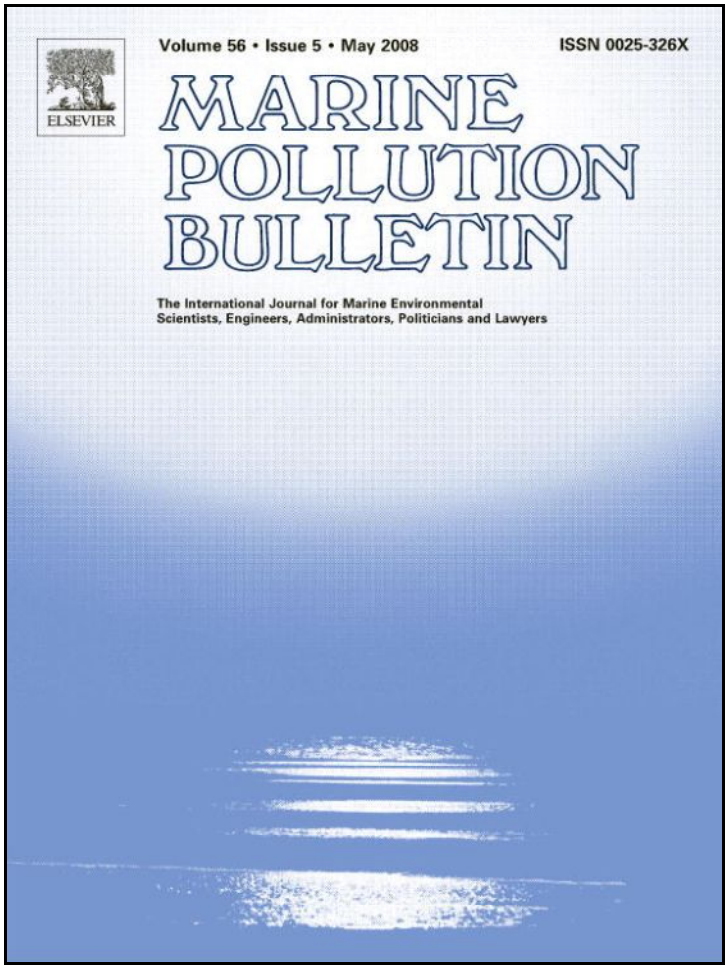
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Baseline

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The objective of BASELINE is to publish short communications on different aspects of pollution of the marine environment. Only those papers which clearly identify the quality of the data will be considered for publication. Contributors to Baseline should refer to 'Baseline—The New Format and Content' (*Mar. Pollut. Bull.* **42**, 703–704).

Status of pollution in mangrove ecosystems along the coast of Tanzania

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Worldwide, mangrove forests are under threat of the accumulation of pollutants, which may be imported into mangrove ecosystems through the waters from rivers and streams. The distribution, behaviour, and accumulation of these imported chemicals in the ecosystem are largely defined by the hydrology of the mangroves, the geochemical properties of sediments, and the class of pollutants (e.g. heavy metals, organotins, organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs)). The properties of the mangrove sediments provide good binding opportunities for a number of these pollutants: hydrophobic organic pollutants adsorb to the extensive surfaces that are provided by the fine particulate sediments of estuaries and mangroves. Metals are trapped in mangrove sediments through the formation of complexes with sulphides (Lacerda et al., 1991), particulate organic carbon, or iron oxyhydroxides (Chapman et al., 1998). As a consequence, anthropogenic pollutants are filtered from the water layer and accumulate in the sediments of estuaries and mangroves (Bayen et al., 2005; Bhattacharya et al., 2003; Tam and Wong, 1995; Tam and Yao, 2002). Depending on the speciation of chemicals, the pollutants can accumulate in the tissues of biota.

Along the coast of Tanzania, mangrove stands are found in most river mouths, estuaries, and sheltered bays. Due to this position and the capacity of mangrove sediments to trap chemicals, the pollutant levels in the mangrove ecosystem are likely to reflect the use of pollutants in the coastal area and the hinterlands. A study on heavy metals in brown algae in the Zanzibar Channel revealed that the highest concentrations occurred near river mouths on the Tanzanian mainland (Engdahl et al., 1998). Among the waterways in the urban area of Dar es Salaam, the Msimbazi River has been identified as heavily polluted (Ak'habuhaya and Lodenius, 1988; De Wolf et al., 2001; Machiwa, 1992a), but also the harbour of Dar es Salaam, located within the Mtoni Estuary, has been reported to contain elevated levels of pollutants (Machiwa, 1992b; Mwevura et al., 2002). De Wolf et al. (2001) have recently determined the level of heavy metals in sediments and in the periwinkle *Littoraria scabra* from mangroves along the coast of Tanzania. The Msimbazi River was identified as the most polluted sampling site, but no correlations were found between pollution levels and differences in morphology.

In the present study, an assessment was made on the levels of several anthropogenic pollutants in sediments and tissues of the barred mudskipper (*Periophthalmus argentilineatus* Valenciennes) in six mangrove stands on the Tanzanian coast. The mangroves are situated at various distances from Dar es Salaam, the largest city of Tanzania, and were expected to differ as to the influence of industrial

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and agricultural activities. Kruitwagen et al. (2006) compared the different mudskipper populations of the same mangroves and found a deviating growth pattern and eye malformalities in one of the mangroves, adverse effects that were associated with coastal pollution. In the current assessment, quantifications were made of heavy metals since these natural elements are used in high concentrations in many industrial processes. PCBs were included in this study as key representatives of industrial persistent organic pollutants (POPs). Hexachlorobenzene (HCB) was included since it is known to be a by-product of a wide variety of industrial processes and in incomplete combustion, but it is also present in some pesticides (Bailey, 2001), while dichlorodiphenyl-trichloroethane (DDT) and hexachlorohexanes (HCHs) are representatives of agrochemical POPs.

Study areas: Samples were collected in the mangroves of Mtoni, Kunduchi, Mbweni, Chwaka, Makoba, and Rufiji along the coast of Tanzania (Fig. 1). Though heavily polluted (De Wolf et al., 2001), the mangrove stand at the mouth of the Msimbazi River was not included in this study, because the mudskipper is absent from its sandy river basin.

The harbour of Dar es Salaam is located in the Mtoni Estuary, a large estuary that receives water from two tributaries, the Kizinga and the Mzinga. The Kizinga Stream is the largest tributary (30 km long) and is suspected to carry mixed wastes from household, agricultural, as well as industrial origin. The Kizinga reaches the Mtoni Estuary as a narrow stream. After passing a small bridge, the stream widens into a large mangrove stand in which no fish was found. The stream winds through the Mtoni mangroves and passes over the mudflat before the Mzinga joins the Kizinga stream. After the confluence of both streams, about 2 km downstream from the bridge, a mangrove stand is found in which mudskippers were present. The different sampling locations in the Mtoni Estuary will be referred to as Mtoni (1) to Mtoni (5) (Fig. 1).

At 25 and 40 km north of the Dar es Salaam harbour, respectively, the mangroves of Kunduchi and Mbweni are located along the Zanzibar Channel. The area surrounding the Kunduchi mangrove is currently being developed as the northernmost suburb of the city of Dar es Salaam. Several hotels and some industries are located in the proximity of the mangroves. The Mbweni mangrove is located north of Kunduchi, next to a small fishing village with no apparent influences of the city of Dar es Salaam.

