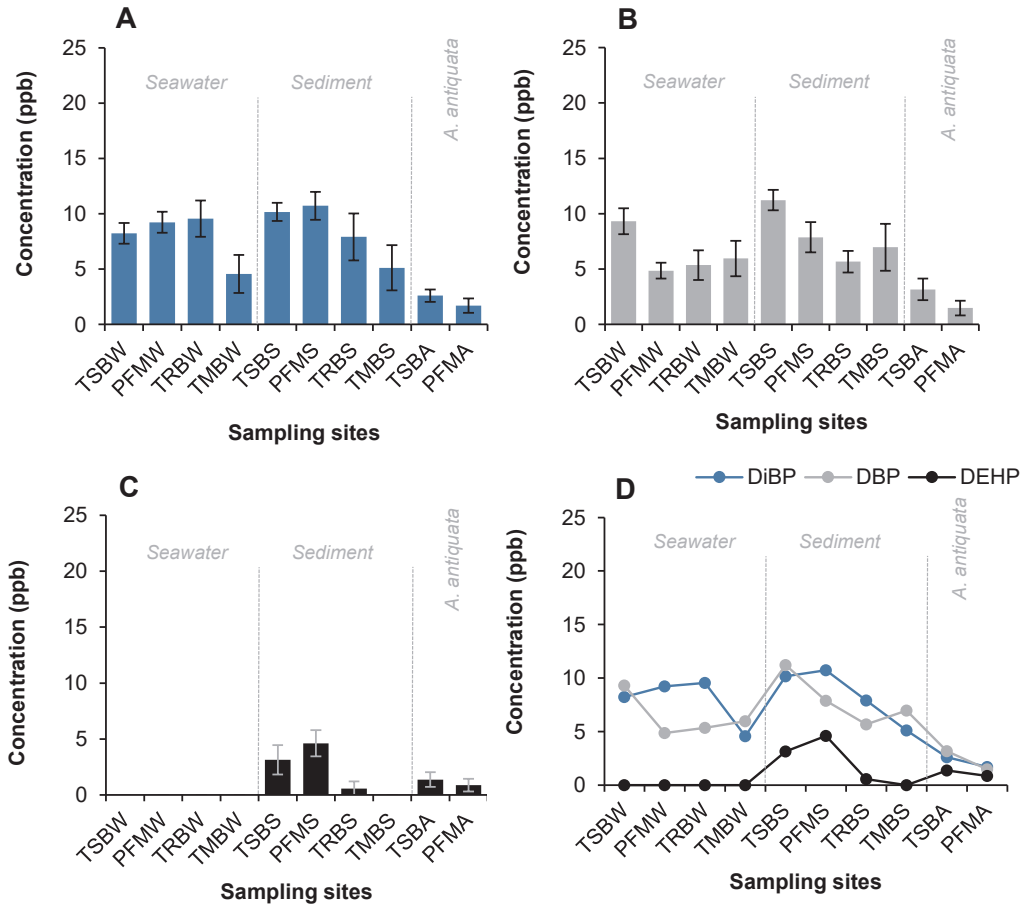

Figure 4. Concentrations of phthalates along the coast of Tanga. A: Diisobutyl phthalate (DiBP) B: Dibutyl phthalate (DBP), C: Bis(2-ethyhexyl) phthalate (DEHP), D: DiBP, DBP and DEHP concentration comparison. TSBW: Tanga Sahare Fish Market Beach -Water, TSBS: Tanga Sahare Fish Market Beach - Sediment, TSBA: Tanga Sahare Fish Market Beach-*A. antiquata*, PFMW: Pangani Fish Market Beach-Seawater, PFMS: Pangani Fish Market Beach - Sediment, PFMA: Pangani Fish Market Beach-*A. antiquata*, TRBW: Tanga Raskazone Beach-Seawater, TRBS: Tanga Raskazone Beach-Sediment, TMBW: Tanga Mkongeni Beach-Seawater, TMBS: Tanga Mkongeni Beach-Sediment. Error Bar= Standard deviation (SD, n=3). Part per billion (ppb)= ng/mL for seawater, ng/g dw (dry weight) for sediment), ng/g fw (fresh weight) for *A. antiquata.*

