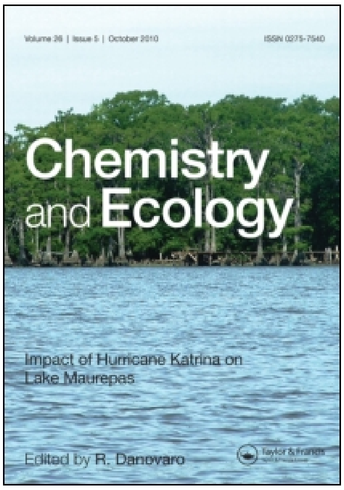

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Heavy-metal distribution and risk assessment of sediment and fish from El-Mex Bay, Alexandria, Egypt

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Heavy metals are increasingly being released into natural waters from geological and anthropogenic sources. The distribution of several heavy metals (Cr, Cu, Cd, Pb, Zn, and Hg) was investigated in muscle, gill, and liver in two different fish species seasonally collected in El-Mex Bay (autumn 2004–summer 2005). In order to evaluate the pollution status of the Bay, the concentrations of the selected metals in the labile and total fractions were analysed in sediment samples collected from eight sites in El-Mex Bay during autumn 2004. Also, the Index of Geoaccumulation (I_{geo}) for the sediment was estimated. The total and labile fractions of the selected metals in sediment samples were 15.2 and 62.8 $\mu g\,g^{-1}$ dw for Cu, 1.8 and 5.0 $\mu g\,g^{-1}$ dw for Cd, 79.1 and 130.3 $\mu g\,g^{-1}$ dw for Zn, 0.2 and 1.2 $\mu g\,g^{-1}$ dw for Hg, 35.8 and 93.0 $\mu g\,g^{-1}$ dw for Pb, and 13.9 and 31.0 $\mu g\,g^{-1}$ dw for Cr. The concentrations of all metals were lower in flesh than those recorded in liver and gill due to their physiological roles. The metal pollution index for fish was calculated. Health hazard calculations for the contaminated sediments and fish consumption were calculated to evaluate the effect of pollution on health.

Keywords: Heavy metals; Sediments; Fish; Risk assessment; El-Mex Bay; Egypt

1. Introduction

Interest in the problems related to contamination of the environment due to a wide variety of chemical pollutants (i.e. heavy metals) has increased in the last few years [1]. Heavy metals from geological and anthropogenic sources are increasingly being released into natural waters [2]. Contamination of aquatic ecosystems with heavy metals has seriously increased worldwide attention, and a large number of studies have been published on heavy metals in the aquatic environment [3, 4]. Under certain environmental conditions, heavy metals may accumulate to toxic concentrations and cause ecological damage.

Fish constitute an important low-cholesterol source of protein and other nutrients for humans throughout the world [5]. Fish provide omega-3 (n-3) fatty acids that reduce cholesterol levels

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and the incidence of heart disease [6, 7]. Fish are also popular tools in heavy-metal monitoring programmes in marine environments because their sampling, sample preparation, and chemical analysis are usually more simple, rapid, and less expensive than alternative investigations in water and sediments [8].

Sediments are composite materials, consisting of inorganic components, mineral particulates, and organic matter in various stages of decomposition. Sediment samples are sensitive and useful indicators of changes due to natural and anthropogenic events [9]. Sediments provide a temporal integrated indication of the aquatic environmental conditions and act as a major reservoir for metals, though some sediments can also act as a source of contaminants. Furthermore, they have a high physical–chemical stability, and their characteristics usually represent the average condition of the system, often being representative of the average water quality. Soils, along with rocks, are the terrigenous sources of elements to adjacent sediments and can indicate a local hot spot [10]. They are usually regarded as the ultimate sink for heavy metals discharged into the environment [11].

Distribution and accumulation of heavy metals are influenced by sediment texture, mineralogical composition, reduction/oxidation state, adsorption and desorption processes, and physical transport. Moreover, metals can be absorbed from the water column onto fine particles surfaces and thereafter move towards sediments; metals participate in various biogeochemical mechanisms, have a significant mobility, can affect ecosystems through bio-accumulation and bio-magnification processes, and can be toxic to the environment and to humans [12].

The leachable metal fraction is defined as the anthropogenic fraction of metals involved with the sediment particles. The assessment of trace metals on the acid-leachable elements is of great interest as the results are more informative as to the extent of trace-metal enrichment than total sediments, which include the residual or non-residual or non-polluted fraction [13]. The present study aims to determine the distribution of different heavy metals (Cr, Cu, Cd, Pb, Zn, and Hg) in muscle, gill, and liver in two fish species seasonally collected in El-Mex Bay (autumn 2004 to summer 2005). The total and labile fractions and the Index of Geoaccumulation (I_{geo}) in sediment samples are also estimated. Finally, we calculate the health hazards resulting from contaminated sediments and fish consumption.

2. Materials and methods

2.1 *Study area*

El-Mex Bay is considered one of the most important hot spot areas in Alexandria. It is located between longitude 29° 47.1′ to 29° 50.4′ E and latitude 31° 7.5′ to 31° 9′ N (figure 1) and subject to large quantities of untreated industrial and domestic sewages. El-Mex Bay is also important economically for fishing. Two commercially fish species (*Siganus rivulatus* and *Sargus sargus*) belonging to Siganidae and Sparidae, respectively, were seasonally collected in El-Mex Bay (between autumn 2004 and summer 2005). Sediment samples were collected in selected stations (eight sites) in summer 2005 in order to estimate the pollution distribution due to industrial and other activities (figure 1).