The sites of both Chwaka and Makoba are located in the rural areas of Unguja Island (Zanzibar), which is located 30 km from the mainland coast and has little industry. Chwaka Bay is a large shallow bay on the east of the island, which is bordered by small fishing villages. A large mangrove forest fringes the closed southern end of the bay. The Makoba mangroves are located in a bay in the northwest of Unguja Island. The Makoba Bay is fed by two streams, the Zingwezingwe and Mwanakombo. In the proximity of the estuary, some agricultural farms and mariculture ponds are located.

The Rufiji site is located 100 km south of Dar es Salaam city in the wide delta of the Rufiji River. This river has a catchment area of 177400 km^2 and is over 640 km long

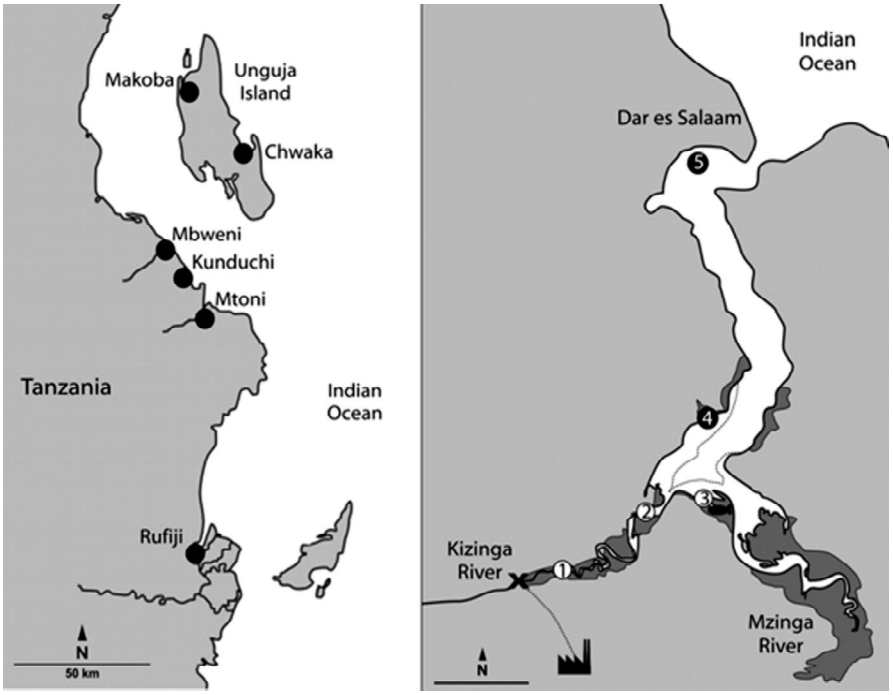


Fig. 1. Map of the Indian Ocean coast of Tanzania with the indication of the sampling sites (left). Sampling locations within the Mtoni Estuary near Dar es Salaam (right). Black dots indicate additional sediment sampling points for organotin analysis. In the right panel, the location of a textile dyeing mill is indicated.

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(UNEP, 2001). In the upstream part of its catchment area, some small towns are located. The downstream part is free of industries, but in the delta various pesticides are being used in mangrove sections that have partially been cleared for rice cultivation (Taylor et al., 2003). Samples were collected from a rice paddy and from the adjacent mangrove creek.

Sampling: Sediment samples analysed for OCPs, heavy metals, and organotins were collected in May 2003, June 2004, and June 2005, respectively. Fish samples for OCP and heavy metal analysis and a rice sample for the analysis of OCPs were collected in the same periods.

Sediments for the analysis of OCPs and heavy metals were collected from fine grained mud in the major mangrove stands. For organotin analysis, sediments were collected over a transect in the Mtoni Estuary. In Mbweni, a sediment sample was collected to be used as a control. The sampling effort focussed on Mtoni, since this is the only coastal system in the present study that is subject to commercial shipping activity, a potential source of organotin pollution.

Samples were collected from the top 5 cm of sediment. Each sample consists of a pool of five points spaced one meter apart. Sediments for the analysis of OCPs and PCBs were air-dried at room temperature, while those destined for the analysis of organotin compounds were immediately frozen after collection. These sediments were freeze-dried and subsequently ground in a mortar and sieved over a 100 μm mesh. Sediments for heavy metal analysis were dried in an oven at 70 °C for 24 h. Before analysis, all sediments were sieved over a <63 μm mesh to obtain the fine fraction.

Barred mudskippers, *P. argentilineatus* (5.1–13.2 cm), were caught at random with scoop nets during low tide on the exposed mudflats in all mangroves. In Mtoni, mudskippers could only be found at site 3 (Fig. 1). For OCP and PCB analyses, fillets of the muscle tissues of the mudskippers were collected and stored at −20 °C until analysis. For heavy metal analysis, whole body samples of mudskipper were collected and oven dried at 70 °C for 24 h. Prior to heavy metal analysis, the fish samples were ground to a homogeneous powder in a blender. Muscle tissues and whole body samples were used for analysis because the small size of the individual mudskippers and the small size of the populations did not enable the use of organs in which a higher accumulation rate of pollutants is expected.

In Rufiji, a rice sample harvested from the same rice paddy, where sediments and fish were collected, was also obtained. The rice had been dried in the sun and husks had been removed by the local farmers. This sample was processed and analysed for POPs according to the method described for the mudskipper tissues.

Heavy metals: Sediment and whole body mudskipper samples were digested in a mixture of HNO_3 and H_2O_2 (4:1, v/v) in a Milestone MLS microwave with Teflon bombs and stored at 4 °C until analysis. Sediment and whole body samples were analysed for cadmium, chromium, copper, lead, aluminium, zinc, iron, cobalt, tin, and nickel, using a SpectroFlame ICP-AES (Spectro Analytical Instruments, Kleve, Germany). Analytical accuracy was checked with standard reference material for marine sediment (IAEA-356) and mussel tissue (Mytilus edulis, BCR278R). Recovery values for standard reference material are given in Tables 1 and 2. When recovery values for the reference material deviated from the certified values by more than 10%, the results for samples were corrected for the deviation.

Organochlorine pollutants: Samples were analysed for the following OCPs: α-, γ-isomers of HCHs, HCB, p,p′-DDE, p,p′-DDD and p,p′-DDT (expressed here as DDTs). The following PCB congeners (IUPAC numbers) were targeted: 28, 52, 101, 118, 138, 153, 156, 170, 180, and 187. Internal standards used were PCB 46, PCB 143, and ε-HCH (100 pg/μl). All individual standards of PCBs and OCPs were obtained from Dr. Ehrenstorfer Laboratories (Augsburg, Germany).