Fish Market Beach. In seawater, DBP concentrations ranged from 4.86 ± 0.71 to 9.32 ± 1.16 ng/mL, with the highest level found at Tanga Sahare Fish Market Beach. *A. antiquata* from Tanga Sahare Fish Market Beach also exhibited a higher DBP concentration (3.17 ± 0.97 ng/g fw) compared to those from Pangani Fish Market Beach (1.48 ± 0.67 ng/g fw). Figure 4D shows that DBP had the highest concentrations, followed by DiBP, while DEHP had the lowest levels. Statistical analysis confirmed significant differences in mean concentrations amongst the sampling sites in Tanga ($p<0.05$) (Table 3), with DiBP showing significantly higher levels compared to DBP and DEHP.

Phthalates in Zanzibar samples

Figure 5 compares the concentrations of phthalates in sediments and seawater from four sites in Zanzibar (Pwani Mchangani, Zanzibar Ferry Beach, Zanzibar Bwawani Komba, and Zanzibar Mazizini Fish Market). The results showed varying concentrations of DiBP, DBP, and DEHP across the sampling locations (Table 3). DiBP concentrations ranged from 4.72 ± 0.51 to 12.87 ± 2.45 ng/g dw in sediments, with the highest concentration observed at the Zanzibar Ferry Beach. In seawater, DiBP concentrations ranged from 3.07 ± 1.46 to 9.87 ± 2.02 ng/mL, with the highest concentration again found at Zanzibar Ferry Beach. The concentration of DiBP in *A. antiquata* from Zanzibar Mazizini Fish Market was 2.97 ± 0.93 ng/g fw. For DBP, sediment concentrations ranged from 4.44 ± 2.54 to 9.54 ± 2.45 ng/g dw, while seawater concentrations ranged from 5.23 ± 0.93 to 6.78 ± 1.13 ng/mL. DEHP concentrations in sediments and seawater were quantifiable at various sites. DiBP had the highest concentrations among the phthalates analysed (Fig. 5D). Statistical analysis indicated no significant differences in phthalate

