HEAVY METALS AND ORGANIC POLLUTANTS IN SEDIMENTS OF DAR ES SALAAM HARBOUR PRIOR TO DREDGING IN 1999

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ABSTRACT

Heavy metals and organic contaminants were analysed in the sediments of the inner area of the Dar es Salaam harbour. Complementary analytical parameters, such as, the organic carbon content and the silt/clay fraction of the sediments showed good positive correlation (r = 0.64). Stations that had high content of fine grain material in the sediment also indicated relatively high level of organic carbon and pollutants. The Florida criteria *(MacDonald 1993) for assessment of pollution of tropical marine sediments was adopted in oredr to evaluate the extent of pollution in Dar es Salaam harbour sediments. The* Florida criteria *is one of the established references for sediment quality assessment. Heavy metals that had concentrations above the* Florida no effect level *were chromium, copper, lead, mercury and zinc. Mercury exceeded the* Florida no effect level *(0.1 $mgkg^{-1}$) at 18 of 22 sampling stations, but the* Florida probable effect level *(1.4 $mgkg^{-1}$) was not closely reached at any station. Lead and chromium exceeded the* Florida no effect level *(21 $mgkg^{-1}$ and 33 $mgkg^{-1}$ respectively) at 15 stations. Copper and zinc exceeded the* Florida no effect level *(28 $mgkg^{-1}$ and 68 $mgkg^{-1}$ respectively) at 12 and 16 stations respectively. Levels of pollutants in the study area were generally lower than in the sediments of some major harbours of the world.*

INTRODUCTION

Tanzania coastal environment is a narrow strip extending between latitudes 5^{o} and 10^{o} S, about 800 km. The biotic coastal environment is characterised by coral reefs, macro and microalgae, seagrass meadows, mangrove forests and the associated fauna. Dar es Salaam city has one of the largest harbours and is the biggest commercial centre along the eastern Africa coast. The coastal strip

of Dar es Salaam is interrupted by a number of streams, most of which also drain residential and industrial locations of the city. The inner harbour is a deep, narrow, sheltered inlet. Therefore, tidal flushing is limited, causing long residence time of water, resulting into accumulation of contaminants in the sediment. The area is under the influence of several sources of contaminants. Point source discharges include the TIPER crude oil refinery, storm and sewage out-falls and fresh water tributaries such as Msimbazi, Mzinga and Gerezani creeks. Non-point source discharges include accidental and deliberate oil spills, ship and boat waste discharges as well as runoff from the city. The outer harbour is affected by sewage discharges, storm water runoff and possible oil leakage from the Single Buoy Mooring. Dar es Salaam harbour is a partially enclosed lagoon with a narrow entrance channel. Main biotopes of concern adjacent to the harbour are mangrove wetlands, coral reefs and seagrass meadows. Artisanal fishing is conducted in the inner harbour, particularly near the mangroves of the southern creek. During 1999 substantial amounts of sediments were dredged from the port and transferred to the outer harbour dump. Consequently, concentration of heavy metals and organic pollutants in the port sediment in 2000 should be lower than those of 1993 which are reported in this study.

Levels of toxic metals and organic pollutants in the sediments of Dar es Salaam harbour prior to the 1999 dredging are presented. Organic pollutants include base-neutral extractables (phthalates), polyaromatic hydrocarbons (PAH), chlorinated hydrocarbons, polychlorinated biphenyls (PCBs), and organochloride pesticides. Concentrations of pollutants in the sediment are compared with the *Florida criteria* for assessment of sediment quality (MacDonald 1993), in a tropical coastal environment. However, accurate prediction of the effects of toxic substances on ecosystem structure and function is difficult (O'Neill *et al.* 1982). This data will serve as a benchmark that will be used in future (year 2000 onwards) comparative studies to determine whether there is a decrease or increase of discharge of pollutants in the coastal waters off the city of Dar es Salaam.

MATERIALS AND METHODS

Duplicate sediment cores (6 cm diameter) were retrieved from the inner harbour by frogmen aboard a boat in 1993. Sampling stations (Fig. 1) were selected in accordance with possible routes of contaminants. Pre-selection of sites was necessary in order to determine the sources and to assess the level of accumulation of pollutants. Topmost and the lowermost 5 cm sections of the cores were retained for moisture content, grain size, metals and organic carbon determination. Length of cores varied with type of substrate. Surface sediment sub-samples were also used for analysis of organic pollutants. Sediment samples were kept at 5°C until analysis. Glass sample containers were

prepared in a manner suitable for collection and analysis of all parameters of interest. All sample containers were constructed of silicate glass fitted with teflon lined lids. The silicate containers were acid washed, solvent rinsed and baked dry at 250°C. Heavy metals and organic pollutants analyses were carried out in Canada by ASL Analytical Service Laboratories Ltd. (EVS ref. No. 3/377-03). Sediment extractions for heavy metals and organic pollutants were carried out in accordance with (Anon. 1992). An extensive quality assurance/quality control programme was conducted during analysis. Procedure included the analysis of quality control samples to define precision and accuracy. Analysis was also performed to demonstrate contamination control for the sediment samples and for the various types of parameters that were investigated. Quality control samples that were analysed included method blanks, sample replicates, certified and standard reference materials, analyte spikes and surrogate spikes.

