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Occurrence of tributyltin compounds and characteristics of heavy metals

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ABSTRACT: Surface sediment samples were collected from Tanzanian major commercial ports and studied for the distribution and behavior of tributyltin (TBT) compounds and heavy metals. The content of TBT in sediments ranged from ND-3670 ng (Sn) g^1dry wt (1780 ± 1720) (Mean ± SD) at Zanzibar and from ND-16700 ng (Sn)g^1 dry wt (4080 ± 7540) at Dar es Salaam ports, respectively. Maximum TBT levels were detected inside the both ports. Metabolic degradation of butyltin compounds (BTCs) showed that MBT + DBT > TBT %, this may be attributed by the warm ambient water and intense sunlight in the tropical regions. A sequential extraction procedure was undertaken to provide detailed chemical characteristics of heavy metals in the sediments. The procedure revealed that about 50 % of Fe in the both ports is in immobile fraction (residual fraction) while other metals; Cd, Cu, Ni, Co, Zn, Pb, and Mn were mostly found in exchangeable or carbonate fractions and thus can be easily remobilized and enter the aquatic food chain. This paper provides basic information of TBT compounds contamination and chemical characteristics of heavy metals in the marine ecosystem in Tanzania. To our knowledge, this is the first documentation of Organotin compounds (OTCs) in marine environments in East Africa and suggests the importance of further detailed OTCs studies in other sub-Saharan Africa regions

Key words: *TBT, heavy metals, sequential extraction, OTCs, port, Zanzibar, Dar es Salaam*

INTRODUCTION

Tanzania is a tropical country located in Eastern Africa between longitude 29° and 41° East. It is an important hub for marine transportation in Eastern and Central African landlocked countries. The country faces a serious problem of the environmental degradation (Hans de Wolf, *et al.*, 2001; Machiwa, 1992a; Mgana and Mahongo, 1997; Machiwa, 1992b; Mohammed, 2002; Kishe and Machiwa, 2003). Environmental awareness about the effects of organotin compounds has increased considerably in recent years (Morabito and Massanisso, 2000). Organotin compounds have been widely used as biocdes, PVC stabilizers, agrochemicals and wood preservatives. Tri butyl tin (TBT) is of particular importance because of its widespread use as a biocide in antifouling paints on ships and in wood preservative (Fent, 2003). In addition, TBT is extremely toxic to aquatic organisms. It may cause imposex and calcification anomalities in mollusks (Alzieu, 1989). Significant disturbances caused by TBT were observed in Crassotrea Gigas oysters farms in the Arachan Bay, France (Alzieu, 1989). TBT is simultaneously degraded by chemical, photochemical and biochemical pathways successively in to di butylin (DBT), mono butylin (MBT) and inorganic tin (Sn IV). Rates of photodegradation and biodegradation of organotins in water are dependent upon environmental conditions. Due to toxicity of TBT compounds, many countries have imposed regulations on the usage of TBT containing paints. In 1982, French Authorities prohibited the use of tin-containing paints for pleasure boats under 25 m long except those with aluminium hulls (Pierre-Marie, *et al.*, 1995). Similar actions on the usage of TBT in paints were also taken by the UK, USA, Switzerland, the Netherlands, Australia, New Zealands, South Africa, Japan and most of the European countries (Sergi Diez, *et al.*, 2005). However, the legislative restrictions on the use of TBT-based marine paints in Tanzania are not clearly defined. Heavy metals are introduced in to the aquatic systems as a

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result of weathering of soil rocks, from volcanic eruption and variety human activities (Jain, 2004). Sediments are a principal sink for heavy metals in the aquatic environment (Kishe and Machiwa, 2003; Izquierdo, *et al.,* 1997). Measurement of total heavy metal concentration may not be able to provide information on exact dimension of metal pollution (Jain, 2004; Marika and Markku, 2003; Tokalioglu, *et al.,* 2000; Pagnanelli, *et al.,* 2004; Izquierdo, *et al.,* 1997; Abd El-Azim, *et al.,* 2005). Sequential extraction of heavy metals provides detailed information to evaluate the bioavailability and toxicity of the elements in environment and can distinguish those metals with a lithogenic origin from those with an anthropogenic origin (Izquierdo, *et al.,* 1997). Although the fate of organotin compounds and chemical characteristics of heavy metals have been widely investigated in developed countries. Limited studies have considered the prevalence of TBT compounds and speciation of heavy metals in sub-Saharan African harbors, Tanzania in particular. The primary objectives of this study were to investigate; (a) the contamination levels and metabolic degradation of TBT compounds, and (b) the speciation of heavy metals in sediments at the Dar es Salaam and the Zanzibar ports.