2.2 *Sampling*

About 20 specimens of the two studied species were collected during the period of study (autumn 2004 to summer 2005). Fish were nearly of the same size and weight. Fish samples were stored in prewashed polyethylene bags and brought to the laboratory on the same day of

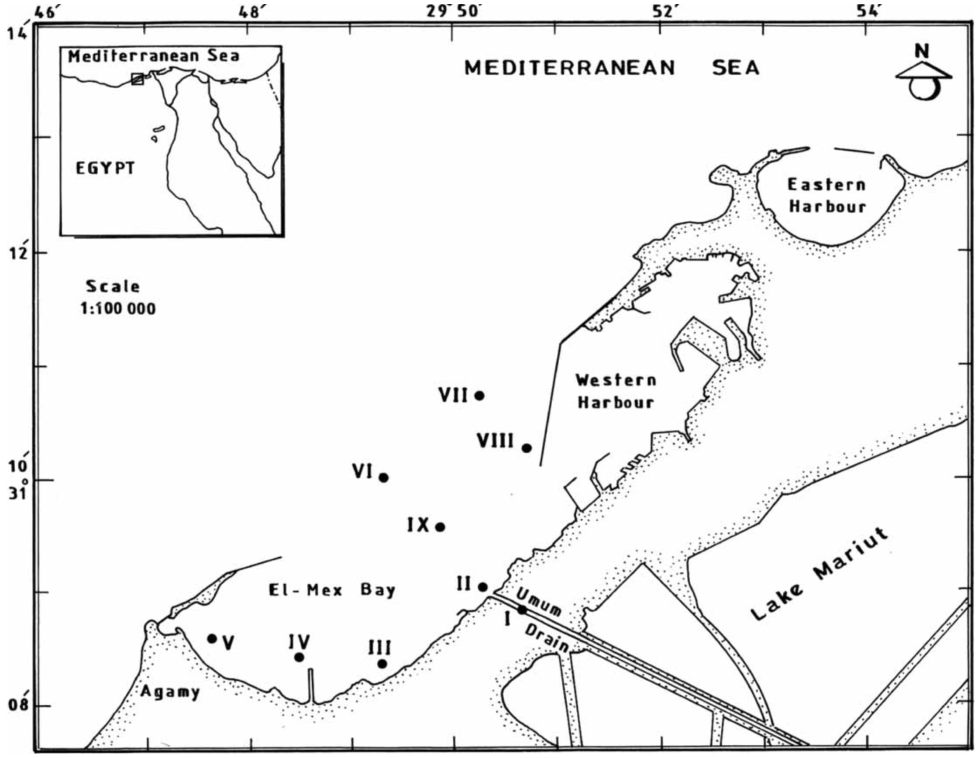

Figure 1. Area of study and sampling locations during autumn 2004 to summer 2005.

capture. In the laboratory, the length and weight of each fish were measured, and the condition factor (CF) for each species was calculated (table 1). Gills and liver are chosen as target organs for assessing metal accumulation. Muscle is chosen because of its public concern. Gills are chosen because of their direct contact with the surrounding water. Different organs (muscle, liver, and gill) were kept separately for each species and homogenized to make a composite sample. Each composite sample was weighed separately in clean, labelled Petri dishes and dried for several days at 50 °C to constant weight. Pulverization and homogenization were achieved by grinding the tissue samples which were analysed for heavy metals according to UNEP/FAO/IAEA/IOC [14].

Table 1. Weight, total length, and condition factor (CF) of *Siganus rivulatus* and *Sargus sargus* from El-Mex Bay during autumn 2004 to summer 2005.

Fish species	No. of samples	Season	Mean total length (cm) ± SD	Mean weight (g) ± SD	CF	CF (average)
Siganus rivulatus	20	Autumn	18.65 ± 3.21	80.6 ± 10.25	1.2	1.1
	20	Winter	19 ± 2.03	58.3 ± 6.45	0.9	
	20	Spring	18.65 ± 1.78	70.6 ± 6.85	1.1	
	20	Summer	19.5 ± 3.02	105 ± 11.08	1.4	
Sargus sargus	20	Autumn	15.2 ± 2.22	45.15 ± 2.92	1.3	1.4
	20	Winter	13.85 ± 1.54	40.85 ± 2.66	1.5	
	20	Spring	17.2 ± 2.45	52.8 ± 3.65	1	
	20	Summer	17.85 ± 2.35	95.25 ± 6.65	1.7	

An exact weight of dry sample (triplicate, each 0.2–0.3 g) was placed in Teflon vessels followed by the addition of 5 ml of nitric acid (Merck) and 2 ml of perchloric acid. The vessels were tightly covered and allowed to predigest over night at room temperature. The digestion block was placed on a preheated hot plate at 90 °C until all the materials were dissolved. The samples were cooled to room temperature and diluted with deionized water, filtered, and the volume made up to 10 ml with deionized water. The resulting solutions were analysed using a flame atomic absorption spectrophotometer (Perkin Elmer, Model 2380).The results were expressed as $\mu g\, g^{-1}$ wet wt.

A mercury analysis was conducted, using cold-vapor atomic absorption (SOLAAR32). One gram of homogenized dry samples was weighed into a previously pre-cleaned Teflon vial, 5 ml of nitric acid and 2 ml of perchloric acid were added, and the mixture was heated at 50 °C until all the materials were dissolved. After cooling to room temperature, the volume was diluted using bidistilled water, filtered and made up to 10 ml, and then subjected to Hg determination with triplicate analysis [14].

The absorption wavelength and detection limits were as follows: 228.8 nm and 0.06 $mg\, kg^{-1}$ for Cd; 324.7 nm and 0.06 $mg\, kg^{-1}$ for Cu; 217.0 nm and 0.8 $mg\, kg^{-1}$ for Pb; 213.9 nm and 0.7 $mg\, kg^{-1}$ for Zn; 357.9 nm and 0.009 $mg\, kg^{-1}$ for Cr; and 253.7 nm and 0.008 $mg\, kg^{-1}$ for Hg.

2.3 *Length–weight relationship and the CF*

The CF was calculated according to the following equation [15]:

$$\frac{W \times 100}{L^3},$$

where W is the weight of the fish, and L is its length.