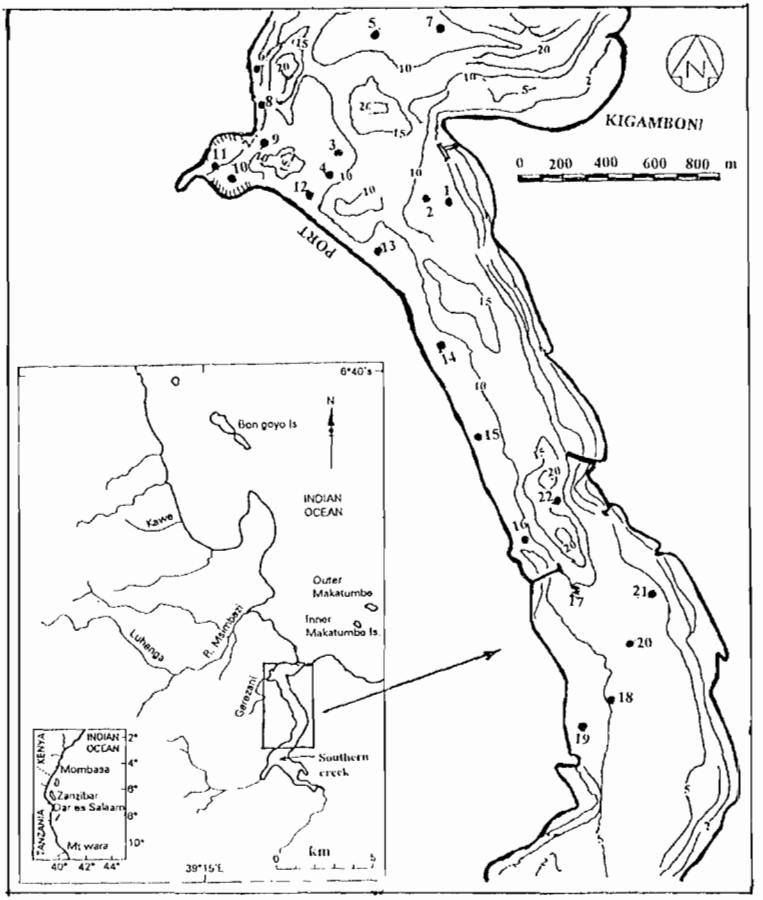

Fig. 1: Map of Dar es Salaam inner harbour showing sampling stations (Bathymetry adopted from British Admiralty Charts 693 and 674 and US Corp. of Engineers series Y941 Dar es Salaam south, Edition 3-AMS)

Determination of moisture, organic carbon and grain size content
Sediment samples for determination of moisture content were dried to constant weight at 103°C. Moisture content was determined gravimetrically. Sediment sub-samples for organic carbon analyses were freeze-dried, finely ground and homogenised. Organic carbon was determined by Gaudette *et al.* (1974) titrimetric method. Sediment samples (0.2 – 0.5 g) were oxidised with Cr (IV) in a highly exothermic reaction followed by addition of concentrated H_2SO_4. Amount of the reduced dichromate was estimated by titration of the excess chromium (IV) with ammonium iron (II) sulphate.

Samples for grain size analyses were wet sieved on sieves of sizes 2000 µm, 500 µm and µm. Particles of the three grain size fractions were then oven dried to constant weight. The molten which was less than 63 m materials (fine grain fraction) consisted of clay and silt particles, the grain size fraction between 63 µm and 500 µm (medium grain fraction) consisted of fine to medium sand particles and the grain size fraction between 500 µm and 2000 µm (coarse grain fraction) consisted of medium to coarse sand particles.

Analysis of heavy metal and organic pollutants
Sediment samples for metal and organic pollutants analyses were freeze-dried, finely ground and homogenised. Sub-samples of the dried sediment were digested using Aqua Regia (Jacobs & Keeney 1974). Supernatant solution was bulked to volume with deionised-distilled water. Analysis was performed on Atomic Absorption Spectrophotometer (Spectra AA 20).