The methods for the determination of PCBs and OCPs in fish and sediment samples have been previously described and validated by Jacobs et al. (2002) and Covaci et al. (2005). The whole amount of available fish muscle

Table 1
Average metal concentrations in sediments collected in June 2004 at various sites (μg/g dw ± SE) and recovery values for standard reference material (average ± SE)

	Mtoni (1)	Mtoni (2)	Mtoni (3)	Kunduchi	Mbweni	Chwaka	Makoba	Rufiji	% recovery of reference sample
n	2	3	5	2	2	2	1	3	
Al	5430 ± 5790^{a}	61900 ± 4130^{a}	18600 ± 3250^{b}	2370 ± 68^{c}	8150 ± 544^{c}	4310 ± 3^{c}	10300	13400 ± 2750^{b}	
Zn	2450 ± 101^{a}	178 ± 29^{b}	43.9 ± 11.2^{bc}	13.1 ± 1.0^{c}	21.4 ± 1.4^{c}	18.4 ± 9.3^{c}	66.6	57.1 ± 2.5^{bc}	96.1 ± 1.9
Fe	59100 ± 1830^{a}	28300 ± 499^{b}	8070 ± 1010^{c}	2020 ± 141^{c}	7490 ± 1060^{c}	2540 ± 388^{c}	14200	32500 ± 2670^{ab}	94.2 ± 3.2
Pb	385 ± 209^{ab}	110	47.2 ± 3.8^{a}	23.8 ± 12.1^{ab}	13.0 ± 0.8^{b}	23.3 ± 2.8^{ab}	13.8	47.0 ± 3.2^{a}	109.8 ± 6.3
Cd	28.1	14.9	0.9 ± 0.3	1.3 ± 0.4	0.7 ± 0.3	1.0 ± 0.2	2.3	1.4 ± 0.3	107.5 ± 5.3
Cu	4050 ± 207^{a}	14.7 ± 1.8^{b}	3.7 ± 0.8^{c}	1.0 ± 0.1^{c}	2.8 ± 0.1^{c}	3.1 ± 1.1^{c}	4.4	18.6 ± 1.2^{b}	101.4 ± 2.1
Co	14.1 ± 1.0^{a}	21.5 ± 11.5^{ab}	1.9 ± 1.0^{ab}	1.7 ± 0.0^{b}	3.0 ± 1.4^{ab}	1.3 ± 0.1^{b}	3.1	15.3 ± 0.6^{a}	90.8 ± 4.3
Cr	6240 ± 3^{a}	61.5 ± 11.9^{bc}	14.4 ± 1.8^{d}	4.5 ± 0.5^{e}	14.6 ± 0.0^{d}	24.8 ± 0.2^{c}	30.8	46.1 ± 2.5^{b}	59.7 ± 1.8
Sn	174	153 ± 63.9	0.8 ± 0.5	6.7 ± 0.6	6.4 ± 2.0	9.0 ± 6.0	9.3	4.5 ± 0.4	
Ni	156 ± 6.5^{a}	23.2 ± 6.7^{bc}	7.9 ± 1.7^{cd}	2.7 ± 0.4^{d}	8.9 ± 0.4^{cd}	12.0 ± 1.4^{cd}	13.5	32.8 ± 1.0^{b}	

Sites with different letters are significantly different.

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Table 2
Average metal concentrations in fish tissues in June 2004 at various sites (μg/g dw ± SE) and recovery values for standard reference material (average ± SE)

	Mtoni (1)	Mtoni (2)	Mtoni (3)	Kunduchi	Mbweni	Chwaka	Makoba	Rufiji	% recovery of reference sample
n	–	–	14	6	5	5	7	12	
Al	n/a	n/a	300 ± 91.5^{a}	57.4 ± 34.3^{ab}	26.8 ± 4.1^{b}	198 ± 71.5^{ab}	173 ± 107^{ab}	62.2 ± 14.4^{b}	
Zn	n/a	n/a	219 ± 8.7^{a}	153 ± 21.8^{ab}	161 ± 8.1^{b}	165 ± 31.8^{ab}	170 ± 17.4^{ab}	148 ± 16.0^{b}	130 ± 4.0
Fe	n/a	n/a	295 ± 42.4^{a}	129 ± 11.4^{b}	147 ± 25.4^{ab}	169 ± 40.9^{ab}	132 ± 9.4^{b}	141 ± 14.3^{b}	117 ± 3.4
Pb	n/a	n/a	8.9 ± 1.0^{b}	4.5 ± 1.2^{bc}	7.3 ± 2.7^{abc}	5.9 ± 2.2^{abc}	1.9 ± 0.4^{c}	20.9 ± 3.8^{a}	95 ± 0.7
Cd	n/a	n/a	0.2 ± 0.1^{c}	0.4 ± 0.1^{bc}	0.9 ± 0.2^{ab}	0.5 ± 0.0^{b}	0.6 ± 0.2^{abc}	1.5 ± 0.2^{a}	105
Cu	n/a	n/a	4.9 ± 0.7^{a}	3.5 ± 0.5^{ab}	5.5 ± 1.8^{ab}	2.9 ± 0.1^{b}	5.0 ± 0.7^{ab}	3.6 ± 0.5^{ab}	107 ± 4.3
Co	n/a	n/a	0.7 ± 0.1^{b}	0.3 ± 0.1^{b}	0.3 ± 0.1^{b}	0.6 ± 0.1^{b}	0.3 ± 0.1^{b}	2.5 ± 0.4^{a}	
Cr	n/a	n/a	3.2 ± 0.2	3.6 ± 0.9	2.0 ± 0.3	2.4 ± 0.2	2.3 ± 0.2	$3.1 \pm .03$	117 ± 9.0
Sn	n/a	n/a	3.2 ± 0.2^{b}	1.6 ± 0.3^{b}	2.3 ± 0.3^{b}	3.5 ± 1.3^{b}	1.9 ± 0.4^{b}	18.6 ± 3.8^{a}	
Ni	n/a	n/a	2.0 ± 0.3^{ab}	1.3 ± 0.2^{b}	2.3 ± 0.8^{ab}	1.4 ± 0.2^{b}	1.4 ± 0.3^{ab}	3.1 ± 0.4^{a}	

n/a = not applicable.
Sites with different letters are significantly different.

(typically around 4 g) or 3 g sediment was homogenized with anhydrous Na_2SO_4, spiked with internal standards (ε-HCH, PCB 46 and 143) and extracted for 2 h with 100 ml hexane/acetone (3:1, v/v) using an accelerated Soxhlet extractor B-811 (Buchi, Switzerland). Fish extracts were cleaned up after lipid determination on 8 g acidified silica, while the sediment extract was cleaned up on 6 g acidified silica topped with 3 g of copper powder. After elution with 15 ml hexane and 10 ml dichloromethane, the cleaned extracts were concentrated to 100 μl. The cleaned extracts were analysed on a Hewlett Packard 6890 GC-μECD (Palo Alto, CA, USA), which was equipped with a 25 m × 0.22 mm × 0.25 μm HT-8 capillary column (SGE, Zulte, Belgium). The identification of OCPs and PCBs was based on their relative retention times to the internal standard used for quantification. The content of OCPs could not be analysed in sediment samples from Mtoni (1) due to the high sulphur content of the sediments at this location.

The analytical procedures were validated through the regular analysis of laboratory reference material (fish tissue) and through participation in Quasimeme interlaboratory tests (PCBs and OCPs determination in sediment and fish). The method limits of quantification (LOQ) for individual compounds ranged between 0.1 and 0.3 ng/g wet weight (ww) for fish and 0.2 ng/g dry weight (dw) for sediment. The analyses were carried out at the Toxicological Centre of the University of Antwerp, Belgium.

The ratio between α-HCH and γ-HCH indicates whether lindane or technical HCH has been used, while the ratio between p,p′-DDT and its breakdown-products p,p′-DDE and p,p′-DDD gives an indication of the historical use of DDT.