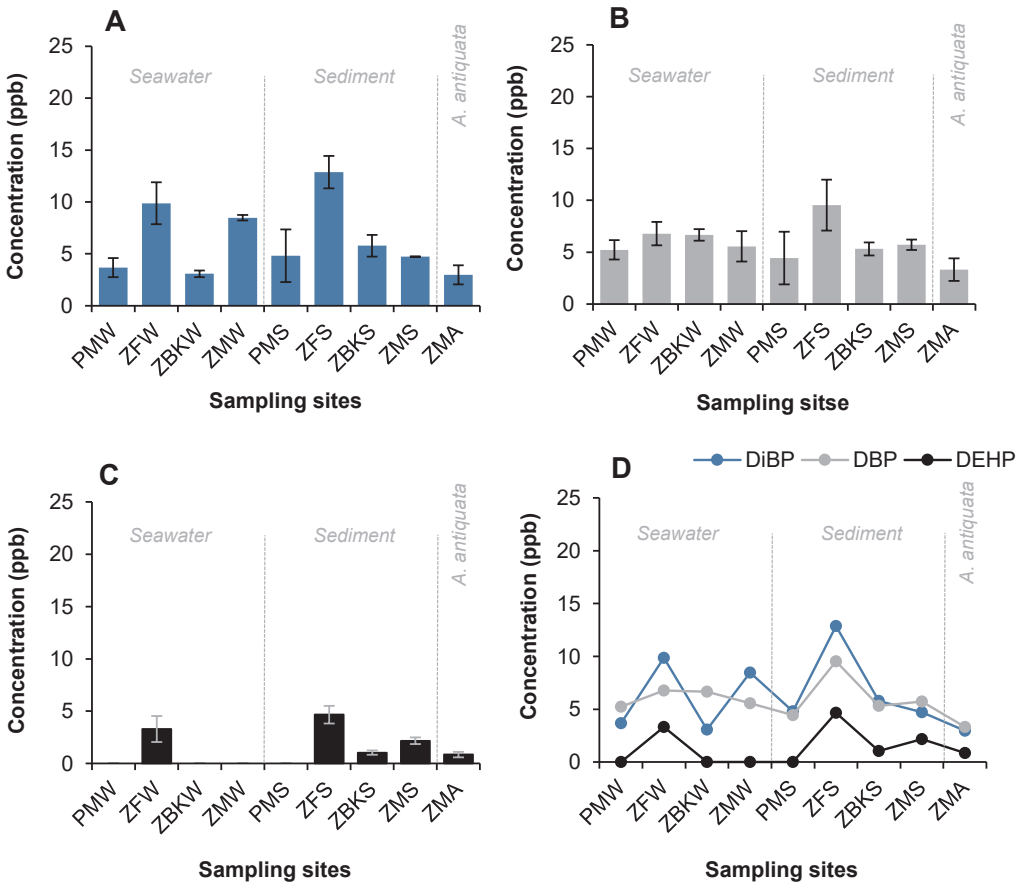

Figure 5: Concentrations of phthalates in Zanzibar. A: Diisobutyl phthalate (DiBP) B: Dibutyl phthalate (DBP), C: Bis(2-ethyhexyl) phthalate (DEHP), D: DiBP, DBP and DEHP concentration comparison. PMW: Pwani Mchangani-Seawater, PMS: Pwani Mchangani-Sediment, ZFW: Zanzibar Ferry Beach-Seawater, ZFS: Zanzibar Ferry Beach-Seawater, ZBKS: Zanzibar Bwawani Komba-Sediment, ZBKW: Zanzibar Bwawani Komba-Seawater, ZMW: Zanzibar Mazizini Fish Market-Seawater, ZMS: Zanzibar Mazizini Fish Market-Sediment, ZMA- Zanzibar Mazizini Fish Market-*A. antiquata*. Error Bar= Standard deviation (SD, n=3). Part per billion (ppb)= ng/mL for seawater, ng/g dw (dry weight) for sediment), ng/g fw (fresh weight) for *A. antiquata*.

concentrations between sediments and seawater ($p > 0.05$), but there were significant differences observed amongst the phthalates in seawater ($p < 0.05$) (Table 3).

Cumulative concentration of phthalate in sediment, seawater and Anadara antiquata

Due to their similar mode of toxicity, it has been recommended that the cumulative concentration of phthalates in the environment should also be considered (Araki *et al*., 2020, Chen *et al*., 2020 and Sumner *et al*., 2019). Higher concentrations of phthalates were evident in samples collected from Dar es Salaam sites, particularly at Selander Bridge (45.20 and 44.57 ng/mL in seawater and sediment, respectively). Generally, seawater, sediment and *A. antiquata* samples from Dar es Salaam sites exhibited higher cumulative concentrations than samples from other sites (Figure 6). However, statistically, there was no significant difference in the concentrations of phthalates between seawater and sediment matrices ($p > 0.05$).

Bioconcentration of phthalates in the cockle Anadara antiquata

Table 4 presents the bioconcentration factor (BCF) and biota sediment accumulation factor (BSAF) values of phthalates (DiBP, DBP, and DEHP) in *A. antiquata* at various sampling sites. The BCF values ranged from 0.18 at Pangani Fish Market Beach to 0.95 at Kawe Beach. Similarly, the BSAF values vary, with the lowest value of 0.16 at Pangani Fish Market Beach and the highest of 1.02 at Kawe Beach. These findings indicate variations in the accumulation potential of phthalates in *A. antiquata* across different sampling sites.

Correlation analysis

Table 5 shows Pearson's correlation coefficients of phthalates (DiBP, DBP, DEHP) and physico-chemical parameters in seawater and sediment samples, respectively. The finding depicts the extent and direction of associations among DiBP, DBP and DEHP and temperature, pH, EC and TDS. The findings show