All glassware used for organic pollutant analyses were rinsed prior to analysis with acetone followed by hexane and then methylene chloride. Aliquot of 10 to 20 g dry weight of sediment sample was Soxhelet extracted for 48 hours and concentrated on a Kuderna Danish evaporating apparatus to about 1 ml. Total phthalates in the sediment were determined by extraction with acetonitrile. The extract was then solvent exchanged to hexane followed by an alumina column clean-up. The final extract was analysed by dual capillary column gas chromatography with electron capture detection. Polynuclear aromatic hydrocarbons were analysed using a procedure involving a triple solvent with dichloromethane. Silicagel column chromatography was used for clean-up of final extract. This clean-up procedure effectively removed aliphatic and heterocyclic hydrocarbons which could potentially interfere with the analysis. The final extract was analysed by capillary column gas chromatography with mass spectrometric detection.

Polychlorinated biphenyls analyses of sediments followed the method of Brownawell and Farrington (1986). Sediment samples for organochloride and PCBs determination were solvent extracted using acetonitrile. The extract was solvent exchanged to hexane followed by an alumina column cleanup. The

final extract was analysed by a high resolution dual capillary column gas chromatography (Hewlett-Packard 5840) with electron capture detection.

RESULTS

Grain size composition and moisture content

Grain size analysis showed that, generally surface samples contained a high proportion of fine grain material, presumably silt and clay fraction (< 63 μm) compared with bottom sediment (Table 1). Surface sediment samples from the mouth of the channel (stations 5, 6, 7, and 8) had a relatively low proportion of fine grain material (between 31% and 59%) compared with samples that were collected adjacent to the southern creek (stations 17, 18, 19, 20 and 21). The fine grain material in the sediment at stations that were close to the southern creek ranged between 93% and 99%. The southern creek area receives discharges from rivers Mzinga and Mtoni. The central part of the channel (stations 1, 2, 3, 4, 9, 10, 11, 12, 13, 14 and 15) was composed of mixed grain sizes (clay/silt/fine sand/ medium sand and coarse sand). Fine grain materials content ranged between 3% and 91% in surface sediment of the central inner harbour area.

Moisture content of the samples varied between 18.4% and 80.5% (Table 1). The surface sediment samples that had a high content of fine grains also had a correspondingly high amount of moisture.

Table 1: Mean (±S.D.) of moisture content (%), organic carbon concentration (%) and grain size distribution (%) in the surface (0 – 2.5 cm) and bottom (between 25 and 50 cm) sediment samples at the Dar es Salaam harbour, Tanzania, 1993

	Surface sediment	Bottom sediment
Moisture content	56.7 ± 18.9	ND
Organic carbon	1.78 ± 0.86	1.31 ±1.17
< 63 μm grain size	57 ± 34	40 ± 34
63 – 500 μm grain size	26 ±19	35 ± 23
> 500 μm grain size	18 ± 26	25 ± 27

ND = not determined

Organic carbon content

Concentration of organic carbon in the port entrance channel was generally low, as expected of areas with high amount of coarse grain composition of the sediment. Surface sediment samples had high amount of organic carbon than bottom sediment samples (Table 1). Generally the organic carbon concentration co-varied positively (r = 0.64) with the fine grains content of the

surface sediment (Figure 2). Stations that had high organic carbon content (> 1.5%) in the surface sediment were 2, 5, 6, 7, 8, 10, 12, 14, 15, 16,17, 18, 19, 20, 21 and 22. Samples that were collected close to the southern creek had relatively high concentration of organic carbon. Bottom (21 – 24 cm) sediment samples from station 11 had highest amount of organic carbon (4.71%) despite their having low amount of fine grain material (46.9%). This discrepancy was due to presence of oil-like organic constituents in this sample. There was an inverse relationship between organic carbon concentration and the coarse grains fraction (r = - 0.59) as well as the medium grains fraction (r = - 0.30) of the sediment.