Organotin compounds: Samples of the sieved sediments (4–5 g) were acidified with HCl, extracted with diethyl-ether/tropolone, derivatized using a Grignard pentylation reaction, purified over deactivated alumina and analysed using gas chromatography with an ion trap mass spectrometric detector (GC-MS and GC-MS-MS; Varian 3400 gas chromatograph; Varian Saturn IV ion trap mass spectrometer; Varian, Walnut Creek, CA, USA) as applied in previous studies (Stäb et al., 1996). Samples were analysed for tributyltin (TBT) and its degradation products dibutyltin (DBT) and monobutyltin (MBT), tetrabutyltin (TeBT), triphenyltin (TPT) and the degradation products diphenyltin (DPT) and monophenyltin (MPT). Analyses were carried out by the Institute for Environmental Studies (IVM) at the Vrije Universiteit Amsterdam, The Netherlands.

Statistical analysis: Differences between the heavy metal concentrations of the various mangroves were analysed by one-way ANOVA. Prior to the analysis, data were log-transformed to achieve homogeneity of variance. Post Hoc comparison tests (Games-Howell) were used to determine which mangroves differed significantly. The amount of sediment collected turned out to be insufficient to perform all chemical analyses on all samples. As a result, no statistical analysis could be performed on the results for organochlorine and organotin compounds. All statistical analyses were performed with software-package SPSS© 11.5 and statistical significance was accepted at $P \leqslant 0.05$. Significant differences between groups are indicated in tables with letters; differences between groups sharing the same letter are not significant.

The average metal concentrations for sediment and whole body samples of mudskippers are given in Tables 1 and 2, respectively. The data show that the highest average sediment concentrations of zinc, iron, lead, copper, chromium, and nickel were found in Mtoni (1). Particularly, the concentrations of copper, chromium, nickel and tin were elevated in the sediments of Mtoni (1) compared to the other sampling sites. The concentrations of lead, copper, chromium, and nickel in Mtoni (2) were significantly lower than that in Mtoni (1), but still higher than that in Mtoni (3), Chwaka, Kunduchi, Mbweni, and Makoba. The concentrations for lead and chromium in the sediments of Rufiji were lower than Mtoni (2), but the concentrations of the other metals were similar to Mtoni (2). The

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Table 3
Concentrations of organochlorine pollutants in sediments of various sites (ng/g dw ± SE)

	Mtoni (2)	Mtoni (3)	Kunduchi	Mbweni	Chwaka	Makoba	Rufiji
n	1	3	2	2	2	1	5
α-HCH	n.d.	0.51 ± 0.07	n.d.	n.d.	0.47 ± 0.47	n.d.	0.34 ± 0.09
γ-HCH	0.53	4.75 ± 0.56	0.24 ± 0.24	0.21 ± 0.21	1.52 ± 0.20	0.84	1.97 ± 0.63
Sum HCHs	0.53	5.26	0.24	0.21	1.99	0.84	2.30
γ-HCH/sum HCH	1.00	0.91	1.00	1.00	0.77	1.00	0.85
HCB	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
pp′-DDE	0.66	2.79 ± 0.81	0.13 ± 0.13	n.d.	0.59 ± 0.13	5.17	0.37 ± 0.37
pp′-DDD	1.30	1.45 ± 0.51	n.d.	n.d.	0.14 ± 0.14	2.05	0.71 ± 0.54
pp′-DDT	0.76	0.46 ± 0.46	n.d.	n.d.	2.49 ± 1.78	1.43	0.58 ± 0.42
Sum DDTs	2.72	4.70	0.13	–	3.23	8.64	1.65
pp′-DDT/sum DDT	0.36	0.12	0.00	–	0.77	0.17	0.35
CB 28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CB 52	1.03	0.99 ± 0.02	n.d.	n.d.	0.80 ± 0.45	n.d.	n.d.
CB 101	0.21	0.25 ± 0.03	n.d.	n.d.	n.d.	n.d.	n.d.
CB 118	0.44	0.48 ± 0.05	n.d.	n.d.	0.43 ± 0.02	n.d.	n.d.
CB 153	0.47	0.49 ± 0.06	n.d.	n.d.	0.88 ± 0.50	n.d.	n.d.
CB 138	0.37	0.34 ± 0.06	n.d.	n.d.	0.22 ± 0.22	n.d.	n.d.
CB 187	0.39	0.21 ± 0.08	n.d.	n.d.	n.d.	n.d.	n.d.
CB 156	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CB 180	0.35	0.32 ± 0.04	n.d.	n.d.	n.d.	n.d.	n.d.
CB 170	0.39	0.14 ± 0.09	n.d.	n.d.	n.d.	n.d.	n.d.
Sum PCBs	3.65	3.08	–	–	2.33	–	–

n.d. = below LOQ.

Table 4
Concentrations of organochlorine pollutants in fish tissues and a rice sample of various sites (ng/g lipid weight ± SE)

	Mtoni (3)	Kunduchi	Mbweni	Chwaka	Makoba	Rufiji	
Sample type	Fish tissue	Fish tissue	Fish tissue	Fish tissue	Fish tissue	Fish tissue	rice
n	4	4	9	7	6	6	1
Lipid content (%)	0.46 ± 0.02	0.54 ± 0.03	0.48 ± 0.02	0.44 ± 0.01	0.51 ± 0.03	0.51 ± 0.01	0.92
α-HCH	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	100
γ-HCH	2570 ± 625^{a}	18 ± 18^{b}	527 ± 74^{b}	62 ± 62^{b}	21 ± 13^{b}	633 ± 51^{b}	15300
Sum HCHs	2570 ± 625^{a}	18 ± 18^{b}	527 ± 74^{b}	62 ± 62^{b}	21 ± 13^{b}	633 ± 51^{b}	15400
γ-HCH/sum HCH	1.00	1.00	1.00	1.00	1.00	1.00	0.99
HCB	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
pp′-DDE	799 ± 141^{a}	n.d.	24 ± 17^{c}	n.d.	269 ± 48^{b}	39 ± 14^{c}	27
pp′-DDD	166 ± 37^{a}	n.d.	8 ± 8^{c}	n.d.	104 ± 11^{b}	n.d.	171
pp′-DDT	118 ± 46	n.d.	n.d.	n.d.	n.d.	n.d.	56
Sum DDTs	1080 ± 213^{a}	–	37 ± 26^{c}	–	373 ± 49^{b}	39 ± 14^{c}	253
pp′-DDT/sum DDTs	0.11	–	0.00	–	0.00	0.00	0.22
CB 28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	89
CB 52	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	112
CB 101	n.d.	300 ± 146^{a}	n.d.	26 ± 17^{b}	n.d.	n.d.	250
CB 118	10 ± 10^{b}	136 ± 60^{a}	n.d.	16 ± 11^{b}	n.d.	n.d.	52
CB 153	135 ± 12^{b}	952 ± 404^{a}	30 ± 10^{b}	187 ± 82^{b}	81 ± 11^{b}	n.d.	102
CB 138	98 ± 7^{b}	917 ± 380^{a}	32 ± 10^{b}	203 ± 91^{b}	74 ± 11^{b}	n.d.	69
CB 187	45 ± 10^{b}	454 ± 193^{a}	n.d.	90 ± 52^{b}	18 ± 8^{b}	n.d.	n.d.
CB 156	9 ± 9^{b}	238 ± 92^{a}	n.d.	52 ± 37^{b}	n.d.	n.d.	n.d.
CB 180	89 ± 9^{b}	1330 ± 469^{a}	22 ± 7^{b}	357 ± 203^{b}	127 ± 20^{b}	n.d.	n.d.
CB 170	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum PCBs	428 ± 31^{b}	5040 ± 1970^{a}	84 ± 27^{b}	1149 ± 606^{b}	365 ± 58^{b}	–	674

n.d. = below LOQ; lipid content concerns the extractable lipids.
Sites with different letters are significantly different.

concentrations of aluminium and iron were very high in the sediments of Mtoni (2), Mtoni (1), and Rufiji. The metal concentrations in Chwaka, Kunduchi, Mbweni, and Makoba were generally low.