MATERIALS AND METHODS

Area of study and sampling

Zanzibar port is located at 6 °10' S, 39 ° 11' E and handles more than 90% of Zanzibar's trade. Dar es Salaam Port is situated at Latitude 6 °49' S, Longitude 39° 19' E. It is the principle port and a major sea for landlocked countries. About 100 g of sediments samples were collected between June 22-26, 2004 from 8 sites (D1-D8) in Dar es salaam, and 5 sites (Z1-Z5) in Zanzibar port as shown in Fig. 1. All sediment samples were collected using a grab sampler (or by stainless spoon when possible) and were stored in glass bottles under 4 °C and shipped to Japan for analysis. The samples were subsequently freeze-dried by FRD-51, IWAKI and stored at-20 °C in the dark until analysis.

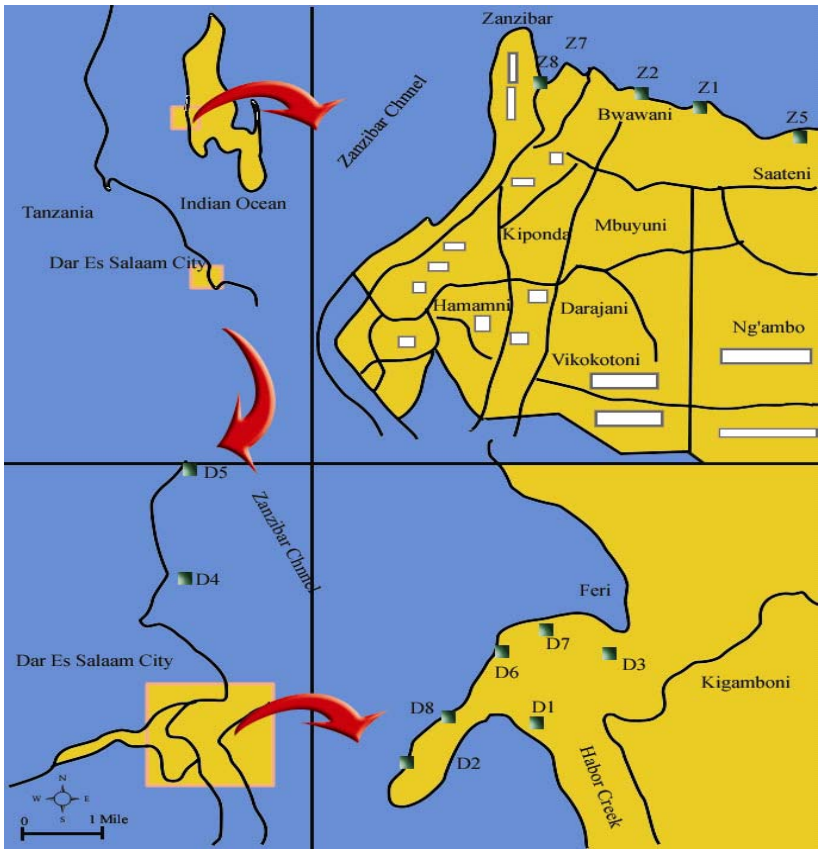

Fig. 1: Sampling locations

Reagents

Organotin standards: Tripropyltin chloride (TPrT, 98 %), Monobutyltin trichloride (MBT, 95 %), Dibutyltin dichloride (DBT, 96 %), and Tribuyltin chloride (TBT, 96 %) were purchased from Merck. Stock solutions 1000 mg (Sn)/L of organotin compounds and were prepared in methanol (pesticide analysis grade), then stored at +4 °C. Working solutions were prepared weekly by diluting the stock solutions. Sodium tetraethylborate 98 %, hydrochloric acid (Sn < 0.1 pg/mL, acetic acid (ultrapure grade), anhydrous sodium sulphate, tetramethyl ammonium hydroxide (TMHA, 25%, Sn < 20 pg/mL) and ammonium solution (ultrapure grade) were obtained from Kanto Chemicals Tokyo, Japan.