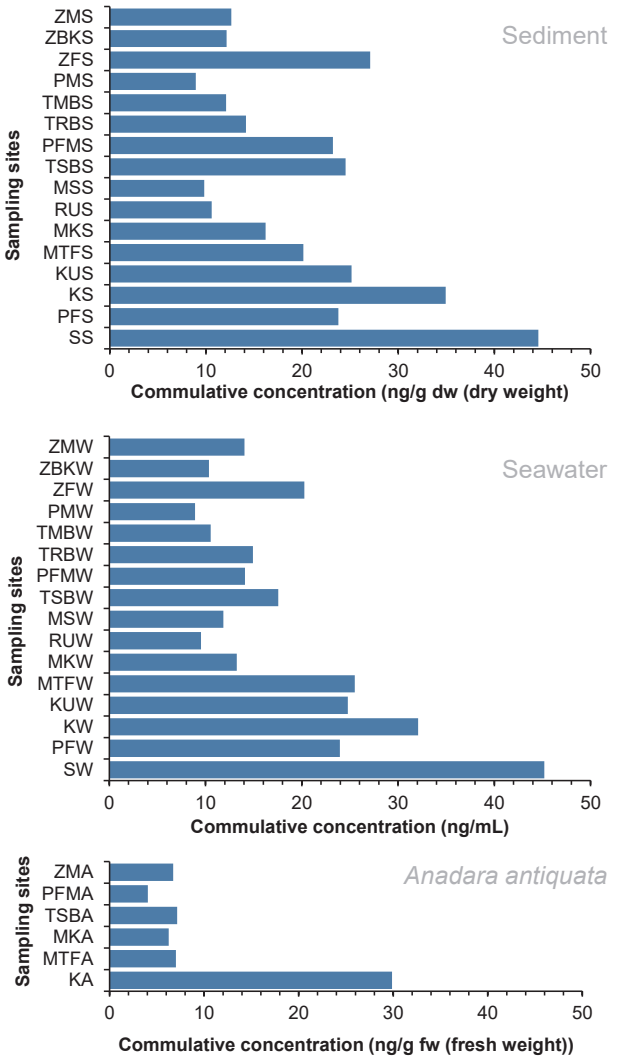

Figure 6. Cumulative concentration of Diisobutyl phthalate (DiBP), dibutyl phthalate (DBP) and Bis (2-ethylhexyl) phthalate) in marine sediment, seawater and *A. antiquata* along the Indian Ocean Coast. **A**: Diisobutyl phthalate (DiBP) **B**: Dibutyl phthalate (DBP), **C**: Bis(2-ethyhexyl) phthalate (DEHP), **D**: DiBP, DBP and DEHP concentration comparison. SW: Selander Bridge-Seawater, SS: Selander Bridge-Sediment, PFW: Posta Ferry Beach-Seawater, PFS: Posta Ferry Beach-Sediment, KW: Kawe Beach-Seawater, KS: Kawe Beach-Sediment, KUW: Kunduchi Beach-Seawater and KUS: Kunduchi Beach-Sediment. MTFW (Mtwara Ferry Fish Market Beach -Seawater), MTFS (Mtwara Ferry Fish Market Beach-Sediment), MTFA (Mtwara Ferry Fish Market Beach -*A. antiquata*), MKW (Mikindani-Seawater Sample), MKS (Mikindani-Sediment), MKA (Mikindani-*A. antiquata*), RUW (Ruvula-Seawater), RUS (Ruvula-Sediment), MSW (Msimbati-Seawater) and MSS (Msimbati-Sediment). TSBW: Tanga Sahare Fish Market Beach-Seawater, TSBS: Tanga Sahare Fish Market Beach-Sediment, TSBA: Tanga Sahare Fish Market Beach-*A. antiquata*, PFMW: Pangani Fish Market Beach-Seawater, PFMS: Pangani Fish Market Beach-Sediment, PFMA: Pangani Fish Market Beach-*A. antiquata*, TRBW: Tanga Raskazone Beach-Seawater, TRBS: Tanga Raskazone Beach-Sediment, TMBW: Tanga Mkongeni Beach-Seawater, TMBS: Tanga Mkongeni Beach-Sediment. PMW: Pwani Mchangani-Seawater, PMS: Pwani Mchangani-Sediment, ZFW: Zanzibar Ferry Beach-Seawater, ZFS: Zanzibar Ferry Beach-Seawater, ZBKS: Zanzibar Bwawani Komba-Sediment, ZBKW: Zanzibar Bwawani Komba-Seawater, ZMW: Zanzibar Mazizini Fish Market -Seawater, ZMS: Zanzibar Mazizini Fish Market-Sediment, ZMA-Zanzibar Mazizini Fish Market-*A. antiquata*.

that DiBP in seawater had a slightly positive correlation with DBP (r = 0.66) and a weak positive correlation with DEHP (r = 0.40), while DBP demonstrated a strong positive correlation with DEHP (r = 0.77). Correlations between phthalates and physical-chemical parameters are generally weak in both seawater and sediments, with some negative correlations noted between pH and phthalates, and weak positive correlations between EC and DEHP (r = 0.42). In sediment samples (Table 5), DiBP exhibited a strong positive correlation with DBP (r = 0.84) and a moderate positive correlation with DEHP (r = 0.58). On the other hand, a strong positive correlation between the concentrations of DBP and DEHP was evident (r = 0.73).