2.4 *Metal Pollution Index*

The overall metal contents of the two fishes were compared, using the metal pollution index (MPI) calculated with the following formula [16, 17]:

$$\mathrm{MPI} = (M_1 \times M_2 \times M_3 \times \cdots \times M_n)^{1/n},$$

where M_n is the concentration of metal n expressed in $\mu g\, g^{-1}$ of wet weight.

2.5 *Determination of total heavy metals in sediment*

The determination of total heavy metals in sediments was measured according to the reported method of analysis [18]. An exact weight of dry sample (about 0.2 g) of sediment was completely digested in Teflon vessels using a mixture of HNO_3, HF, and $HClO_4$ (3:2:1) (triplicate digestions were made for each sample). The final solution was diluted to 25 ml with double-deionized distilled water. All digested solutions were analysed in triplicate using an atomic absorption spectrophotometer (Perkin Elmer, Model 2380). The results were expressed in $\mu g\, g^{-1}$ (ppm) dry weight.

2.6 *Determination of total mercury in sediment*

Mercury was determined in sediment samples following the conventional published method [18]; 0.5 g of homogenized air dry sample was digested with 3 ml of aqua regia

(9:1 HNO_3:HCl) in Teflon vessels. The mixture was heated for 1 h at 50 °C. After cooling to the room temperature, the mixture was diluted to 25 ml with double-deionized distilled water.

2.7 *Determination of leachable heavy metals in sediment*

An aliquot of 0.5 ± 0.05 g of dry sediment was treated with 40 ml of 1 N HCl at room temperature and the mixture stirred for 2 h, centrifuged at 5000 rpm for 2 min, then filtered in 50 ml polypropylene bottles ready for analysis [19].

2.8 *Reagents and quality assurance*

All reagents used were of analytical grade (Merck). The digestion and analytical procedures were checked by analysis of standard reference materials sediment: (SD – M – 2/TM, marine sediment) and for fish: (DORM-1 for dog fish) provided by the National Research Council of Canada. A replicate analysis of these reference materials showed a good accuracy, with recovery rates for metals between 92% and 104% for fish and 92% and 98% for sediment. To prevent contamination, all used plastic vessels were previously washed in diluted nitric acid and deionized water.

2.9 *Grain-size analysis*

A grain-size analysis was carried out using the conventional method [20]. About 30 g of washed and quartered dried sample was subjected to the combined technique of dry sieving and pipette analysis (according to the texture of the sediment).

2.10 *Determination of organic carbon*

Organic-carbon content was determined using the acid/dichromate titration method as described by Gaudette *et al.* [21]. This method utilizes exothermic heating and oxidation in the presence of potassium dichromate and concentrated H_2SO_4, and titration of excess dichromate with a standard 0.5 N ferrous ammonium sulfate solution. The concentrations were calculated according to the following equation:

$$\text{Percentage organic carbon} = 10\left(1 - \frac{T}{S}\right)\left(0.003 \times \frac{100}{W}\right),$$

where T = ferrous solution (ml); S = standardization blank; W = weight of sediment sample (g).

The organic carbon is converted to organic matter by multiplying the organic carbon values by the factor of 1.724.

3. Results and discussion

3.1 *Length–weight relationship and the CF*

The length–weight relationship is affected by various factors such as the availability of food, rate of feeding, development of gonads, and spawing. The CF for both species was higher in the summer than in other seasons (1.4 and 1.7) for *Siganus rivulatus* and *Sargus sargus*, respectively (table 1). This may be due to the spawning activity of the fish [22, 23].

3.2 *Heavy metals in fish*

The concentrations of heavy metals (Cu, Pd, Hg, Zn, Cr, and Cd) expressed as $\mu g\,g^{-1}$ wet weight in muscle, liver, and gill of the two selected species are summarized in table 2. In both species, the concentration of the six metals under investigation was higher in the summer than in other seasons. Similar increases in metal levels in tissues of some invertebrate and fish species were observed during the summer. These were related to the increased metabolism due to high temperatures [24].

Because Cu is an essential trace nutrient, most marine organisms have evolved mechanisms to regulate concentrations of this metal in their tissues in the presence of variable concentrations in the ambient water, sediments, and food [23]. Liver had accumulated the highest level of Cu, while the muscle had the lowest content. The average concentrations of copper were 31.94 ± 8.87, 8.5 ± 3.46, and $2.34 \pm 0.73\,\mu g\,g^{-1}$ wet weight for *Siganus rivulatus* in liver, gill, and muscle, respectively, and 16.95 ± 5.06, 3.45 ± 1.94, and $1.64 \pm 0.37\,\mu g\,g^{-1}$ wet weight) for *Sargus sargus* in liver, gill, and muscle, respectively (table 2). The higher level of copper observed for *Siganus rivulatus* compared with that in *Sargus sargus* is due to the food habit where the first is herbivorous, and the second feeds mainly on crustaceans and molluscs as well as small fishes. These results were highly comparable with those reported by Khaled [25].

Zn is an essential micronutrient in all marine organisms, being a cofactor in nearly 300 enzymes. Therefore, marine animals are able to regulate tissue Zn at the concentrations in sea water and sediment from normal ambient levels to incipient lethal levels [26]. The zinc concentration in different organs can be ordered as follows: liver > gill > muscles. The bioaccumulation of zinc is greatly affected by the types of tissues analysed, with higher concentrations in gills and liver, and lower concentrations in bones and muscles.