Butyltin compounds extraction

The extraction of organotion from sediments was performed as follows (Ramaswamy, *et al.*, 2000). 0.5 g of freeze-dried sediment contained in a centrifugal tube, a 100 µL of TPrT (50 µg/L) was added as an internal standard. After 10 min, 2 g of NaCl, 12 mL of toluene containing 0.1 % tropolone and 10 mL of 1mol/L HCl methanol were added. The capped tubes were mixed for 60 min after which 10 mL of milli Q water was added and again shaken for a further 10 min and then centrifuged at 2000 rpm for 3 min. The toluene part was concentrated to 5 mL for further analysis. NaBEt4 was applied as derivatization agent for organotin compounds in sediments as follows; 5 mL of 1mol/L acetate buffer of pH 5 was added to the acetone part. Fifteen ml of milli Q water and 1ml of 5% NaBEt4 were added to the extract and shaken for 10 min for ethylation and extraction, then centrifuged. The hexane layer was collected using pesteur pipette from the centrifugal tube and dried by Na_2SO_4. Finally, the extract was concentrated to 100 µL for OTCs analysis. The gas chromatography (GC) used was Hewllett Parckard HP 6890 Series equipped with HP-1 methyl siloxane column (30 m length, 320 µm i.d., 0.25 µm film thickness) with flame photo detector (FPD) fitted with a 610 nm optical filter. The carrier gas was He 2.0 mL/min, in splitless mode and sample of 1 µL was automatically injected to the GC. The temperature of the detector and injector were 240 and 250 °C respectively. Quality control of results was monitored by preparing calibration curves per week and injecting a derivatized standard with all butyltin species every day to test the instrument signal. The method for butyl tin compounds in sediments was validated by analyzing certified reference material obtained from National Meteorological Institute of Japan, CRM 7301 a for butyltins in Marine sediments. Recoveries obtained were as follows; TBT and DBT was 74 % and 106 %, respectively. Detection limits of entire procedure were determined as 3ó of blanks, was 0.3 ng/g for butyl tin compounds in sediment samples.

Sequential extraction procedure for metals

A sequential extraction procedure for heavy metals was performed according to Jozsef, *et al.*, (2004). The metals (Cd, Cu, Ni, Co, Zn, Pb, Mn and Fe) were extracted from 1 gram of freeze dried sediment after division of five fractions as follows;

(i) Exchangeable fraction (F 1) (1M CH3COONH4 at pH 7) (ii) Carbonate bound fraction (F 2) (1 M acetic acid at pH 5), (iii) Reducible fraction (F 3) (1M NH2OH.HCl at pH 2), (iv) Oxidizable fraction (F 4) (30% v/v H_2O_2/ CH3COONH4 at pH 2) (v) Residual fraction (F 5) (HF, HClO4, HNO3).

Each extraction was carried out in three days at room temperature. After each successive extraction, the supernatant was separated by centrifuging the suspension at 4,500 rpm for 30 min. About 2 mL of conc. HNO3 was added and then boiled to near dryness. The residues were dissolved with 0.1N HCl and then diluted to 100 mL with Milli Q water. Heavy metal concentrations of the supernatants from sequential extraction were analyzed by Atomic Absorption Spectrophotometer (AAS Thermo Elemental Solaar 969) equipped with a flame atomizer. The method for total concentration of the heavy metals was validated by analyzing a reference material CRM 7302-a for trace elements in marine sediments obtained from National Meteorological Institute of Japan and the recoveries were between 68-123 % for most metals. The fractionation total concentration was comparable with the total digestion concentration. The detection limits for the metals were as follows; Fe (0.0006), Mn (0.0003), Cu (0.0007), Ni (0.0004), Zn (0.0003) and Co (0.001 mg/kg).

RESULTS

Spatial distribution of BTCs

The contents of butyl tin compound (BTCs) species including MBT, DBT and TBT in sediment samples are summarized in Table 1.

ΣBTCs ranged from 2 to 101000 (22800ng ± 42500, Mean ± SD) Sn/g.dry wt at the Dar es salaam port with the mean concentrations of dry wt. Minimum butyl tin contents were detected at D4 (Salender bridge) and D5 (Oyster Bay) . TBT levels ranged from ND-16700 ng Sn/g.dry wt (5450± 8425 (n=8)) (mean ± SD). The highest TBT values were observed at center of the port D 6 (16700 ng Sn/g and D 7(15900 ng Sn/g. TBT was not detected at Stations D 4 (Salender bridge) and D5 (Oyster Bay).