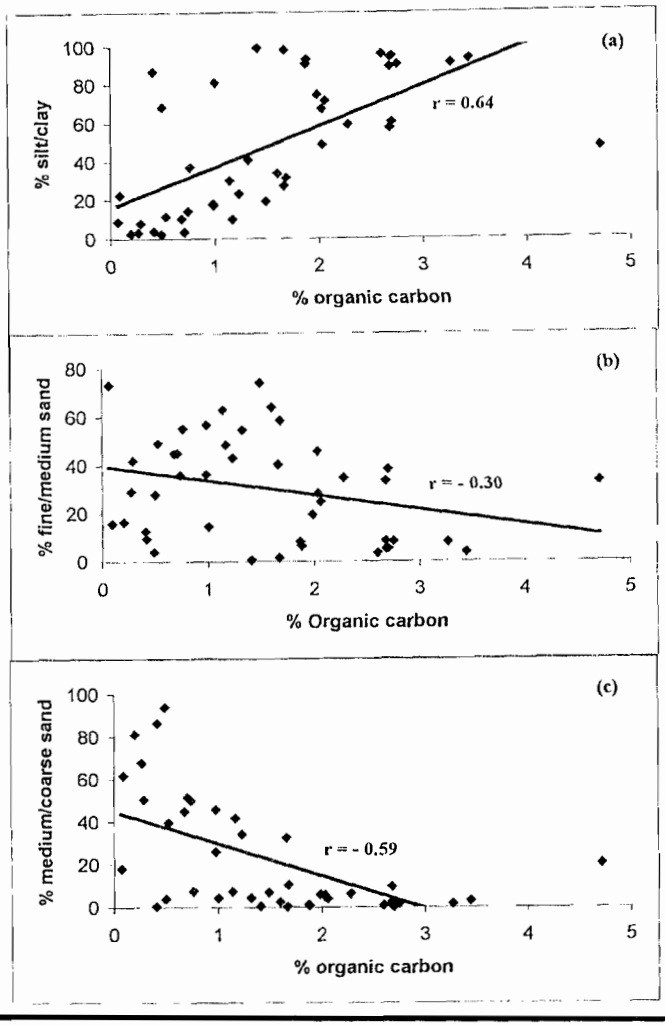

Fig. 2: Plots of organic concentration vs grain size content of the sediment (a) Silt and Clay fraction (< 63 μm); (b) fine to medium sand fraction (63 μm-500 μm; (c) medium sand to coarse fraction (500 μm-2000 μm)

Heavy metals

Of the common heavy metals (As, Cd, Cu, Pb, Hg, Ni, Ag and Zn), only Pb, Zn, Cr and Hg had elevated levels at some stations (Table 2). Pb was highest (1061±944 $mgkg^{-1}$) in the bottom sediment (37 – 42 cm) at station 20 which is close to the southern creek. Apparently, station 20 also had the highest amount of fine grain material in the sediment, ranging between 89% and 99% from the surface to 44 cm below the surface. High Pb concentration (123 $mgkg^{-1}$) in the surface sediment was found at station 10, which had 91% fine grain material. Similar co-variation of lead concentration with clay content of the sediment has been reported by Scrudato and Estes (1975). The *Florida no effect level* (MacDonald 1993) for Pb (21 $mgkg^{-1}$) was exceeded in the surface sediments of station nos. 1, 2, 3, 5, 6, 8, 10, 14, 15, 16, 17, 18, 19, 20 and 21 (see Appendix I). In the bottom sediment (37 – 42 cm) of station no. 20, Pb concentration (1061±944 $mgkg^{-1}$) exceeded the *Florida probable effect level* (160 $mgkg^{-1}$).

Table 2: Mean (±S.D.) of heavy metal concentration in bulk sediment from Dar es Salaam harbour, Tanzania for the surface (0 – 2.5 cm) and bottom (between 25 and 50 cm) samples. Other values are for the surface sediment in New York harbour (Feng *et al.* 1998), Mombasa coastal area (Oteko 1989) and Townsville harbour (Reichelt and Jones 1994). Flor. Neff =Florida no effect level and Flor. Peff. = *Florida probable effect level*, all values are in $mgkg^{-1}$. 1993

	Surface sediment	Bottom sediment	Flor. Neff.	Flor. peff	New York Harbour	Mombasa Area	T'ville Harb.
As	5.26±2.46	6.41±3.87	8	64	-	-	-
Cd	0.12±0.09	0.10±0.02	1	7.5	0.5–2.0	0.05-0.2	-
Cr	42.8±23.0	26.9±21.9	33	240	-	-	-
Co	6.6±3.3	3.6±2.5	-	-	-	-	-
Cu	28.9±17.3	14.6±12.1	28	170	40-150	22-84	30-70
Pb	36.1±24.3	220.8±555.3	21	160	50-190	18-43	<5-53
Hg	0.301±0.141	0.309(0.228	0.1	1.4	-	-	-
Ni	14.7±7.8	9.6±7.9	-	-	-	-	60-139
Se	<50	<50	-	-	-	--	-
Ag	<2.0	<2.0	0.5	2.5	1.0–6.5	-	-
Sn	<30	<30	-	-	-	-	-
V	34.8±20.7	20.8±18.5	-	-	-	-	-
Zn	109.1±58.8	48.5±43.5	68	300	100-250	56-311	160-460

Highest concentration of zinc (288 $mgkg^{-1}$) was detected in the surface sediment of station 10, where the concentration of Zn approached the *Florida probable effect* criterion (300 $mgkg^{-1}$). Sediments with pollutant level above

the *probable effect* is considered not safe for marine life. All other stations with the exception of stations 4, 9, 11, 12, 13 and 22 had high Zn concentration in the surface sediment above the *Florida no effect level.*