Pb is a non-essential element, being a toxic metal that can affect humans when ingested or inhaled in high doses, causing encephalopathy, colic, renal diseases, and anaemia. In particular, children are susceptible to lead toxicity, with numerous epidemiological studies reporting neurocognitive functions to be inversely correlated with blood or tooth-lead levels [27]. In fish, lead can cause deficits or decreases in survival, growth rates, development, and metabolism, in addition to increased mucus formation [28]. According to the present study (table 2), the gills show a high accumulation of lead. This could be attributed to the similarity of lead and calcium in their deposition and mobilization from gills [29, 30]. The high content of lead in gills is approved by the NRCC [31], and the lower pH value at the gill surface due to the respired CO_2 may dissolve lead, changing it into a soluble form which could diffuse into the gill tissues. The relatively low rate of binding lead with the SH group explained the low Pb content in the muscle of the tested fish species. The accumulation pattern of Pb in different organs follows the order: gill > liver > flesh.

Cadmium is a serious environmental contaminant that is also transported atmospherically. In fish, it can cause anaemia and vertebral fractures, osmoregulatory problems, decreased digestive efficiency, haematological and biochemical effects, erratic swimming, and mortality [28]. The distribution pattern of cadmium in *Siganus rivulatus* and *Sargus sargus* is in the descending order liver > gill > muscle. The liver recorded the highest concentration of cadmium. This is in agreement with WHO–IPCS–Environmental Health criteria for Cd which reported that Cd is stored in the body in various tissues, but the main site of accumulation in aquatic organisms is in the kidney and liver [32].

Mercury is one of the most toxic metals for marine fauna. It is listed as a priority pollutant by international agencies in charge of marine environmental protection [33]. Hg accumulation in fish is affected by water chemistry (e.g. pH, temperature, turbidity), the chemical form of Hg in the environment and food-chain structure [34]. The different feeding behaviour of two fish species may explain the differences in terms of Hg concentrations.

Table 2. Concentrations of heavy metals (μg/g wet weight) of *Siganus rivulatus* and *Sargus sargus* collected from El-Mex Bay during autumn 2004 to summer 2005.

Species	CSeason	Organ	Heavy-metal concentration ($\mu g\,g^{-1}$ wet weight) Cu	Pb	Hg	Cd	Zn	Cr	MPI
Siganus rivulatus	Autumn	Liver	31.25	7.88	0.55	1.6	200.21	2.05	6.68
		Gill	10.09	9.03	0.11	0.93	24.65	1.92	2.76
		Flesh	2.26	1.83	0.06	0.39	9.24	1.21	1.01
	Winter	Liver	23.22	4.56	0.25	1.9	131.87	1.94	4.84
		Gill	5.55	6.38	0.1	0.48	36.14	0.81	1.92
		Flesh	1.65	1.1	0.07	0.3	7.26	0.32	0.67
	Spring	Liver	29.06	5.77	0.15	0.73	115.12	1.05	3.61
		Gill	5.72	7.96	0.1	0.2	19.53	1.42	1.71
		Flesh	2.09	1.37	0.04	0.13	8.94	0.64	0.66
	Summer	Liver	44.23	9.04	1.1	2.56	283.04	5.71	11.05
		Gill	12.63	11.97	0.71	0.69	52.42	3.22	4.82
		Flesh	3.36	2.48	0.22	0.42	14.28	1.26	1.55
	Mean ± SD	Liver	31.9 ± 8.9	6.81 ± 2.0	0.51 ± 0.4	1.7 ± 0.8	182.6 ± 76.43	2.69 ± 2.06	6.53 ± 3.26
		Gill	8.5 ± 3.46	8.83 ± 2.4	0.25 ± 0.3	0.58 ± 0.3	33.19 ± 14.6	1.84 ± 1.02	2.8 ± 1.4
		Flesh	2.34 ± 0.7	1.69 ± 0.6	0.1 ± 0.08	0.38 ± 0.2	9.93 ± 3.03	0.86 ± 0.46	0.97 ± 0.42
Sargus sargus	Autumn	Liver	19.47	5.22	0.19	0.73	97.05	2.17	3.97
		Gill	4.32	8.4	0.05	0.71	17.84	0.8	1.62
		Flesh	1.82	1.12	0.03	0.28	5.04	0.42	0.58
	Winter	Liver	14.38	1.22	0.06	0.53	59.7	1.02	1.8
		Gill	1.23	8.13	0.03	0.37	13.04	0.72	1.01
		Flesh	1.82	1.03	0.01	0.11	4.03	0.38	0.38
	Spring	Liver	11.32	2.28	0.09	0.68	84.08	1.33	2.37
		Gill	2.6	6.21	0.02	0.25	10.06	0.39	0.83
		Flesh	1.12	1.09	0.03	0.19	4.32	0.23	0.44
	Summer	Liver	22.61	3.14	0.33	1.87	111.23	2.94	4.93
		Gill	5.65	7.06	0.08	1.07	23.66	1.26	2.16
		Flesh	1.98	1.43	0.05	0.36	6.75	0.77	0.8
	Mean ± SD	Liver	16.9 ± 5.06	3.95 ± 2.7	0.17 ± 0.1	0.95 ± 0.62	88.02 ± 21.89	1.87 ± 0.68	3.22 ± 1.41
		Gill	3.45 ± 1.9	6.6 ± 2.6	0.04 ± 0.03	0.6 ± 0.37	16.15 ± 5.94	0.79 ± 0.36	1.4 ± 0.6
		Flesh	1.64 ± 0.4	1.17 ± 0.2	0.03 ± 0.02	0.24 ± 0.11	5.03 ± 1.22	0.45 ± 0.23	0.55 ± 0.19

The distribution of chromium in fish is similar to that for Zn, Cu, Hg, Pb, and Cd. The bioaccumulation of Cr is mainly in the liver and gills. The Cr concentration in *Siganus rivulatus* is higher than that in *Sargus sargus*. The two studied species showed Cr in their flesh ($0.86 \pm 0.46\ \mu g\ g^{-1}$ wet wt.) and ($0.45 \pm 0.23\ \mu g\ g^{-1}$ wet wt.) for *Siganus rivulatus* and *Sargus sargus*, respectively.