Discussion

Occurrences of phthalates on the coast of Tanzania

Three of the 16 targeted phthalates, namely DiBP, DBP, and DEHP, were detected and quantified in seawater and sediments from sampling sites in two regions of the Tanzanian mainland (Dar es Salaam and Tanga) and at Zanzibar Island, whereas only DiBP and DBP were detected in samples from the Mtwara area. Statistical analysis using One Way ANOVA revealed that the cumulative concentrations of DiBP, DBP, and DEHP were generally higher in sediments and seawater at Dar es Salaam beaches (Selander Bridge, Kawe Beach, Posta Ferry Beach and Kunduchi Beach) than at Mtwara, Tanga, and Zanzibar.

The high prevalence of phthalates at the Dar es Salaam sites can be explained by the highest level of anthropogenic activities in the region, which include 532 industries and 5,383,728 inhabitants that account for 5.4 % of the population in Tanzania (NBS, 2022). The Msimbazi River, which runs for 35 km through Dar es Salaam has been identified as the main channel for the flow of organic pollutants to the city's coast. Domestic wastes and wastewater from nearby factories in Tabata and Ubungo, landfill sites, and horticultural activities in the river basin contribute to the pollution (Nchimbi *et al*., 2022). The Dar es Salaam coast also receives water from the Zinga and Kizinga rivers flowing through the industrial suburbs of Kurasini, Mbagala, and Kigamboni. Industrial effluents, garage waste, pesticides from nearby horticulture sites, and domestic plastic waste in these river basins are potential sources of phthalate contamination (Nchimbi *et al*., 2022). Phthalate contamination may also come from recreational and fishing activities on Dar es Salaam's popular beaches, where swimwear and plastic fishing nets are common.

Table 4. Bioconcetration factor (BCF) and biota sediment accumulation factor (BSAF) of individual phthalates in *A. antiquata*. X – could not be calculated.

Sampling site	Concentration factor	DiBP	DBP	DEHP
Kawe Beach (K)	BCF	0.95	0.89	0.97
	BSAF	1.02	0.77	0.78
Mtwara Ferry Fish Market Beach (MTF	BCF	0.4	0.18	X
	BSAF	0.30	0.46	X
Mikindani (MK)	BCF	0.5	0.38	X
	BSAF	0.35	0.42	X
Tanga Sahare Fish Market Beach (TSB)	BCF	0.32	0.34	X
	BSAF	0.26	0.28	X
Pangani Fish Market Beach (PFM)	BCF	0.18	0.3	X
	BSAF	0.16	0.89	X
Zanzibar Ferry Beach (ZF)	BCF	0.35	0.45	X
	BSAF	0.62	0.58	X

The presence of phthalates in the protected mangrove forests of Ruvula and Msimbati, which are 43 and 36 kilometres from Mtwara town, respectively, can find support in a study by Mayoma *et al.* (2020) along the Tanzanian coastline, which reported the presence of microplastics. The microplastics could potentially be a source of phthalate contamination in these protected coastal areas (Weideman *et al.*, 2013; Kida and Koszelnik, 2021). The findings indicate that phthalate pollution is a widespread problem along Tanzania's coast and indicates the need for control and monitoring efforts.

The findings of the current study indicate significant associations between phthalates in both seawater and sediment samples, as revealed by Pearson's correlation coefficients (Table 5). The positive correlations between DiBP, DBP, and DEHP suggest that these phthalates originate from similar pollution sources. Notably, the strength of these relationships is stronger in sediment samples (Table 5), suggesting similar adsorption properties of these chemicals in sediments. These observations agree with the literature on phthalate sorption behaviour (Staples *et al.*, 1997). It is commonly recognised that the sorption of phthalate esters (PAEs) to soil, sediment, or suspended solids is influenced by their relative hydrophobicity (Staples *et al.*, 1997). Furthermore, a study in JiangHan Plain reported that DiBP, DBP and DEHP coexisted in soil, sediments, and groundwater (Liu et *al.*, 2013).