The concentrations in the whole body samples of mudskippers exhibited only minor variations, but the concentrations were generally low and similar. The fish at Mtoni (3) had higher concentrations of aluminium and iron.

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The concentrations of OCPs in sediments and mudskipper muscle tissues are shown in Tables 3 and 4, respectively. The concentration of total HCH (γ-HCH and α-HCH) was highest in the sediments at Mtoni (3) followed by Rufiji. While both γ-HCH and α-HCH were found in Mtoni (3), Chwaka, and Rufiji, only γ-HCH was found in Mtoni (2), Kunduchi, Mbweni, and Makoba. The ratio of γ-HCH/sum HCH was higher than 0.77 in the sediments from all sites. In the mudskipper muscle tissues, γ-HCH was the only HCH isomer that could be detected: the highest levels were found in the fish from Mtoni (3), followed by Rufiji and Mbweni. HCB was not detected in any of the sediments (Table 3) or fish samples (Table 4).

The highest sum of DDT and its metabolites in sediments was found at Makoba with the highest contribution of DDE (Table 3). A similar ratio between the derivates was found at Mtoni (3). In all fish samples, DDE was present in higher concentrations than DDT. The highest sum of DDT was found in fish from Mtoni (3) followed by Makoba.

PCBs could not be detected in the sediments of Kunduchi, Mbweni, Makoba, and Rufiji, nor in the fish muscle tissues from Rufiji (Tables 3 and 4, respectively). In the sediments of Mtoni (2), Mtoni (3), and Chwaka, the congeners 52, 118, and 153 were most abundant. In the fish tissues from all five sites where PCBs were detected, congeners 153, 138, and 180 were present in the highest concentrations. The total sum of PCBs in fish muscle tissues was highest in Kunduchi, followed by Chwaka and Mtoni (3).

The Rufiji rice sample had a very high concentration of γ-HCH and a low concentration of α-HCH (Table 4), which resulted in a γ-HCH/sum HCH-ratio of 0.99. The sample contained all derivates of DDT and the DDT/sum DDT-ratio was 0.22. A number of PCB congeners could be detected in the rice sample, of which CB 101 was found in the highest concentration.

The results from the analysis of organotin compounds in the sediments of Mtoni are presented in Fig. 2. The data show that the concentrations of MBT, DBT, and TBT decreased within the Mtoni Estuary with increasing distance from Dar es Salaam harbour. The highest concentrations of MPT were observed in the proximity of a textile dyeing plant. TeBT was not detectable in any of the sediments that were analysed. DPT and TPT were only detectable in the sample that was collected at Mtoni (4).

In the present study, the main differences in the concentration of pollutants between the various sites were observed for the heavy metals. Their concentrations were highest in the mangroves of Mtoni, where heavy metals occur in concentrations that indicate heavy industrial pollution. The samples taken at different locations within the Mtoni mangroves reveal a concentration gradient that increased in the direction of the Kizinga Stream, where a textile dyeing mill is located nearby. With increasing distance from the effluent discharge pipe of the mill in the downstream direction, the concentration of heavy metals in the sediments decreased rapidly. This decrease over a relatively short distance reveals a strong capacity and effectiveness of the sediments to remove heavy metals from the water layer. Mangrove sediments are generally reduced, anaerobic and characterized by high sulphide and iron concentrations (Tam and Wong, 1996). These conditions favour the immobilisation of heavy metals through the formation of metal-sulphide complexes by sulphate-reducing

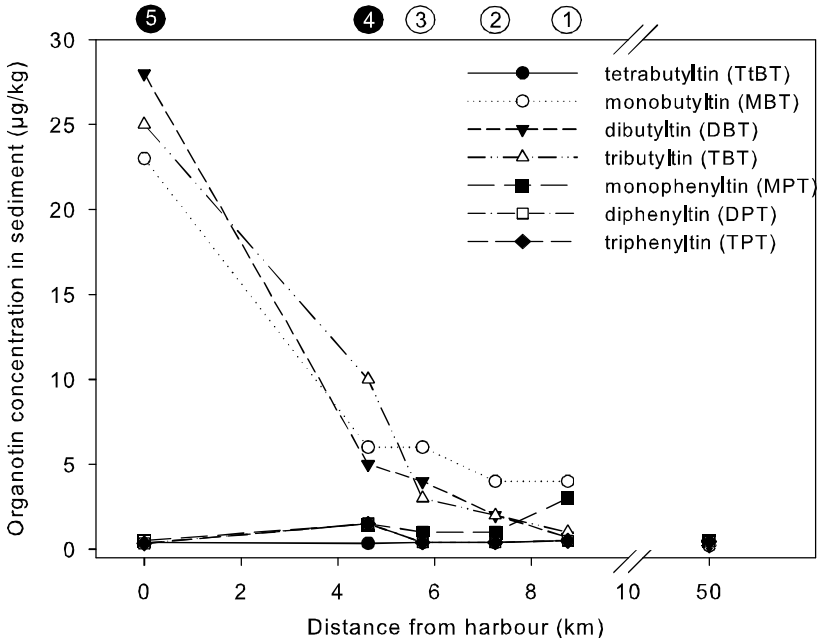


Fig. 2. Concentrations of organotin compounds (in µg/kg) in sediments collected in June 2005 in relation to the distance to the Dar es Salaam harbour. Numbers correspond to sampling locations in Mtoni (see Fig. 1). The sample at 50 km distance was collected in the Mbweni mangroves and was used as a reference sample.

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bacteria (Chapman et al., 1998; Marchand et al., 2004), which are abundant in the sediments of the Mtoni mangroves (Lyimo et al., 2002).

In the samples from the mangrove sites other than Mtoni, only aluminium, iron and zinc were present in relatively high concentrations. However, these metals are most likely not from anthropogenic origin, but can be attributed to the high content of aluminium and iron oxides in the soils of the East African region (FAO, 1998). These heavy metal concentrations comply with the concentrations that are commonly found in South African coastal sediments (Mzimela et al., 2003).

Organotin compounds have various applications in industries and agriculture and are mostly from anthropogenic origin (Fent, 1996). In the present study, organotin concentrations were only determined in the sediments of Mtoni, where butyltin compounds appeared to be present in a gradient of concentrations that increased from the Kizinga stream in the direction of the harbour. The direction of the gradient suggests that the butyltin compounds in the environment are derived from shipping activities that are concentrated in the estuary mouth. The organotin concentrations decrease over distance due to sorption of organotins to sediments close to their release site (Langston and Pope, 1995). Tidal flushing of the estuary may also contribute to the observed distribution gradient in the estuary. The ratios between the different butyltin compounds suggest that TBT is gradually debutylated within the estuary (Yonezawa et al., 1994) at a rate similar to the release of TBT into the environment. The observed butyltin concentrations correspond to an average shipping density of less than five ships of 100 gross tons per day according to the method used by Ten Hallers-Tjabbes et al. (2003) for shipping activity in the North Sea and the Skagerrak, which corresponds to the reported total of 1039 deep sea ship calls to the Dar es Salaam harbour in the year 2003/2004 (Tanzania Ports Authority, 2006). Monophenyltin was detected in the sediments of the Kizinga Stream in addition to butyltin compounds. Phenyltins are used as fungicide in agriculture and may occur in coastal sediments as a result of run-off (Stäb et al., 1996). The presence of monophenyltin in the Kizinga Stream indicates agricultural activities in the hinterland of the stream.