Mercury concentration in surface sediment ranged between 0.015 and 0.561 $mgkg^{-1}$) it did not exceed the *Florida no effect level* (0.1 $mgkg^{-1}$) only at stations 4, 9, 11 and 12 (see Appendix I). However, the probable effect criterion (1.4 $mgkg^{-1}$) was not closely approached. In the surface sediment highest concentration of Hg (0.6 $mgkg^{-1}$) was detected at station no. 2. In the subsurface sediment, highest concentration of Hg (0.7 $mgkg^{-1}$) was detected at station 1 in the 49 – 59 cm depth zone. The concentration of Hg was 0.6 $mgkg^{-1}$ at station 19 between 43 and 48 cm in the sediment. At station 21 the concentration of mercury was 0.5 $mgkg^{-1}$ at 36 – 41 cm in the sediment. In subsurface samples, Hg concentration ranged between 0.012 and 0.746 $mgkg^{-1}$, it exceeded the *Florida no effect level* in all but station no. 9, but the *probable effect concentration* was not exceeded at all (Table 2).

The concentration of chromium was below the *Florida no effect level* (33 $mgkg^{-1}$) only at stations 4, 8, 9, 11, 13 and 22. Highest concentration of Cr (75.5 $mgkg^{-1}$) was detected in the surface sediment of station 19 (Appendix I).

The *Florida no effect criterion* for copper (28 $mgkg^{-1}$) was exceeded at stations 1, 6, 8, 10, 14, 15, 16, 17, 18, 19, 20 and 21. Highest concentration of Cu (78.2 $mgkg^{-1}$) was detected in the surface sediment of station 10, which also contained elevated levels of Pb and Zn. This station receives waste material from municipal discharges via Gerezani creek, the storm-water outfall at the port and effluents from the dock. The concentration of other heavy metals (e.g. Cd, As, Co, Ni, and V) was low, generally below the *Florida no effect criteria.* The concentration of Se, Ag and Sn was below the limit of detection of the instrument (Table 2).

Organic pollutants

Polyaromatic hydrocarbon criteria screening values for one out of a possible total of 16 PAH (Benzo (b) fluoranthene) was slightly exceeded at five stations, 1, 2, 6, 11 and 14. The high concentrations were not considered to be biologically significant as they were well below the criteria of rejection (*Florida Probable effect,* Table 3, Appendix I).

Table 3: Mean ± S.D. of concentrations ($mgkg^{-1}$) of petroleum hydrocarbons in the bulk surface sediment (0 –5 cm) samples (n = 22) at the Dar es Salaam harbour, Tanzania. 1993

	Concentration in sediment	*Florida No effect*	*Florida Probable effect*
Base – neutral extractable compounds			
Benzyl butyl phthalate	0.106±0.096	-	-
Bis (2-ethylhexyl) phthalate	0.277±0.167	-	-
Di-n-butyl phthalate	1.309±0.674	-	-
Di-n-octyl phthalate	< 0.020	-	-
Diethyl phthalate	< 0.5	-	-
Dimethyl phthalate	< 0.5	-	-
Polyaromatic Hydrocarbons			
Acenaphthene	< 0.020	0.022	0.45
Acenaphthylene	< 0.020	-	-
Anthracene	0.020±0.001	0.085	0.74
Benzo (a) anthracene	0.046±0.035	0.16	1.3
Benzo (a) pyrene	0.061±0.056	0.23	1.7
Benzo (b) fluoranthene	0.085±0.077	-	-
Benzo (ghi) perylene	0.055±0.046	-	-
Benzo (k) fluoranthene	0.036±0.026	-	-
Chrysene	0.039±0.029	0.22	1.7
Dibenzo (a,h) anthracene	0.022±0.007	0.31	0.32
Fluoranthene	0.064±0.055	0.38	3.2
Fluorene	0.021±0.003	0.018	0.46
Indeno (1,2,3-cd) pyrene	0.054±0.044	-	-
Naphthalene	0.021±0.003	0.13	1.1
Phenanthrene	0.038±0.033	0.14	1.2
Pyrene	0.067±0.054	0.29	1.9

Polychlorinated biphenyls were below detection limit except at station 21, where PCB 1254 was just above the detection limit (Table 4). This station was adjacent to an oil refinery plant (TIPER), but no wastewater outfall from the plant was located. Other polychlorinated hydrocarbons (e.g. Hexachlorobenzene, Hexachlorobutadiene, Hexachlorocyclopentadiene, Hexachloroethane and 1,2,4-Trichlorobenzene) were not detected at the stations in the surface sediments, suggesting that there was no source of these pollutants to the harbour.