Table 5. Person correlation coefficients for diisobutyl phthalate (DiBP), butyl phthalate (DBP), and bis(2-ethylhexyl phthalate) (DEHP) and temperature (TEMP), pH, electrical conductivity (EC), and total dissolved solid (TDS) in seawater and sediment samples. Perfect positive correlation: r = 1, Strong positive correlation: 0.7 ≤ r ≤ 0.99, Slightly positive correlation: 0.4 ≤ r ≤ 0.69, Weak positive correlation: 0.1 ≤ r ≤ 0.39, No correlation: -0.1 ≤ r ≤ 0.1, Weak negative correlation: -0.1 ≥ r ≥ -0.39, Slightly negative correlation: -0.4 ≥ r ≥ -0.69, Strong negative correlation: -0.7 ≥ r ≥ -0.99, Perfect negative correlation: r = -1.

	Parameters	DiBP	DBP	DEHP	TEMP	pH	EC	TDS
Seawater	DiBP							
	DBP	0.66						
	DEHP	0.41	0.77					
	TEMP	0.47	0.53	0.39				
	pH	-0.31	-0.23	-0.16	-0.59			
	EC	-0.14	0.11	0.42	0.12	0.13		
	TDS	-0.34	-0.23	-0.16	-0.59	0.99	0.13	
Sediment	DiBP							
	DBP	0.84						
	DEHP	0.58	0.73					
	TEMP	0.153	0.19	0.17				
	pH	-0.09	0.16	-0.20	-0.01			
	EC	0.16	0.31	0.35	0.48	0.29		
	TDS	-0.199	-0.28	-0.18	-0.03	-0.51	-0.25	

Moreover, it has been shown that dispersion and partition coefficients increase with the carbon chain length of phthalates (Liu *et al.,* 2013). Specifically, the sorption rate of DiBP and DBP was found to be approximately 10 %, compared to 1 % for DEHP (Liu *et al.,* 2013). The findings reported by Liu *et al*. (2013) agree with the strong correlation observed between DiBP and DBP in the present study, as compared to DEHP. By considering the collective evidence from the literature, the findings from this study contribute to the understanding of the fate and behaviour of phthalate contaminants in coastal areas, particularly along the coast of Tanzania.

Comparison with other studies

Table 6 provides a comparison between phthalate concentrations recorded in the current study and other relevant studies from the marine environment in different regions of the world. The table specifically highlights the concentrations of DiBP, DBP, and DEHP in water, sediments and biota. It can be observed in Table 6 that the present study reveals contrasting concentration ranges of phthalates in seawater compared to findings from other studies. Mackintosh *et al.* (2006) found lower concentrations of these phthalates in water from False Creek Harbor, Vancouver. Similarly, Jebara *et al.* (2021) reported relatively lower concentrations along the north-eastern coastline of Tunisia. Sánchez-Avila *et al.* (2012), who investigated the Bay of Biscay in Spain and the Port Sea in the Mediterranean Sea, also observed lower concentrations of these phthalates. Additionally, Fossi *et al.* (2012) who examined the Mediterranean Sea in Italy, reported lower concentrations of these phthalates in studied areas.

Table 6. Comparison of DiBP, DBP, and DEHP concentrations with other studies.