PCBs are the only pollutants typical of industrial pollution that were found outside the city of Dar es Salaam. In Kunduchi, a relatively high load of PCBs was found in the muscles of the mudskippers, which is most likely derived from plastics manufacturers that are located in the proximity. The PCBs have, however, not been found in the sediments from Kunduchi. These divergent results might be due to the low content of organic matter in the sandy sediments of Kunduchi. The presence of PCBs in the mangroves of Chwaka Bay is most likely the result of the use of outboard engines in the semi-enclosed bay since there are no industries in the area.

The presence of HCHs and DDT and their derivates is directly related to agricultural activities (Mmochi and Mberek, 1998). HCHs were present in the highest concentrations in the sediments and in the fish samples from Mtoni and Rufiji. In all samples, including the rice sample from the paddy in the Rufiji mangroves, HCHs were mostly present as γ-HCH, indicating the use of lindane rather than technical HCH as a pesticide in the rice paddies (Willett et al., 1998). The high content of HCHs in the rice sample reveals that this pesticide is used in considerable quantities during the growing season. This is not necessarily reflected by its environmental concentrations since the HCHs are very volatile and susceptible to breakdown by solar radiation in tropical agriculture (Abdullah et al., 1997; Ritter et al., 1995). DDT is also subject to these processes and may be broken down to the derivates DDE and DDD (Abdullah et al., 1997). The highest total concentrations of DDT and its breakdown-products were encountered in the sediments of Makoba and Mtoni. With the exception of the sediments of Chwaka, all analysed samples contained higher concentrations of the breakdown-products DDE and DDD than DDT, which indicates that the DDT derivates in the samples are the result of the past use of DDT. Only the ratios between DDE, DDD, and DDT in the sediment samples from Chwaka indicated more recent use.

The variations in pollutant concentrations in the sediments were only reflected to a limited extent in the fish tissues. At all locations where mudskippers were collected, heavy metal levels in the sediments were low and consequentially did not result in elevated levels of metals in the mudskipper tissues. The low concentrations of the lipophilic organochlorine pollutants in the fish tissues and the limited variation in the concentrations suggest that these pollutants were only available for uptake in limited amounts. Apart from the low environmental concentrations, the accumulation of lipophilic compounds in the muscle tissues of the mudskipper would also be limited by the low fat content of the mudskipper muscle tissue. The average fat content of 0.49% in the muscle tissues is much lower than that for most fish species (Manirakiza et al., 2002), but is similar to fat percentages found in related gobiid fishes (Mwevura et al., 2002; Voorspoels et al., 2004). The low fat content thus reduces the sensitivity of the mudskipper to the accumulation of lipophilic pollutants from the coastal environment in its muscle tissues. It is likely that the analysis of pollutant concentrations in kidneys or livers would have yielded higher concentrations of pollutants than the concentrations that were found in the mudskipper muscle tissues and whole body samples. However, the amount of kidneys and livers that could be collected was too small to enable analysis in these organs. Since no bioaccumulation was observed in the muscle tissues, no relation could be found between bioaccumulation and the adverse effects that were previously observed in mudskippers from the Mtoni population (Kruitwagen et al., 2006). Direct exposure to high levels of pollution, such as the high metal concentrations that were found in Mtoni, could however also have induced the observed adverse effects.

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When the pollutant concentrations in the sediments, fish tissues, and the rice sample are considered, it appears that the distribution of industrial and agricultural pollutants over the mangrove sites closely follows the actual distribution of industries and agriculture: industrial influence is found in Mtoni and Kunduchi, while agricultural pollutants occur in Mtoni, Makoba, Rufiji and Chwaka. Mtoni is not only the site with the highest pollutant concentration, but also the only site where both industrial and agricultural pollutants can be found. In contrast, neither industrial nor agricultural pollutants were found in the samples from Mbweni. Simultaneously, the results show that the geographical range over which the effects of industrialisation and urbanisation are observed is still relatively limited.

Heavy metal concentrations of 65–5300 μg Cu/g and 25–190 μg Pb/g have been found in coastal sediments in Hong Kong (Blackmore, 1998), while concentrations of 131 μg Cu/g and 372 μg Pb/g were present in the sediments of the Tees estuary in Great Britain, an estuary notorious for its high pollutant concentrations in the 1970s (Jones and Turki, 1997). In the present study, only the sediment heavy metal concentrations at the hot spot in the Kizinga Stream reached similar levels. The concentrations at the other sampling locations are also surpassed by the heavy metal concentrations of 50–229 μg Cu/g and 55–165 μg Pb/g in the mangrove sediments of the Makupa Creek in Mombasa, Kenya (Muohi et al., 2003a), but are similar to the concentrations of 2–20 μg Cu/g and 9–46 μg Pb/g found in the mangrove sediments of the relatively pristine Shirazi Creek 70 km south of Mombasa (Muohi et al., 2003b) as well as to the concentrations of <1–17 μg Cu/g and 3–28 μg Pb/g found in Richards Bay, South Africa (Mzimela et al., 2003). This comparison indicates that the mangrove sediments that were analysed in the present study were relatively unpolluted by heavy metals, with the exception of the Kizinga Stream.

Compared to the concentrations reported for Hong Kong (0.1–2.3 ng HCH/g, 1.4–311 ng total DDT/g, and 0.1–16.0 ng total PCB/g; Hong et al., 1995) and concentrations found in the Scheldt Estuary (<0.3 ng HCH/g, 11.8–21.0 ng DDT/g, and 167–238 ng PCB/g; Covaci et al., 2005), the levels of organochlorine pollutants in the sediments of the mangroves of Tanzania were relatively low. Organochlorine concentrations of similar magnitudes were found in the mangroves of Singapore (Bayen et al., 2005) and the Hugli Estuary in India (Guzzella et al., 2005). The organochlorine concentrations that were found in the tissues of the barred mudskipper in the present study are similar to the levels of pollutants in mudskippers in relatively unpolluted areas of Japan and Singapore (Bayen et al., 2005; Nakata et al., 2002).

The concentrations in the sediments reported here are very similar to the heavy metal concentrations found in previous investigations in the same study area (De Wolf et al., 2001; Machiwa, 1992b), except for the high heavy metal levels found in Mtoni (1) and Mtoni (2). The concentrations of PCBs in the Mtoni Estuary have decreased during the last decade relative to the concentrations reported by Machiwa (1992b). Concentrations of DDT and its derivates have decreased as well since the previous investigation, but DDT still shows the same ratio in relation to total DDT-related compounds (Mwevura et al., 2002), indicating that the breakdown of DDT has continued. The concentrations of γ-HCH found in the present study were higher than the concentration of <0.8 ng/g reported for the Mtoni Estuary by Mwevura et al. (2002). In 1992, Machiwa anticipated an increase in population and industries and predicted that this would result in an increase in the level of pollution in the Mtoni Estuary (Machiwa, 1992b). Since the study by Machiwa (1992b), the population of Tanzania in general and of the coastal zone in particular has increased (National Bureau of Statistics, 2002), but nonetheless no changes in the general pollution levels were noticed, except for the occurrence of a heavy metal hot spot following the establishment of a textile mill on the banks of the Kizinga stream.