Higher metal concentrations were found in liver tissue, while the lowest were detected in muscle tissues because the liver is the major organ involved in xenobiotic metabolism in fish. Organisms retain metals through specific binding proteins known as metallothioneins in their liver. Metallothioneins play an important role in metal homeostasis and in protection against heavy-metal toxicity. The low concentrations of the examined metals in the muscles of the fish species may reflect the low levels of these binding proteins in the muscle [35].

The observed variability of metal levels in different species depends on the feeding habits, ecological needs, metabolism, age, size, and length of the fish and their habitats [36]. The higher metal concentration in the gill could be because of the element complexing with the mucus (which is impossible to remove completely from the lamellae) before the tissue is prepared for analysis [37].

In the present study, the metal concentrations found in edible parts of the two species under investigation are still within the permissible limits proposed by different organizations [38–43].

The lowest metal pollution indexes (MPI) were recorded for *Sargus sargus* (figure 2). MPI recorded its maximum value for the liver of both species, followed by the gill, and finally the muscles.

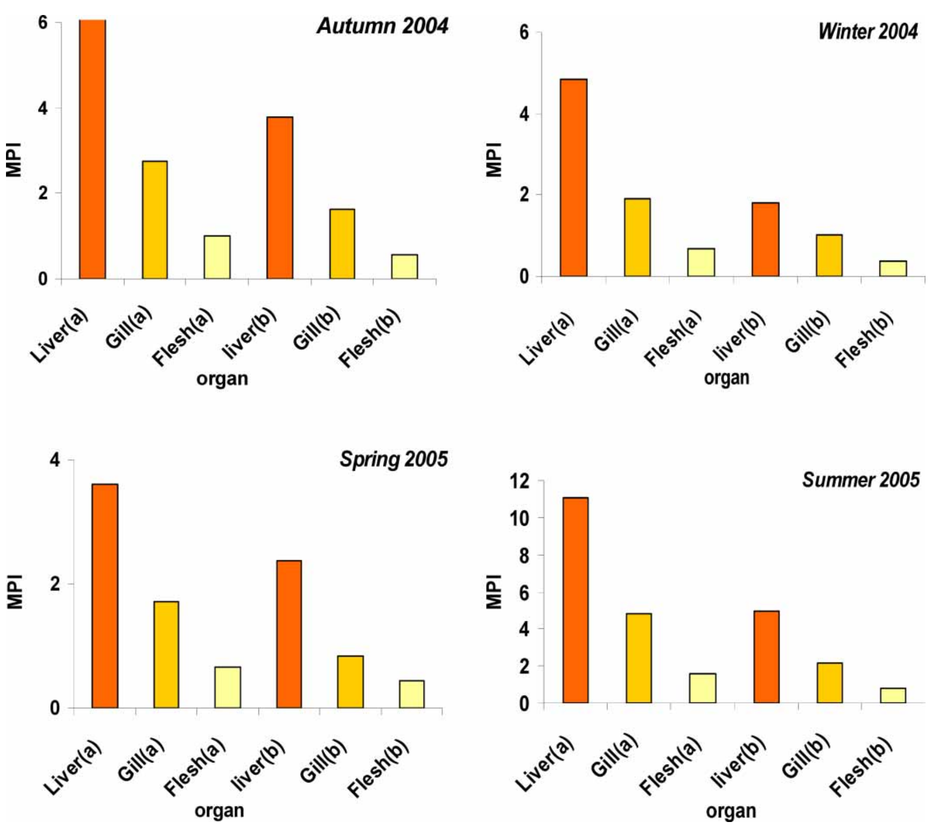

Figure 2. Metal pollution index (MPI) for the two selected species: (a) *Siganus rivulatus*; (b) *Sargus sargus*.

3.3 *Grain-size analysis*

The grain size of the sediment is a specific parameter. The mean grain size and the median diameter may reflect the general characteristics of granule metric composition of sediment. While the values of skewness and kurtosis reflect the uniformity of the distribution of sediment composition, the distribution of sediment composition depends on the equilibrium between gravity of sediment and water forces. This is one of the major controlling factors for the distribution of trace metals in coastal areas [44].

Table 3 lists the grain sizes of the sediment samples. All sediment types are sand except for station VIII (because of the ecology of the region under study), where the major part of sediment is sand, and the minor part is clay.

3.4 *Heavy metals in sediment*

Bottom sediments can serve as a reservoir for heavy metals and deserve special consideration in the planning and design of aquatic pollution research [45]. One advantage of the use of sediment analysis rather than water analysis is the evaluation of the degree of contamination in aquatic medium, which gives a stable image over time compared with the huge temporal variability in the levels of contaminants in water.

The ratio of the heavy-metal concentrations in the labile fraction to the total concentration of metals in the sediment is expressed as a percentage, known as the percentage of extractability. The labile fraction is usually defined as exchangeable carbonate-bound, iron and manganese oxide bound and organically bound fractions. The ratio between labile and total heavy metals may be referring to the anthropogenic input or the new input percentage (NIP).

Figure 3 summarizes the concentrations of selected heavy metals in total and leachable fractions. Copper is sorbed rapidly to sediment, resulting in high residue levels. Most copper in the particles is either as a constituent of mineral phases or adsorbed to oxide surfaces or organic matter depending on the type of sediment, pH, competing cations, and the presence of legends and Fe/Mn oxides. The average concentration of total copper in sediment was 41.53 $\mu g\,g^{-1}$, at station II in front of El-Umum drain; this may be due to the discharge of effluents via the El-Mex pumping station. The antifouling paints used for ships and boats are regarded as one of the important sources, which increased the level of copper in El-Mex Bay. The distribution of leachable Cu (non-residual Cu) showed the same pattern of total sediment, affected by the anthropogenic activities. Therefore, it is the non-residual metal concentration which truly reflects the extent to which the sediments have been subjected to heavy-metal pollution.