In Zanzibar port, ΣBTCs contents ranged from 21 to 65300 (28700 ± 2860) ng Sn/g dry wt. The highest concentration of BTCs was recorded at station Z7 (Malindi) inside the port. TBT concentration ranged between ND-3670 ng Sn/g dry wt (1780 ± 1720) (Mean ± SD). The highest concentration of TBT was detected

Table 1: The concentrations of butyltin species in sediments (ng Sn/g dry wt)

Sampling port	Sampling station name	*Date of collection	MBT	DBT	TBT	∑BTs	MBT/∑BTs
Zanzibar	Z 1	40625	96	7190	3670	10900	0.01
Port	Z2	40625	82	10700	3600	14400	0.01
	Z5	40625	1.02	20	ND	21	0.05
	Z7	40626	975	63600	755	65300	0.01
	Z8	40626	976	51300	875	53100	0.02
Mean			424	26500	1780	28700	0.02
± SD			500	28700	1720	2860	0.01
percentage composition			1.4	92.2	6.21		
Dar es Salaalm	D1	40622	39	29	15	80	0.46
Port	D2	40622	32	1	3	40	0.71
	D3	40622	46	30	8	80	0.55
	D4	40622	15	4	ND	20	0.79
	D5	40622	ND	2	ND	2	-
	D6	40622	5900	58900	16700	81500	0.07
	D7	40622	5810	79300	15900	101000	0.06
	D8	40622	17	32	37	80	0.19
Mean			1480	17200	4080	22800	0.4
± SD			2690	32400	7540	42500	0.3
percentage composition			6.4	75.6	17.8		

ND= Not detected
*yy/mounth/day

Table 2: Concentrations of TBT compounds in sediments from various regions of the world

Site	Concentration ng (Sn)/g drywt.	Reference
Suva Habour,Fiji	72200-360 000	Maata and Koshy, 2001
Sado Estuary,Portugal	6-213	Quevauviller, *et al.*, 1988
Hong kong Marina	317, 200	Ko, *et al.*, 1995
Port of Osaka, Japan	2-966	Harino, *et al.*, 1997
Chinhae Bay, Korea	7 - 68.5	Hwang, *et al.*,1999
Portland and Boothbay Harbour USA	24-12400	Page, *et al.*, 1995
Malaysia (1997-1998)	2.8-1100	Sudaryanto, *et al.*, 2004
Suva harbour, Fiji	<5-38,000	Stewart and de Mora,1992
Western Meditterenian	ND-9260	Tolosa, *et al.*, 1992
Vietnam	0.89-34	Midorikawa, *et al.*, 2004
Poole Harbour, UK	8-213	Langston, *et al.*, 1987
Spain	<0.6-140	Gomez Ariza, *et al.*, 2000
Okinawa commercial harbors	10-640	Wang, 2004
Itoman fishing port, Japan	ND-172	Sawano, 2002
Dar es salaam port	ND- 16700	This study
Zanzibar port	ND- 3670	This study

ND = Not detected

at Z 1(3670 ng Sn/g.dry wt). TBT was not detected at Z 5 (Saateni) which located far from Port.

The ratio of MBT / Σ BTCs from Zanzibar and Dar es Salaam port are presented in Table 1. In Zanzibar port sediment samples, the calculated ratio ranged from 0.01 to 0.05 with the mean of 0.02 while Dar es Salaam Ports, ratio were greater than 0.36 except D6, D7 and D8 , that have the ratios less than 0.36.

Total heavy metals

The heavy metals were detected in all sediment samples in Dar es Salaam and Zanzibar port as shown in Table 3.

In Zanzibar port, levels varied in the ranges of Fe (67500 – 12400 mg/kg), Zn (3600 – 339 mg/kg), Mn (812 -537 mg/kg), Pb (1150– 228 mg/kg), Co (111 – 75 mg/kg), Ni (113– 27 mg/kg), Cu (75 – 4 mg/kg) and Cd (20 – 10 mg/kg). The mean metal concentration of Zanzibar samples decreased in the order of Fe > Zn > Mn > Pb > Co > Ni > Cu > Cd. The highest value of most metals analyzed was found at station Z1.

Heavy metal concentrations for the sediments collected from Dar es Salaam port varied in the ranges Fe (43300-7040 mg/kg), Zn (3190-107 mg/kg), Mn (725-277mg/kg), Pb (488-45 mg/kg), Co (76-33 mg/kg), Ni (92-25 mg/kg), Cu (36-N/D mg/kg) and Cd (9-5 mg/kg). The mean concentration of metal of Dar es Salaam samples decreased as Fe > Zn > Mn > Pb > Co > Ni > Cu > Cd. The highest metal contents of Fe, Mn, Pb, and Cu were recorded at D6.