The low concentrations of industrial pollutants suggest that the level of industrialisation along the Tanzanian coast is limited. Industrial activities are concentrated to the urban area of Dar es Salaam, whereas agricultural activities are widespread and are even found within the boundaries of the city of Dar es Salaam. All over the African continent, industrialisation is concentrated in the major centres of commerce, which have primarily emerged along the coasts of the Indian and Atlantic Oceans (Biney et al., 1994; Scheren et al., 2002). If the control of waste disposal and the treatment of wastes are limited, such a concentration of industrial activities increases the chances of pollution of the local environment. The establishment of new industries can thus rapidly create hot spots of pollution, as is shown by the heavy metal pollution in Mtoni. This pollution suggests that treatment of the wastes of the textile dyeing mill is insufficient, even though proper treatment methods for such wastewater exist (El Geundi, 1997; Volesky and Holan, 1995). This study reveals that environmental pollution levels along the coast of Tanzania due to industrial waste disposal and agricultural run-off are limited. The pollution hot spot in Mtoni should be considered as an example of the large impact that may be expected to occur if the level of industrialisation of the urban area of Dar es Salaam continues, and insufficient measures of waste treatment are taken to prevent increasing environmental impact.

References

Abdullah, A.R., Bajet, C.M., Matin, M.A., Nhan, D.D., Sulaiman, A.H., 1997. Ecotoxicology of pesticides in the tropical paddy field ecosystem. Environmental Toxicology and Chemistry 16, 59–70.

Ak'habuhaya, J., Lodenius, M., 1988. Metal pollution of river Msimbazi, Tanzania. Environment International 14, 511–514.

Bailey, R.E., 2001. Global hexachlorobenzene emissions. Chemosphere 43, 167–182.

Author's personal copy

Bayen, S., Wurl, O., Karuppiah, S., Sivasothi, N., Lee, H.K., Obbard, J.P., 2005. Persistent organic pollutants in mangrove food webs in Singapore. Chemosphere 61, 303–313.

Bhattacharya, B., Sarkar, S.K., Mukherjee, N., 2003. Organochlorine pesticide residues in sediments of a tropical mangrove estuary, India: implications for monitoring. Environment International 29, 587–592.

Biney, C., Amuzu, A.T., Calamari, D., Kaba, N., Mbome, I.L., Naeve, H., Ochumba, P.B.O., Osibanjo, O., Radegonde, V., Saad, M.A.H., 1994. Review of heavy metals in the African aquatic environment. Ecotoxicology and Environmental Safety 28, 134–159.

Blackmore, G., 1998. An overview of trace metal pollution in the coastal waters of Hong Kong. Science of the Total Environment 214, 21–48.

Chapman, P.M., Wang, F.Y., Janssen, C., Persoone, G., Allen, H.E., 1998. Ecotoxicology of metals in aquatic sediments: binding and release, bioavailability, risk assessment, and remediation. Canadian Journal of Fisheries and Aquatic Sciences 55, 2221–2243.

Covaci, A., Gheorghe, A., Voorspoels, S., Maervoet, J., Redeker, E.S., Blust, R., Schepens, P., 2005. Polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in sediment cores from the Western Scheldt river (Belgium): analytical aspects and depth profiles. Environment International 31, 367–375.

De Wolf, H., Ulomi, S.A., Backeljau, T., Pratap, H.B., Blust, R., 2001. Heavy metal levels in the sediments of four Dar es Salaam mangroves; accumulation in, and effect on the morphology of the periwinkle, *Littoraria scabra* (Mollusca: Gastropoda). Environment International 26, 243–249.

El Geundi, M.S., 1997. Adsorbents for industrial pollution control. Adsorption Science and Technology 15, 777–787.

Engdahl, S., Mamboya, F., Mtolera, M., Semesi, A.K., Björk, M., 1998. The brown macroalgae *Padina boergesenii* as an indicator of heavy metal contamination in the Zanzibar channel. Ambio 28, 694–700.

FAO, 1998. Digital Soil Map of the World and Derived Soil Properties. FAO, Rome.

Fent, K., 1996. Ecotoxicology of organotin compounds. Critical Reviews in Toxicology 26, 3–117.

Guzzella, L., Roscioli, C., Vigano, L., Saha, M., Sarkar, S.K., Bhattacharya, A., 2005. Evaluation of the concentration of HCH, DDT, HCB, PCB and PAH in the sediments along the lower stretch of Hugli estuary, West Bengal, northeast India. Environment International 31, 523–534.

Hong, H., Xu, L., Zhang, L., Chen, J.C., Wong, Y.S., Wan, T.S.M., 1995. Environmental fate and chemistry of organic pollutants in the sediment of Xiamen and Victoria Harbours. Marine Pollution Bulletin 31, 229–236.

Jacobs, M.N., Covaci, A., Schepens, P., 2002. Investigation of selected persistent organic pollutants in farmed Atlantic salmon (*Salmo salar*), salmon aquaculture feed, and fish oil components of the feed. Environmental Science and Technology 36, 2797–2805.

Jones, B., Turki, A., 1997. Distribution and speciation of heavy metals in surficial sediments from the Tees Estuary, north-east England. Marine Pollution Bulletin 34, 768–779.

Kruitwagen, G., Hecht, T., Pratap, H.B., Wendelaar Bonga, S.E., 2006. Changes in morphology and growth of the mudskipper (*Periophthalmus argentilineatus*) associated with coastal pollution. Marine Biology 149, 201–211.

Lacerda, L.D., Rezende, C.E., Aragon, G.T., Ovalle, A.R., 1991. Iron and chromium transport and accumulation in a mangrove ecosystem. Water Air and Soil Pollution, 513–520.

Langston, W.J., Pope, N.D., 1995. Determinants of TBT adsorption and desorption in estuarine sediments. Marine Pollution Bulletin 31, 32–43.

Lyimo, T.J., Pol, A., Op den Camp, H.J.M., 2002. Sulfate reduction and methanogenesis in sediments of Mtoni mangrove forest, Tanzania. Ambio 31, 614–616.

Machiwa, J.F., 1992a. Heavy metal content in coastal sediments of Dar es Salaam, Tanzania. Environment International 18, 409–415.

Machiwa, J.F., 1992b. Anthropogenic pollution in the Dar es Salaam harbour area, Tanzania. Marine Pollution Bulletin 24, 562–567.

Manirakiza, P., Covaci, A., Nizigiymana, L., Ntakimazi, G., Schepens, P., 2002. Persistent chlorinated pesticides and polychlorinated biphenyls in selected fish species from Lake Tanganyika, Burundi, Africa. Environmental Pollution 117, 447–455.

Marchand, C., Baltzer, F., Lallier-Verges, E., Alberic, P., 2004. Pore-water chemistry in mangrove sediments: relationship with species composition and developmental stages (French Guiana). Marine Geology 208, 361–381.

Mmochi, A.J., Mberek, R.S., 1998. Trends in the types, amounts, and toxicity of pesticides used in Tanzania. Ambio 27, 669–676.

Muohi, A.W., Onyari, J.M., Omondi, J.G., Mavuti, K.M., 2003a. Heavy metals in sediments from Makupa and Port-Reitz creek systems: Kenyan coast. Environment International 28, 639–647.

Muohi, A.W., Onyari, J.M., Omondi, J.G., Mavuti, K.M., 2003b. Heavy metal distribution in surface sediments from Mtwapa and Shirazi creeks, Kenyan coast. Bulletin of Environmental Contamination and Toxicology 70, 1220–1227.