The high concentrations of total lead recorded in El-Mex Bay, may be related to the release of Pb from the freshwater discharge of El-Umum Drain (carrying industrial, agricultural,

Table 3. Grain-size analysis of sediment.

Site no.	Mean size (Φ)	Sorting (σI)	Skewness (Sk1)	Sand (%)	Silt (%)	Clay (%)	Sediment type	TOM
II	1.97	0.81	–	100	–	–	Sand	0.929
III	1.86	1.1	–	100	–	–	Sand	0.404
IV	0.86	1.14	–	100	–	–	Sand	0.875
V	1.78	0.85	–	100	–	–	Sand	1.012
VI	1.12	0.82	–	100	–	–	Sand	0.496
VII	0.82	0.84	–	100	–	–	Sand	0.715
VIII	5.82	1.82	74.87	6.75	74.87	18.38	Clayey silt	5.292
IX	1.6	0.9	–	100	–	–	Sand	0.584

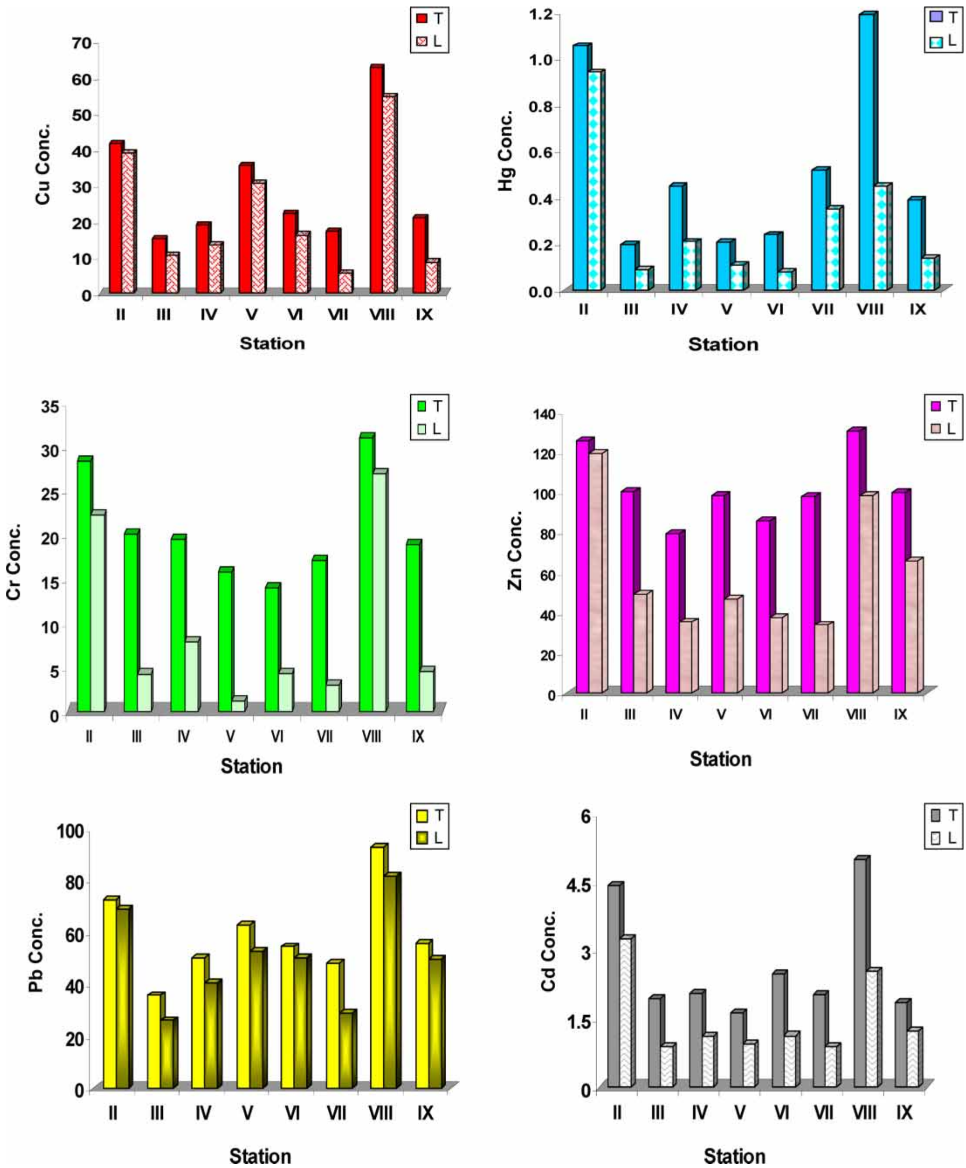

Figure 3. Total and leachable concentrations ($\mu g\ g^{-1}$ dw) fraction of Pb, Cr, Cu, Hg, Zn, and Cd. T: total fraction of heavy metals; L: leachable fraction of heavy metals.

and sewage effluents) and from the atmospheric deposition, where Pb is released from the combustion of gasoline from motor vehicles. Due to the silty texture of sediment at station VIII, a higher content of Pb in both total and labile fractions was recorded. This indicates that more heavy metals were bound strongly in the silt and clay fraction than the sand-sized fraction of the sediments. The metal adsorption capacity was in the order of sand < silt < clay, due to the increase in surface areas as the particle size decreased from sand to clay [46].

The high extractability percentages of Pb recorded in most stations under study indicated a new input in El-Mex Bay, which was probably due to the domestic, industrial effluents and the atmospheric deposition; many reported studies have also indicated elevated levels of heavy metals in aquatic systems receiving effluents from urban areas, domestic, and untreated sewage [45, 47].

The distribution pattern of cadmium is similar to that of lead. Station II, located in the vicinity of El-Umum Drain, has the highest concentration of cadmium (4.41 $\mu g\,g^{-1}$). This may indicate that cadmium is derived from land base activities or from El-Umum Drain. The high concentration of Cd may be due to the use of Cd as pigments in ship painting. Sediment with a silty texture (VIII) contains a higher concentration of total cadmium than sediments with a sandy texture.