Heavy metal speciation

The percentage composition profiles of heavy metal fractions by sequential extraction from the Zanzibar and Dar es Salaam ports are presented in Fig 3. The mean and fractional concentrations of each element are shown in Table 4. Concentrations for Mn, Ni and Co were low in F1, representing > 10% of the all fractions, Mn being comparatively higher. Iron, Pb, Zn and Cd were almost not detected. In F2 most metals showed significant concentrations, Co and Zn had highest concentration values of greater than 40 % of the total in most of the samples. Nickel and Mn were found in appreciable percentages of 32 % where Fe and Pb were less than 10 % of the total. Lead was a dominant in the F3**,** Other metals like Zn, Cd, Ni, Co, Fe and Mn were also found in this fraction in appreciable percentages. Cu was dominantly associated with F4 about (80 %). F5 was dominated by Fe (57 %). Other metals like Zn, Cu, Ni, Cd, Mn and Pb were found in low percentages.

DISCUSSION AND CONCLUSION

Contamination of BTCs was widely spread in the surveyed ports. The levels of TBT in sediments appeared to reflect the activities performed at those sites in both ports.

The high levels of TBT in Dar es Salaam Port can be attributed to leaching from the hulls of mooring vessels, barges and ferry boats. Stations D6 and D7 are the main and busy stations for ferry boats, Repair works concerning maritime activities, slipway, oil jetty, Tanzania harbors Authority's barges, and is near tankers and commercial cargo stations. Some grounded ships were also found adjacent to the port areas during sampling; these can have an impact on the elevated TBT levels in the marine sediments (Andrew, *et al*., 2002). Poor water exchange may also attributed high levels of TBT; the port is situated in a narrow bay, which is almost protected from flushing by seawater circulation (Machiwa, 1992a). Our results are supported by studies of Midorikawa, *et al*., (2004) and Harino, *et al*., (1997).

In Zanzibar port, the levels of TBT may be associated leaching from passengers and fishing boats, and paint waste from the dockyard. To our understanding, Zanzibar dockyard has no technical means to dispose of the paint waste and probably may be directly disposing in to the coastal areas. Based on the distribution of the TBT around Zanzibar port, we suggest that the Zanzibar dock yard could be the main source of TBT. TBT was not detected at sites far from boating activities such as D4 and D5, and Z5. Therefore, these can be regarded as control stations and showed uncontaminated with TBT compounds. Based on Dowson et al (1993), the ports sediments can be classified as grossly contaminated (above 500 ng/g). The results show that the levels of TBT in the Tanzanian commercial ports are likely pose a threat to marine organisms. It was observed that ~750 ng/g sediment TBT is sufficient to course adverse effects in bioassays with juvenile bivalves (Ruiz, *et al.,* 1994).

TBT degradation process may be explained as a sequential loss of alkyl group from TBT to form non toxic in organic tin. The ratio of MBT / Σ BTCs is used to determine whether the discharge is recent, low ratios (0.03-0.1) indicates TBT has been released recently (Maata and Koshi, 2001). Ratios as low as 0.03, show

TBT "hot spots" (Ko, *et al.*, 1995). The mean ratio observed in Zanzibar port was 0.02, this suggests that the TBT contamination in Zanzibar has occurred recently. Furthermore, the ratios of most stations in Zanzibar port were less than 0.03, implying that those stations are "hot spots" of TBT contamination. All sediment samples from Dar es Salaam port showed the ratio of above 0.03, which imply that no "hot spots" were observed at the port.

Significant difference between the proportions of butyltin compounds were observed among the samples collected from Zanzibar and Dar es Salaam ports. DBT was the most dominant in most samples (Fig. 2). The percentage proportions of MBT in total butyltin were 0.5 to 5% and 0 to 75%, DBT was 65.6 to 97.3% and 22 to 100%, TBT was 0 to 33.5% and 0 to 43% for Zanzibar and Dar es Salaam ports respectively.

The average composition (percentage) of the sediment samples for TBT, DBT and MBT were 22.4 %, 64.2 % and 13.4%, respectively. Our results have differed with studies in other countries such as sediments from the USA coastal areas. TBT, DBT and MBT were 71%, 24% and 6% respectively (Krone, *et al.*, 1996). Sediments from Thailand consisted of TBT (52%), DBT (21%) and MBT (27%) (Kan-Atireklap, *et al.*, 1997). On the other hand, our results are comparable to a study by Gomez-Ariza, *et al.* (1998) in the southwest of Spain. The proportions of DBT+MBT ranged from 34-95%. In