Locations	DiBP	DBP	DEHP	References
Seawater (ng/mL)				
Dar es Salaam	11.53-12.4	13.08-20.63	nd-12.57	This study
Mtawara	3.71-14.35	5.82-11.70	nd	This study
Tanga	4.56-9.56	4.86-9.32	nd	This study
Zanzibar	3.07-9.87	5.23-6.78	nd-3.31	This study
False Creek Harbor, Vancouver	0.005	0.11	0.275	Mackintosh *et al.* (2006)
North-Eastern coastline-Tunisia	0.075	0.017	0.071	Jebara *et al.* (2021)
Bay of Biscay, Spain	-	8.3×10^{-5}	64×10^{-4}	Sa'nchez-Avila *et al.* (2012)
Port sea, Mediterranean Sea, Spain	-	-	0.6×10^{-4}–0.006	Sa'nchez-Avila *et al.* (2012)
Sardinian Sea, Mediterranean Sea, Italy	-	-	0.023	Fossi *et al.* (2012)
Ligurian Sea, Mediterranean Sea, Italy	-	-	0.018	Fossi *et al.* (2012)
Sediment (ng/g dw)				
Dar es Salaam	11.54-13.35	12.09-18.65	nd-12.57	This study
Mtawara	4.56-10.42	4.30-9.71	nd	This study
Tanga	5.12-10.72	5.67-7.87	nd-4.61	This study
Zanzibar	4.72-12.87	4.44.9.54	nd-4.67	This study
Kaohsiung Harbor-Taiwan	21.9 - 69.5	37.3 - 259	259-21,559	Chen *et al.* (2017)
North-Eastern coastline-Tunisia	0.219	0.055	4.594	Jebara *et al.* (2021)
Korean bays	0.011	0.003	0.46	Kim *et al.* (2020)
Korean coast	0.009	0.001	0.38	Lee *et al.* (2020)
False Creek Harbor,Vancouver	0.004	0.103	2.9	Mackintosh *et al.* (2006)
Tropical Western Pacific Ocean	1.87 –14.43	2.24 –12.97	2.01–9.19	Zhang *et al.* (2019)
Biota (ng/g fw)				
A. antiquata, Dar es Salaam	11.82	12.19	5.87	This study
A. antiquata, Mtawara	2.6-2.72	3.53-4.43	nd	This study
A. antiquata, Tanga	1.69-2.61	1.48-3.17	0.87-1.37	This study
A. antiquata, Zanzibar	2.97	3.31	0.86	This study
North-Eastern coastline-Tunisia (ng/g))	0.817	1.771	0.921	Jebara *et al.* (2021)
S. aurata, Mahdia coast (fw basis)		<0.01	<0.0125	Beltifa *et al.* (2017)

A similar trend can be observed in the sediment samples. Chen *et al.* (2017) investigated phthalates in Kaohsiung Harbor in Taiwan, where the concentrations were higher than those reported in this study. Jebara *et al.* (2021) examined phthalates in the north-eastern coastline of Tunisia, while Kim *et al.* (2020) and Lee *et al.* (2020) studied Korean bays and the Korean coast, respectively, showing lower concentrations of phthalates compared to the results obtained in this study. A similar comparison can be observed when results obtained from the present study are compared to those reported by Mackintosh *et al.* (2006) who observed lower levels in the False Creek Harbor, Vancouver. Furthermore, Zhang *et al.* (2019) revealed the presence of different concentrations of these phthalates relative to the present study in the Tropical Western Pacific Ocean.

The potential risk of phthalates in the marine ecosystem

Phthalate esters, like other organic pollutants, undergo alkaline hydrolysis and biodegradation in marine ecosystems. The resulting metabolites from alkaline hydrolysis and biodegradation can have potentially harmful ecological impacts on marine ecosystems (Prasad, 2021; Gao and Chi, 2015). These compounds have the ability to acquire estrogenic activity when exposed to light, leading to the production of 4-hydroxy phthalates. Exposure to phthalates, as well as their metabolites, has been found to reduce fertilization rates in marine organisms, primarily due to their endocrine-disrupting properties (Hu *et al.,* 2020; Miller *et al*., 2020; Gobas *et al*., 2003; Burgos-Aceves *et al*., 2021).

The findings of this study on the bioconcentration of phthalates in *A. antiquata* are consistent with studies that have reported significantly varying concentrations of phthalates amongst different marine biota (Miller *et al*., 2020; Sun *et al*., 2021; Rios-Fuster *et al*., 2022) (Table 6). As a filter feeder, *A. antiquata* can accumulate phthalates in their tissues from the water they filter (Miller *et al*., 2020). *A. antiquata*, similar to other bivalves, can also ingest sediment particles along with the associated phthalates, leading to bioconcentration (Miller *et al*., 2020). The bioconcentration of phthalates in marine ecosystems has implications for human health and the environment as they potentially affect the health of the animals and the wider food web (Gobas *et al*., 2003).