Table 4: Levels (mean ± S.D) of chlorinated hydrocarbons and polychlorinated biphenyls ($mgkg^{-1}$) in the surface sediment (0 – 5 cm) samples (n = 22). Dar es Salaam harbour, Tanzania. 1993

Pollutant	Concentration in sediment	*Florida No effect*	*Florida Probable effect*
Chlorinated hydrocarbons			
Hexachlorobenzene	< 0.010	-	-
Hexachlorobutadiene	< 0.010	-	-
Hexachlorocyclopentadiene	< 0.010	-	-
Hexachloroethane	< 0.010	-	-
1,2,4 – Trichlorobenzene	<0.010	-	-
Polychlorinated Biphenyls			
PCB 1242	< 0.050	-	-
PCB 1248	< 0.050	-	-
PCB 1254	< 0.050	-	-
PCB 1260	0.053(0.015	-	-
Total PCBs	0.055±0.016	0.024	0.26

Organochloride pesticides were analysed in all of the surface sediment samples. Only 4, 4' – DDT and its derivatives (4, 4'-DDD and 4, 4'- DDE) were consistently detected (e.g. stations 1, 2, 3, 6, 10, 11, 13, 14, 15, 16, 17, 18 and 19). These pesticides were used for mosquito control and for crop protection. The concentrations were below *Florida probable effect criteria* throughout the harbour (Table 5). The DDT concentration reach levels of concern (0.24 $mgkg^{-1}$) at station 11.

Table 5: Levels (mean ± S.D) of concentration ($mgkg^{-1}$) of organochloride pesticides in the surface sediment (0 – 5 cm) samples (n = 22). Dar es Salaam harbour. 1993

Pollutant	Concentration in sediment	*Florida No effect*	*Florida Probable effect*
Aldrin	< 0.001	-	-
alpha – BHC	< 0.001	-	-
beta – BHC	< 0.002	-	-
gamma – BHC (Lindane)	< 0.001	-	-
delta – BHC	< 0.001	-	-

Table 5 (Continued)

Pollutant	Concentration in sediment	*Florida No effect*	*Florida Probable effect*
cis – Chlordane (alpha)	< 0.001	-	-
4,4'- DDD	0.010(0.023	-	-
4,4'- DDE	0.010(0.027	0.0017	0.13
4,4'- DDT	0.014(0.049	0.0045	0.27
Dieldrin	0.002(0.002	-	-
Endosulfan I	0.002(0.003	-	-
Endosulfan II	0.001(0.0003	-	-
Endosulfan sulphate	< 0.005	-	-
Endrin	< 0.005	-	-
Heptachlor	< 0.002	-	-
Heptachlor Epoxide	< 0.001	-	-
Methoxychlor	< 0.005	-	-
Toxaphene	< 0.030	-	-

DISCUSSION

Pollution of the Dar es Salaam Port is mainly a result of settling of suspended particulate matter in this relatively calm, poorly flushed lagoon. The significance of grain size in partitioning of chemical pollutants in sediments is well documented in the literature (Warren & Zimmerman 1994, Tessier *et al.* 1996). For instance, Cu and Zn are associated with the organic coatings especially of the fine mineral grains. As, V, Ni, Cr and Cd are associated with Iron and Manganese hydroxyoxides coatings especially of clay and silt particles. Lead is associated with the clay minerals both as an adsorbate and a structural element. These associations suggest that sandy sediments are unlikely to contain high concentrations of pollutants compared with fine sediments.

Sampling stations were grouped in order to assess the influence of organic matter and grain size in the areal distribution of pollutants in the surface sediment. Stations 1, 2, 3, 4, 12 and 13 (PA) included the Port area at the dock, stations 6, 8, 9, 10 and 11 (NPA) were in the northern part of the port which includes Gerezani creek and at the dock for fishing boats, ferry boats and merchant dhows and stations 5 and 7 (FA) were at the extreme northern area at the Kigamboni ferry route. Stations 14, 15, 16 and 22 (SPA) were south of the port, stations 17, 20 and 22 (KOJ) were adjacent to Kurasini oil jetty and TIPER areas and stations 18 and 19 (ASC) were at the extreme southern part adjacent to the southern creek area. Generally, the concentration of heavy metals in the surface sediment related with organic carbon and fine grains content of the sediment (Fig. 3). However, metal concentration at the port (PA station group) were high relative to the organic carbon and fine grains content of the sediment suggesting anthropogenic inputs. Possible sources of heavy metals, apart from the port activities of shipping and boating

as well as ship and boat servicing and repairs, included storm water runoff and storm water outfall. With the exception of Zn, concentration of heavy metals in the sediments of Dar es Salaam inner harbour were substantially less than those of New York harbour (Table 2). However, the mean concentration of Zn (109 ± 58.8 mgkg^{-1}), the highly enriched element in the surface sediment was within the concentration ranges 100 to 250 mgkg^{-1} and 56 to 311 mgkg^{-1} of New York harbour (Feng *et al.* 1998) and Mombasa coastal sediments (Oteko 1989) respectively. Zinc concentration in the port sediment was considerably lower than in Townsville harbour sediment in Northern Australia (Reichelt & Jones 1994), where the concentration ranged between 160 and 460 mgkg^{-1} (Table 2).