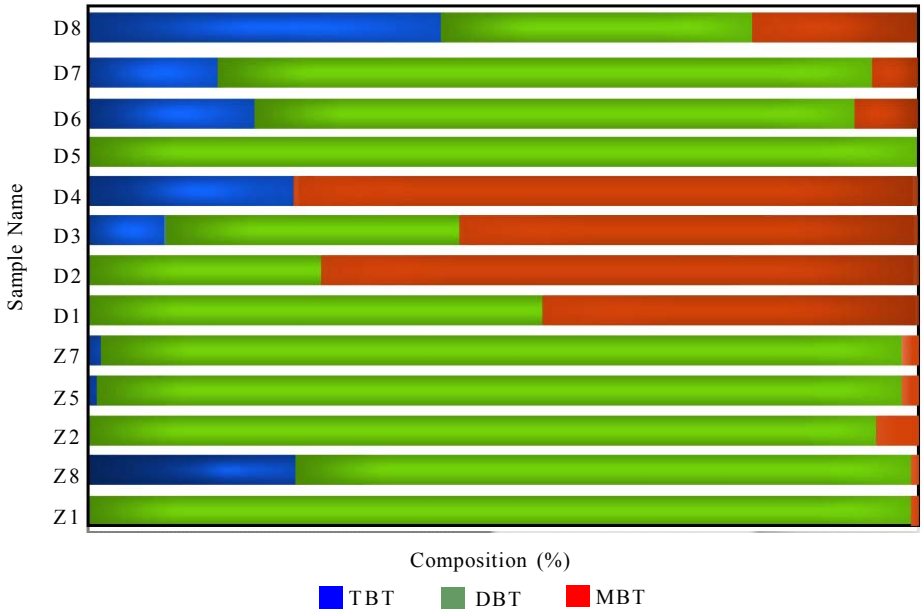

Fig. 2: Proportion composition of butyltin compounds

Table 3: Total metal concentration (mg/kg dry wt) in selected sediment samples

Station	Fe	Zn	Mn	Pb	Co	Ni	Cu	Cd
D6	43300	1260	725	488	48	82	36	6
D7	13300	3190	277	315	33	38	17	6
D8	21200	652	437	205	55	92	1	5
D4	7040	107	372	45	76	25	N.D	9
mean	21210	1300	452	263	53	59.25	18	6.5
± SD	15825	1343	193	186	17	32	17	1.7
Z1	67500	3600	679	1150	75	71	75	20
Z5	12400	339	537	228	99	27	4	10
Z7	44500	2480	812	476	111	113	19	15
mean	41400	2130	676	618	95	70	32	15
± SD	27674	1656	137	477	18	43	37	5