Station II, located near the outfall of El-Umum Drain, which discharges large amounts of agricultural, municipal, and industrial wastes, recorded a high concentration of total mercury.

The total concentration of zinc recorded in this study ranged between 79.05 and 130.26 $mg\,kg^{-1}$ with an average value of $101.98 \pm 17.64\,mg\,kg^{-1}$. The contamination of coastal regions including estuaries and marginal seas is attributed to a number of causes. The most important is direct input from ships and through atmospheric fallout. The concentration of labile Zn (non-residual Zn), ranging between 33.81 and 119.26 $mg\,kg^{-1}$ with $60.72 \pm 31.83\,mg\,kg^{-1}$, shows the same pattern as the total Zn in sediments, indicating that most of Zn is in a leachable form, $Zn(OH)_2$.

The chromium concentration fluctuated between 13.94 and 30.95 $\mu g\,g^{-1}$ with an average value of $20.55 \pm 5.98\,\mu g\,g^{-1}$ in the total fraction, while the non-residual Cr fluctuated between 1.2 and 26.84 $\mu g\,g^{-1}$, with an average value of $9.79 \pm 9.48\,\mu g\,g^{-1}$

3.5 *Total organic matter*

Total organic matter (TOM) is one of the most important collectors of pollutants in the marine sediments. Organic matter tends to form strong organo-metallic complexes with metals, rendering them immobile. An increase in TOM content may result in an increase in levels of metals in marine sediment.

The total organic matter is shown in table 3. A high concentration of TOM is observed in station II, which may be due to the discharge of agricultural and domestic wastewater from El-Umum Drain, which is highly enriched with organic matter. Station VIII, which is of the clayey silt type, shows a higher TOM content.

The composition and structure of the organic matter in the sediment vary due to its origin and geological history in the marine and aquatic environment. Phytoplankton and zooplankton are the most abundant source of organic material in the sediments [48]. The organic-matter content of the sediment is a result of the contribution of teragenous materials and the decomposition of plants and animals by the action of bacteria [49].

Table 4 shows the correlation matrices between TOM and the studied metals in both fractions. The high correlation coefficients observed between the heavy metals and TOM may indicate that metals are highly associated with organic matter and are probably derived from the same origin.

3.6 *Geoaccumulation index(I_{geo})*

The heavy-metal pollution levels in sediment collected were measured using the Index of Geoaccumulation (I_{geo}) [50] (table 5), which consists of six grades. The highest grade reflects 100-fold metal concentration relative to background values:

$$I_{geo} = \log_2 [C_n/(1.5 \times B_n)]$$

Table 4. Correlation coefficients between the total organic matter (TOM), and total and labile fractions of heavy metals ($n = 9$, $p < 0.005$).

	TOM	Cu (T)	Cu (L)	Pb (T)	Pb (L)	Hg (T)	Hg (L)	Cd (T)	Cd (L)	Zn (T)	Zn (L)	Cr (T)	Cr (L)
TOM	1												
Cu (T)	0.87	1											
Cu (L)	0.80	0.98	1										
Pb (T)	0.84	0.97	0.93	1									
Pb (L)	0.73	0.93	0.91	0.97	1								
Hg (T)	0.73	0.80	0.77	0.83	0.77	1							
Hg (L)	0.27	0.53	0.56	0.56	0.55	0.84	1						
Cd (T)	0.75	0.85	0.85	0.84	0.83	0.94	0.77	1					
Cd (L)	0.51	0.76	0.79	0.77	0.82	0.90	0.90	0.93	1				
Zn (S)	0.67	0.82	0.79	0.76	0.72	0.84	0.72	0.84	0.83	1			
Zn (L)	0.51	0.76	0.77	0.75	0.80	0.84	0.82	0.86	0.96	0.91	1		
Cr (T)	0.72	0.78	0.77	0.73	0.71	0.92	0.75	0.90	0.88	0.87	0.88	1	
Cr (L)	0.74	0.81	0.82	0.77	0.76	0.93	0.74	0.97	0.91	0.84	0.87	0.97	1

Note: T: total fraction; L: labile fraction.

Table 5. Index of geoaccumulation (I_{geo}).

Mean	I_{geo}	Sediment state	Background [52]
Cu	1.30	Very little pollution	8
Pb	1.50	Very little pollution	14
Cr	0.00	Unpolluted	17
Zn	0.02	Unpolluted	67
Cd	2.22	Little pollution	0.38

where C_n is the measured concentration of element n in sediment sample, and B_n is the background concentration of element n. A factor of 1.5 is used because of possible variations in background data due to lithogenic effects. This study found I_{geo} values of 1.3, 1.5, 0, 0.02, and 2.22 for Cu, Pb, Cr, Zn, and Cd, respectively, which indicated unpolluted ($I_{geo} < 1$), very little pollution ($1 < I_{geo} < 2$), little pollution ($2 < I_{geo} < 3$), moderately polluted ($3 < I_{geo} < 4$), highly polluted ($4 < I_{geo} < 5$), and very highly polluted ($I_{geo} > 5$) [51].