Chromium concentration was elevated second to Zn in the inner harbour (Fig. 3), however, Cr concentration was also far below the *Florida probable effect level* (Table 2). The distribution of Cr in the harbour was related with the fine grain content of the sediment, it is more likely that the local geology was the source.

Lead, (36.1 ± 24.3 mgkg^{-1}) was the third most available element in the surface sediment of the harbour, its concentration was within the concentration ranges found in New York and Townsville harbours as well as in Mombasa coastal sediments (Table 2). The extremely high concentration of Pb in the bottom sediments of station 20 was possibly due to a non-point source, such as deliberate or accidental disposal of lead containing wastes in the area.

Mercury Hg was detected throughout the sediments of the inner harbour, which suggested a natural source (e.g. the local geology). However, Hg concentration near the dock (station group PA) was high relative to the organic carbon and fine grains content of the sediment, suggesting the possibility of a second source within the city (e.g. battery factory) or spillage at the dock. Since mercury can be bioaccumulated, this contaminant is of concern whenever it is detected.

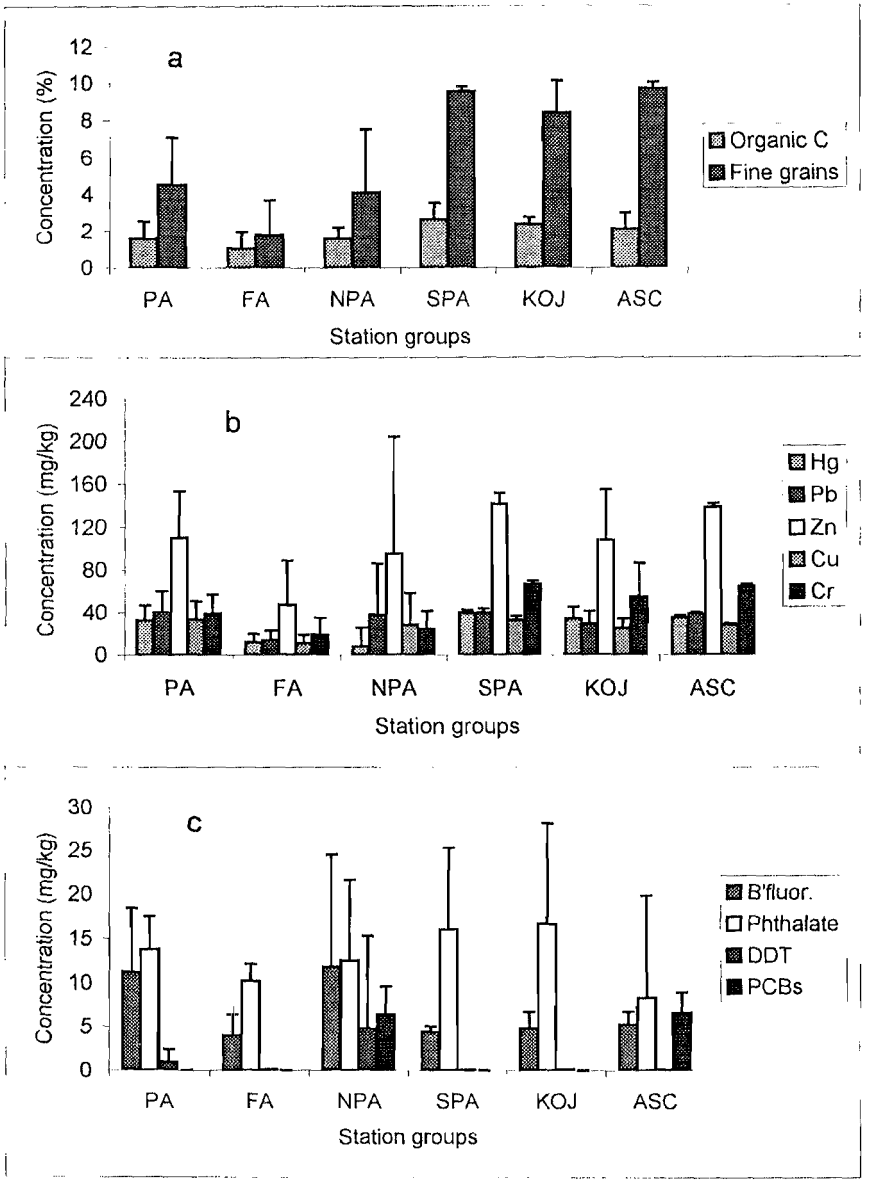

Fig. 3: Comparison of pollutants between groups of stations in relation with the (a) organic carbon (%) and fine grains (% x 10) content of the sediment: PA = stations 1, 2, 3, 4, 12, and 13; NPA = stations 6, 8, 9, 10, and 11; SPA = stations 14, 15, 16, and 22; FA = stations 5, and 7; KOJ = station 17, 20 and 21;and ASC = stations 18 and 19. (b) Heavy metal concentration ($mgkg^{-1}$), except Hg = $mgkg^{-1} \times 10^{-2}$. (c) Concentration of organic pollutants, Di-n-butyl phthalate = $mgkg^{-1} \times 10^{-1}$, Benzo (b) fluoranthene, DDT and PCBs = $mgkg^{-1} \times 10^{-2}$. Dar es Salaam harhour. 1993.