SD= Standard deviation
ND= Not detected

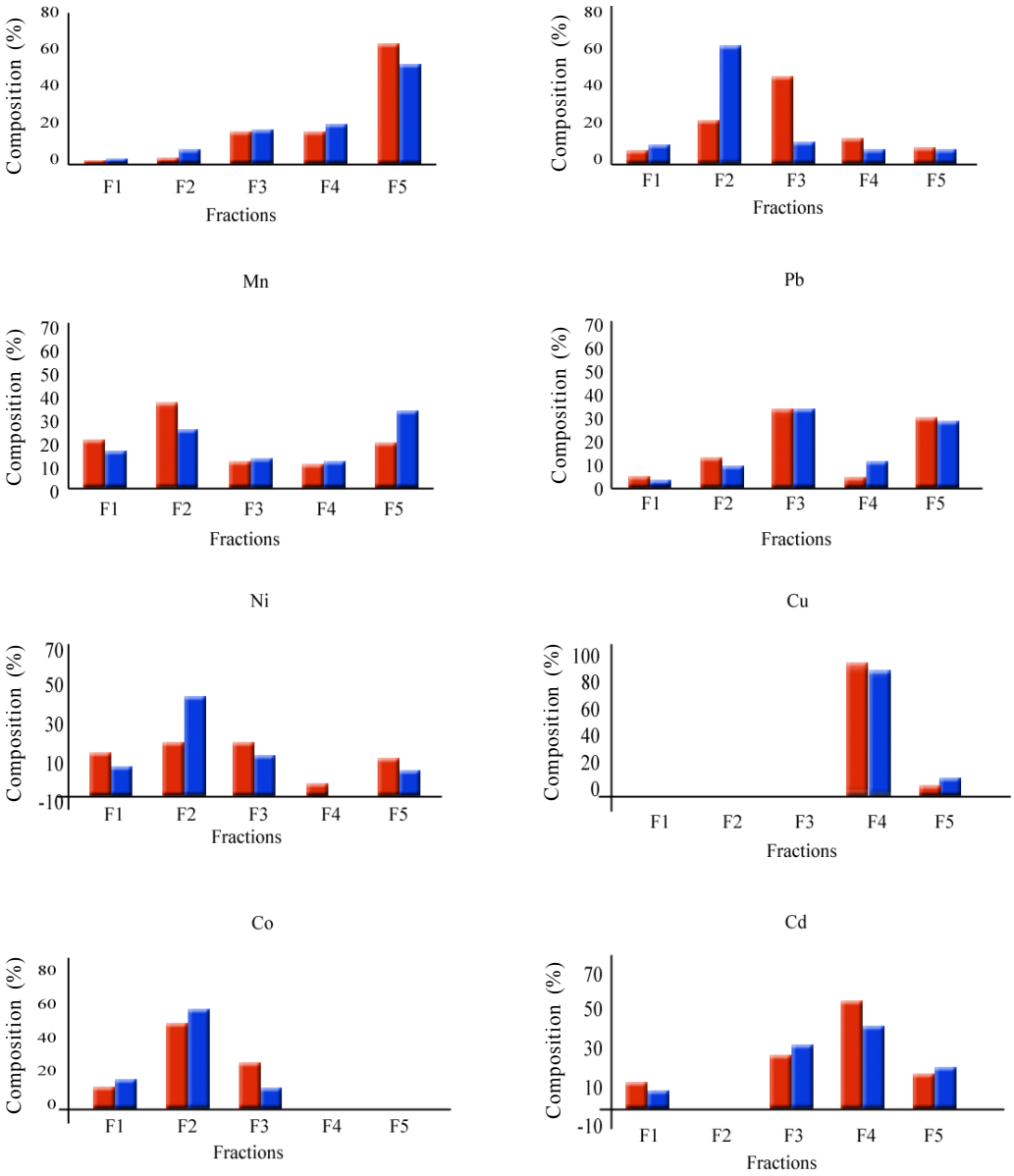

Fig. 3: Profiles of heavy metals composition of in all fractions

addition, Sudarynto, *et al*., (2004) reported percentage proportions in the coastal sediments of Malaysia to be DBT+MBT 58-83% of the total organotin contents. These differences may be caused by the high degradation rate of TBT in coastal waters due to warmer ambient temperature and the intense sunlight in the tropics (Kan-Atireklap, *et al*., 1997, Gomez-Ariza, *et al*. 1998, Quevauville,r *et al*., 1989). This is the most probable reason for higher ratios of MBT and DBT than TBT metabolic compounds in both surveyed ports. Tanzania is a typical tropical country with hot and humid coastal areas. Most parts of the country have a very sunny climate with averaging from seven to ten hours of sunshine a day. The warm ambient water and intense sunlight in the coastal areas could be the main causes of the rapid degradation of TBT to other metabolic compounds (DBT+MBT).

Tabel 4: Concentrations of the metals (mg/kg dry wt) in each fraction

Metal	Sample Code	Exchangeable (F1)	Carbonate (F2)	Reducible (F3)	Oxidizable (F4)	Residual (F5)
Fe	D6	96	375	6890	5190	30600
	D7	124	1020	2700	3080	6240
	D8	171	329	3370	3800	13200
	D4	44	294	1220	2000	3190
	Z1	191	1040	1520	1120	8430
	Z5	191	1040	1520	1120	8430
	Z7	346	1550	6800	11700	24100
Zn	D6	185	415	317	198	147
	D7	91	2860	114	84	17
	D8	161	145	148	69	130
	D4	73	16	ND	6	9
	Z1	97	59	153	10	17
	Z5	97	59	153	10	17
	Z7	236	713	1000	427	103
Mn	D6	131	258	102	96	137
	D7	N.D	141	39	20	77
	D8	136	130	19	63	89
	D4	110	169	44	1	48
	Z1	115	169	118	118	159
	Z5	110	186	45	24	173
	Z7	107	172	80	82	370
Pb	D6	ND	68	219	ND	125
	D7	ND	44	54	33	57
	D8	29	ND	67	ND	73
	D4	N.D	ND	ND	ND	45
	Z1	N.D	ND	622	137	362
	Z5	14	44	41	ND	129
	Z7	16	85	107	113	156
Co	D6	9	21	15	ND	ND
	D7	5	14	14	ND	ND
	D8	0	35	7	ND	ND
	D4	12	37	21	ND	ND
	Z1	12	37	8	ND	ND
	Z5	16	53	10	ND	ND
	Z7	12	53	14	ND	ND
Ni	D6	ND	23	51	8	ND
	D7	2	10	ND	ND	ND
	D8	42	27	9	ND	14
	D4	ND	ND	ND	ND	25
	Z1	ND	56	15	ND	N.D
	Z5	20	ND	ND	ND	7
	Z7	5	28	18	ND	12
Cu	D6	ND	ND	ND	26	5
	D7	ND	ND	ND	11	ND
	D8	ND	ND	ND	ND	ND
	D4	ND	ND	ND	ND	ND
	Z1	ND	ND	ND	66	6
	Z5	ND	ND	ND	ND	ND
	Z7	ND	ND	ND	17	ND
Cd	D6	ND	1	4	1	ND
	D7	ND	2	3	ND	ND
	D8	ND	3	2	ND	ND
	D4	ND	ND	5	3	ND
	Z1	ND	6	9	5	ND
	Z5	ND	5	2	1	ND
	Z7	ND	5	6	3	ND