Mwevura, H., Othman, O.C., Mhehe, G.L., 2002. Organochlorine pesticide residues in sediments and biota from the coastal area of Dar es Salaam city, Tanzania. Marine Pollution Bulletin 45, 262–267.

Mzimela, H.M., Wepener, V., Cyrus, D.P., 2003. Seasonal variation of selected metals in sediments, water and tissue of the groovy mullet, *Liza dumerelii* (Mugulidae) from the Mhlathuze estuary, South Africa. Marine Pollution Bulletin 46, 659–676.

Nakata, H., Sakai, Y., Miyawaki, T., 2002. Growth-dependent and species-specific accumulation of polychlorinated biphenyls (PCBs) in tidal flat organisms collected from the Ariake sea, Japan. Archives of Environmental Contamination and Toxicology 42, 222–228.

National Bureau of Statistics, 2002. Tanzania: 2002 population and housing census. <http://www.nbs.go.tz/>. (accessed 15.04.06).

Ritter, L., Solomon, K.R., Forget, J., Stemeroff, M., O'Leary, C.O., 1995. Persistent organic pollutants: an assessment report on DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls, dioxins, and furans. IPCS assessment report.

Scheren, P.A., Ibe, A.C., Janssen, F.J., Lemmens, A.M., 2002. Environmental pollution in the Gulf of Guinea – a regional approach. Marine Pollution Bulletin 44, 633–641.

Stäb, J.A., Traas, T.P., Stroomberg, G., van Kesteren, J., Leonards, P., Van Hattum, B., Brinkman, U.A.T., Cofino, W.P., 1996. Determination of organotin compounds in the foodweb of a shallow freshwater lake in the Netherlands. Archives of Environmental Contamination and Toxicology 31, 319–328.

Tam, N.F.Y., Wong, Y.S., 1995. Spatial and temporal variations of heavy metal contamination in sediments of a mangrove swamp in Hong Kong. Marine Pollution Bulletin 31, 254–261.

Tam, N.F.Y., Wong, Y.S., 1996. Retention and distribution of heavy metals in mangrove soils receiving wastewater. Environmental Pollution 94, 283–291.

Tam, N.F.Y., Yao, M.W.Y., 2002. Concentrations of PCBs in coastal mangrove sediments of Hong Kong. Marine Pollution Bulletin 44, 642–651.

Tanzania Ports Authority, 2006. Trade and traffic review. <http://www.tanzaniaports.com/>. (accessed 30.06.06).

Taylor, M., Ravilious, C., Green, E.P., 2003. Mangroves of East Africa. UNEP – World Conservation Monitoring Centre, Biodiversity Series No. 13, 25pp.

Ten Hallers-Tjabbes, C.C., Wegener, J.W., Van Hattum, B., Kemp, J.F., Ten Hallers, E., Reitsema, T.J., Boon, J.P., 2003. Imposex and organotin concentrations in *Buccinum undatum* and *Neptunea antiqua* from the North Sea: relationship to shipping density and hydrographical conditions. Marine Environmental Research 55, 203–233.

UNEP, 2001. Eastern Africa Atlas of Coastal Resources: Tanzania. UNEP, Nairobi.

Volesky, B., Holan, Z.R., 1995. Biosorption of heavy metals. Biotechnology Progress 11, 235–250.

Voorspoels, S., Covaci, A., Maervoet, J., De Meester, I., Schepens, P., 2004. Levels and profiles of PCBs and OCPs in marine benthic species

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from the Belgian North Sea and the Western Scheldt Estuary. Marine Pollution Bulletin 49, 393–404.
Willett, K.L., Ulrich, E.M., Hites, R.A., 1998. Differential toxicity and environmental fates of hexachlorocyclohexane isomers. Environmental Science and Technology 32, 2197–2207.
Yonezawa, Y., Fukui, M., Yoshida, T., Ochi, A., Tanaka, T., Noguti, Y., Kowata, T., Sato, Y., Masunaga, S., Urushigawa, Y., 1994. Degradation of tri-*n*-butyltin in Ise Bay sediment. Chemosphere 29, 1349–1356.

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Temporal and spatial changes of total and labile metal concentration in the surface sediments of the Vigo Ria (NW Iberian Peninsula): Influence of anthropogenic sources

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Rias have usually been considered to be coastal systems associated with the northwestern coastlines of Spain and Brittany, the southwestern coast of England and Ireland, several parts of the Mediterranean and the southeastern regions of China and Australia (Fairbridge, 1980; Evans and Prego, 2003). These coasts are being subjected to increasingly dense populations and industrial activities, since these areas are important for business, trade and aquaculture. As such, the present or future anthropogenic impact on these systems can be exemplified by the case of the Vigo Ria.

The Vigo Ria is commonly divided into three morphological zones (Prego and Fraga, 1992): the inner or estuarine; middle; and outer or oceanic zones (Fig. 1). Distributed within Ria areas, are approximately 550 mussel rafts, as well as large cultivated areas of clams and cockles in the San Simón Inlet. The main terrigenous sediment source to the Ria is the Alvedosa River, which drains a basin primarily dedicated to agriculture (Evans et al., 2003). The middle zone is the most affected from an anthropogenic standpoint: both banks are densely populated, the inhabitants numbering some 400,000, 77% of whom belong to the City of Vigo. Inputs occur from food factories and metal industries linked to shipyard and dock activities on the southern bank. The outer zone receives discharges from the two most important of the six sewage treatment plants.

Within the framework of Galicia, several research groups have reported that the concentration of trace metals in sediments dates from the 1980s (Prego and Cobelo-García, 2003). Among these published works, only a few have sampled more than 10 points (e.g. Rubio et al., 2000; Evans et al., 2003) and none of them include the completeVigo Ria. Moreover, there is a lack of information on metal concentrations in sediment fractions and their bioavailability and toxicity to biota, which may help confirm the effects of metal contamination (Ure and Davidson, 2001). If such data were available, it would be possible to evaluate the spatial-temporal variations of sediment total metal concentration and their labile fraction in this Ria by comparison between the year 1999, when around 150 sewers were feeding directly into the Ria, and 2005, six years after the wastewater treatment plants began functioning.

In order to study time-spatial changes of metal concentrations in the Vigo Ria, three sets of sediment samplings (Fig. 1) were carried out on board the R/V *Mytilus*: (1) 51 surface sediment samples (0–1 cm depth) from the uppermost oxic layer were collected by Van Veen grabs on October 1999; (2) the same Ria stations were sampled on May 2005; (3) two Ria cores were sampled in 2005 using a Gravity corer to extract two PVC tubes with 280 cm (core I) and 150 cm (core II) of the sediment column. The cores were sealed just after collection. The surface samples and core were stored at 4 °C until processed in the laboratory.

Following the collection, surface sediment samples were dried gently in an oven below 50 °C and kept in plastic storage for subsequent analyses. Both cores were sectioned in the laboratory; 18 samples – with a slice thickness of 1 cm – were extracted in core I and 13 samples in core II. Afterwards, the core and surface sediments were size fractionated by dry sieving into mud, sand and gravel through 63 and 2000 μm sieves. Then, samples were homogenized and stored in polyethylene containers at room temperature. Metal determinations were carried out in the finest fraction (<63 μm). In order to avoid the contamination of the sediment, these subsamples were taken using acid-washed polyethylene material.

Metals were measured under optimized operating conditions. To determine total metal content in the sediments, samples were previously digested following EPA 3052

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