The bioconcentration of phthalates in marine ecosystems could also have broader ecological implications such as disruption of marine diversity and abundance of marine organisms as a result of their impact on the endocrine system and on reproduction and development of organisms (Gobas *et al*., 2003; Burgos-Aceves *et al*., 2021). Furthermore, with regards to biota contamination, Jebara *et al.* (2021) investigated the north-eastern coastline of Tunisia and reported lower concentrations of phthalates in fish when compared to the concentration in *A. antiquata* obtained in the present study. Beltifa *et al.* (2017) examined *S. aurata* along the Mahdia coast and found lower concentrations of these phthalates. The current findings underscore the importance of taking measures to reduce the use and release of phthalates into the environment to safeguard the health of both marine and human life.

Environmental and policy implications of the results

The differences in phthalate concentrations observed between the current study and other studies indicate the impact of regional and local factors on contamination levels. Factors such as industrial activities, waste disposal practices, and proximity to pollution sources can contribute to the differences in phthalate levels.

The correlation analysis conducted on marine sediment and seawater samples along the Tanzanian coastline revealed no strong correlation between phthalates. The interpretation of correlation coefficients alone does not provide definitive evidence of pollution sources. However, the coefficients indicate potential associations between phthalates (DBP and DEHP) and their occurrence in the analysed samples. To gain an understanding of the pollution sources of phthalates, further investigations that extend beyond the scope and limitations of the current study are needed. Source identification studies, including source apportionment modelling (Giglioli *et al*., 2021) and chemical fingerprinting (Lorgeoux *et al*., 2016), can offer valuable insights into pinpointing specific pollution sources of phthalates in the environment. These additional approaches would contribute to a more accurate assessment of the origins and factors influencing phthalate contamination.

Despite no universally acceptable worldwide guideline for all phthalates, the concentrations of DBP, DiBP, and DEHP in sediments and seawater revealed in this study are a cause for concern as they exceed the minimum allowable concentrations established by various independent environmental regulatory

authorities. For example, in China, DBP and DEHP in drinking water should not exceed 3 and 8 ng/mL, respectively (Ministry of Health of the People's Republic of China, 2006). On the other hand, the National Environment Management Council (NEMC) and Tanzania Bureau of Standards (TBS) have not set limits for Tanzania. It is crucial to note that phthalates are harmful to both the environment and human health, and can be detrimental even at low exposure levels. High concentrations of phthalates can have severe effects on human health and the environment, such as harming aquatic life, disrupting the endocrine system, and impacting reproduction and development (Chen *et al*., 2020).

It is critical to consider the possible danger posed by phthalates and to reduce their concentrations in the environment. The marine ecology of the WIO is a vital component of the biodiversity of our planet, and any negative impacts on it could have repercussions on the larger ecosystem and ultimately on human populations that depend on the resources the ocean provides. In this regard, it is essential that environmental stakeholders and pertinent authorities in the WIO region work together to address this issue. Relevant government agencies in Tanzania may create suitable guidelines to regulate the use and disposal of phthalate-containing materials/products to protect community health and the environment. Furthermore, close monitoring and enforcement of these guidelines, and collaboration with other stakeholders to create public awareness about the potential health risks of phthalate exposure are required.

Conclusions

This study revealed that three phthalates, DiBP, DBP, and DEHP, were prevalent in seawater, sediments and *A. antiquata* collected from the sampling sites in Dar es Salaam, Tanga, and Zanzibar, while DiBP and DBP were prevalent in Mtwara. The Dar es Salaam coast had a significantly higher prevalence of phthalates compared to the other sites. The concentrations of DiBP, DBP, and DEHP exceed the maximum allowable levels established by environmental regulatory authorities in some parts of the world, raising concerns about their potential harm to the environment and human health. The high levels of phthalates in the studied WIO region can be linked to the high density of anthropogenic activities, including industries, agricultural activities, and other waste-producing domestic activities. Therefore, it is crucial for appropriate stakeholders and relevant regulatory authorities to work collectively towards reducing the concentrations of phthalates in the environment by developing and enforcing appropriate regulations and creating public awareness.

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