ND= Not detected

The heavy metals pollution in Zanzibar port is mainly connected with the input of untreated wastewater from Zanzibar municipal, boating activities, and outflow from leather and tanning industries. Mohammed, (2002) reported that untreated wastewater are directly disposed to coastal areas through a sewer network, seepage from pit latrines and septic tanks. Spills of leaded oil probably increase the level of lead in the coastal sediments. Tetraethyl lead gasoline is still used in the East African region (Muohi, *et al*., 2003).

In Dar es Salaam port, sources of heavy metals are probably from industrial waste from city center, and from the rivers Yombo, Kizinga, and Mzinga that pass through industrial and densely populated areas are disposed to the Mzinga Creek and then discharged to the Dar es Salaam harbor areas, heavy traffic of fishing boats and ferries, (Machiwa, 1992a, Sheikh, 1999). The levels of heavy metals detected in both ports are relatively high compared to those reported elsewhere in aquatic systems in East Africa (Mothersill, 1976, Onyari, *et al*., 1985, Kishe, *et al*, 2003, Muohi, *et al*., 2003).

Sequential extraction of heavy metals reveals detailed information on toxicity of the metals in environment and can distinguish different sources of origin (Izquierdo, *et al*, 1997). The sum of metals associated with carbonates and exchangeable ion fractions is extremely important because heavy metals can be easily remobilized by changes of environmental conditions such as pH, and salinity (Izquierdo, *et al*, 1997).

The speciation study shows that the exchangeable and carbonate fractions (F1 and F2) were dominated by Co, Zn, Ni and Mn. These have special affinity for carbonate and may co-precipitate with carbonate minerals (Forstner and Wittmann, 1991). Similar results were found in a previous study (Singh, *et al*., 2005). Lead was dominant in F3 and which has proved to be sensitive to anthropogenic inputs (Modak, *et al*., 1992). Iron and Mn oxide are known to have strong scavenging efficiency and may provide a sink for heavy metals and can thus be said to be good scavengers of Pb. Tokalio?glu, *et al.,* (2000) found a similar results of Pb in significant concentration F3. The high percentage of Cu in F4 is likely to occur as organic complexed metal species. Other metals found in this F4 included Cd, Fe, Zn, Mn, Pb and Ni indicating that the metals occurred in the forms of stable organic complexes and metal sulfides. This is supported by previous studies (Davidson, *et al*., 1994). The high proportion of Fe in F5 in all samples suggests that the source of Fe in all surveyed stations is lithogenic. The remaining metals were mainly detected in F1, F2, F3 and F4, but generally lower in F5, which indicates that they are possibly of anthropogenic origin.

The proportions of metals did not show significant differences between Dar es Salaam and Zanzibar Ports sediment samples, this demonstrate that the heavy metals have common sources in both ports.

A risk assessment code shows that >1% concentrations of the elements in the exchangeable and carbonate (F1and F2) can pose a risk to the environment (Perin, *et al.,* 1985). Our results show that some metals such as Zn, Mn, Co and Ni were detected in relatively high percentages (32 – 51 %) in F1 and F2 in most of the samples from both ports. This may thus pose high risk to the aquatic environment and can easily enter in the food chain (Jain, 2004).

Generally, The results show that the Dar es Salaam and Zanzibar ports are grossly contaminated with TBT. This may thus be a threat to alarm both public and marine ecological health. Rigorous legislative measures are needed to curb the usage of TBT marine paints to protect marine ecosystems and its resources around Tanzanian coasts. The sequential extraction procedure proved that except Fe, the remaining metals (Cd, Cu, Ni, Co, Zn, Pb, and Mn) were introduced in the major ports from anthropogenic sources and may be likely remobilized upon changing environmental conditions. This preliminary information highlight the importance of further works on OTCs in understanding the geochemistry of organotin compounds and heavy metals in aquatic systems in Tanzania.

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