Previous report on sediment sampling and metal analyses for the port of Dar es Salaam (Machiwa 1992) showed that there was no trend of metal contamination with depth in the sediment, suggesting that the sources of metals were not consistent, their fluxes vary with time. For instance, the highest concentration of Cu, Cd, Zn, Cr and Pb at each station were not found at a similar depth, suggesting either presence of excessive bioturbation or absence of diagenetic remobilisation.

Surface sediments of Dar es Salaam harbour in general contained low concentration of heavy metals relative to New York harbour study (Table 2). The extraction techniques for the sediments from the two areas, however, were slightly different. Aqua Regia method used for this study, removed the geochemically available metal fraction, whereas HNO_3-$HClO_4$-HF in a three-step digestion process used by Feng *et al.* (1998) for the New York harbour, was a total digestion method.

Generally, the concentration of organic chemical pollutants was low in surface sediment samples. Concentration of polyaromatic hydrocarbons (Table 3) are of particular interest because they are a constituent of oil and petroleum products that were handled in the port. Detectable amounts of petroleum hydrocarbons (Benzo (b) fluoranthene and Di-n-butyl phthalate) were consistently found throughout the inner harbour and were not related with organic carbon and fine grains content of the sediment (Fig. 3), which suggests that port activities were the main source. The presence of an oil refinery plant (TIPER) in the vicinity of the station group KOJ appeared not to be a point source. Generally, the concentration of petroleum hydrocarbons in the port area was below the *Florida probable effect level* (Table 3).

The concentration of polychlorinated hydrocarbons other than the PCBs was below the limit of detection (0.01 $mgkg^{-1}$) throughout the inner harbour sediments. PCBs were detected in the sediments at stations NPA and ASC (Fig. 3). The concentration of PCBs was not related with the organic carbon and fine grains content of the sediment. Possible source of PCBs (PCB 1260) was either non point or a point source; e.g. a point source would include Gerezani creek north of the port and Mtoni stream at the extreme south of the port. Comparison of data from Feng *et al.* (1998) showed that the concentration of total PCBs in New York harbour sediments (0.3 – 1.3 $mgkg^{-1}$), was higher than that in Dar es Salaam harbour. Generally, the level of PCBs was about an order of magnitude lower than the *Florida probable effect level (*Table 4).

Results on total PCBs and petroleum hydrocarbons are in disagreement with the findings of Machiwa (1992), which showed high concentration (70 $mgkg^{-1}$ and 164 $mgkg^{-1}$ respectively) in the port sediments. Probable cause of differences between the two sets of results include laboratory or

instrumentation errors, or it could be that there was just a small hot spot of sediment contamination which was missed by the present sampling protocol.

With the exception of DDT and its metabolites as well as Dieldrin and Endosulphan I and II, concentration of organochlorine pesticides were generally below the limit of detection (Table 5). Figure 3 shows that 4, 4'-DDT was detected only at the port (PA station group) and north of the port (NPA station group). Insecticides were intensively used in residential areas of Dar es Salaam between late 1980s and early 1990s in an anti-malarial campaign. The occurrence of DDT in the port sediments was probably due to the surface runoff from the city or presence of a storm-water outfall. The sediment from a station group north of the port (NPA) contained all types of organic pollutants (Fig. 3), which suggests that port activities, storm water outfall and the Gerezani creek were the most likely sources of pollutants in the harbour.

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Appendix 1: Status of sampling stations with regard to heavy metal pollution, according to the *Florida criteria*

Heavy Metal	*Florida no effect level*(FEL)		*Florida probable effect level*	
	Stations with Lower Than (FEL)	Stations with Higher Than (FEL)	Stations with Approched (FEL)	Stations with Exceeded (FEL)
As	1-22	-	-	-
Cd	1-22	-	-	-
Cr	4,8,9,11,13,22	1,3,5,7,10,12,14-21	-	-
Cu	2-5,7,9,11,12,13,22	1,6,8,10,14-21	-	-
Pb	4,7,9,11,12,13,22	1,2,3,5,6,8,14-21	10	20
Hg	4,9,11,12	1,2,3,5-8,10,13-22	-	-
Ag	1-22	-	-	-
Zn	4,9,11,12,13,22	1,2,3,5-8,10,14-21	10	-