3.7 *Risk assessment*

The following equations were used for calculate the assessment of human risk [53]:

$$\text{Ingestion of fish } (\text{mg kg}^{-1}\text{day}^{-1}) = \frac{\text{CF} \times \text{IRf} \times \text{FI} \times \text{AF}}{\text{BW}},$$

where CF = concentration of the contaminant in fish (mg kg^{-1} fresh weight (fw)]; IRF = ingestion rate of fish (kg fw day^{-1}) (0.015 and 0.055 kg fw day^{-1}) for child and adult respectively); FI = fraction contaminated (unit less) (0.5 for both child and adult); AF = absorption factor (unit less) (1 for both child and adult); and BW = body weight (kg) (15 and 70 kg for a child and adult, respectively).

$$\text{Daily exposure } (\text{mg kg day}^{-1}) = \left[\frac{6 \times \text{daily exposure}_{\text{child}}}{70}\right] + \left[\frac{64 \times \text{daily exposure}_{\text{adult}}}{7}\right].$$

The hazard index is below 1 for the species (table 6), but in the future human risk may occur depending on the agricultural and industrial development in this region.

$$\text{Ingestion of contaminated sediment (ICS)}(\text{mg kg}^{-1}\ \text{day}^{-1}) = \frac{\text{CS} \times \text{IRs} \times \text{EF} \times \text{AF}}{\text{BW}}$$

$$\text{Dermal contact with contaminated sediment (DCCS)}(\text{mg kg}^{-1}\text{day}^{-1}) = \frac{\text{CS} \times \text{SA}_\text{s} \times \text{AD} \times \text{AS}_\text{s} \times \text{Mf} \times \text{ED}_\text{s} \times \text{EF}}{\text{BW}},$$

where CS = concentration of heavy-metal contaminants in the sediment (mg kg^{-1} dw); IRs = ingestion rate of sediment (0.001 and 0.00035 kg dw per exposure day for a child and adult, respectively); EF = exposure frequency (30 for both a child and adult) (day yr^{-1}); AF = absorption factor (1 for both child and adult); SAs = dermal surface area for sediment exposure (0.17 and 0.28 1 h^{-1} for a child and adult, respectively); AD = dermal adherence rate for sediment (0.51 and 3.75 mg cm^{-2} for a child and adult, respectively); ASs = dermal absorption rate (0.01 and 0.0051 h^{-1} for a child and adult, respectively); Mf = matrix factor (0.15 for both child and adult); EDs = duration of exposure to sediment (8 h day^{-1} for both a child and adult); and BW = body weight (15 and 70 kg for a child and adult, respectively). Table 7 shows the values for the ingestion of sediment and dermal contact with contaminated sediment.

Table 6. Ingestion of fish (mg kg^{-1} day^{-1}) and daily exposure level (mg kg^{-1} day^{-1}).

Species	Metal	Fraction	Adult	Child
Sargus sargus	Cu	Ingestion of fish	6.44×10^{-4}	8.2×10^{-4}
		Daily exposure	5.96×10^{-3}	
		St. range of hazard	0.02–0.05	
	Pb	Ingestion of fish	4.6×10^{-4}	8.85×10^{-4}
		Daily exposure	4.25×10^{-3}	
		St. range of hazard	1.7–4.4	
	Hg	Ingestion of fish	1.17×10^{-5}	1.5×10^{-5}
		Daily exposure	1.08×10^{-4}	
	Cd	Ingestion of fish	9.42×10^{-5}	1.2×10^{-4}
		Daily exposure	8.71×10^{-4}	
		St. range of hazard	0.11–0.16	
	Zn	Ingestion of fish	1.98×10^{-3}	2.52×10^{-3}
		Daily exposure	1.83×10^{-3}	
		St. range of hazard	1.08–1.2	
	Cr	Ingestion of fish	1.77×10^{-4}	2.25×10^{-4}
		Daily exposure	1.64×10^{-3}	
Siganus rivulatus	Cu	Ingestion of fish	9.19×10^{-4}	1.17×10^{-4}
		Daily exposure	8.5×10^{-3}	
		St.range of hazard	0.02 – –0.05	
	Pb	Ingestion of fish	6.64×10^{-4}	8.85×10^{-4}
		Daily exposure	6.14×10^{-3}	
		St. range of hazard	1.7–4.4	
	Hg	Ingestion of fish	3.92×10^{-5}	5×10^{-5}
		Daily exposure	3.63×10^{-4}	
	Cd	Ingestion of fish	1.49×10^{-4}	1.9×10^{-4}
		Daily exposure	1.38×10^{-3}	
		St. range of hazard	0.11–0.16	
	Zn	Ingestion of fish	31.9×10^{-3}	4.97×10^{-3}
		Daily exposure	3.61×10^{-2}	
		St. range of hazard	1.08–1.2	
	Cr	Ingestion of fish	3.38×10^{-4}	4.3×10^{-4}
		Daily exposure	3.13×10^{-3}	

Table 7. Calculation of ingestion of sediment, dermal contact with contaminated sediment, and daily exposure to sediment for children and adults.

Metal	Fraction	Total		Leachable	
		Adult	Child	Adult	Child
Cu	Ingestion of sediment	4.38×10^{-3}	5.84×10^{-2}	3.34×10^{-3}	4.45×10^{-2}
	Dermal contact	7.89×10^{-2}	6.08×10^{-2}	6.01×10^{-2}	4.63×10^{-2}
	Total	8.33×10^{-2}	0.119	6.34×10^{-2}	9.08×10^{-2}
	Daily exposure	0.772		0.587	
	St. range of hazard	0.02−0.05			
Pb	Ingestion of sediment	8.87×10^{-3}	0.118	7.5×10^{-3}	9.99×10^{-2}
	Dermal contact	0.16	0.123	0.135	0.104
	Total	0.168	0.241	0.142	0.204
	Daily exposure	1.55		1.51	
	St. range of hazard	1.7−4.4			
Zn	Ingestion of sediment	1.53×10^{-2}	0.204	9.1×10^{-3}	0.121
	Dermal contact	0.275	0.212	0.164	0.126
	Total	0.291	0.416	0.173	0.248
	Daily exposure	2.69		1.6	
	St. range of hazard	1.08−1.2			
Cd	Ingestion of sediment	3.99×10^{-4}	5.33×10^{-3}	2.24×10^{-4}	2.98×10^{-3}
	Dermal contact	7.2×10^{-3}	5.55×10^{-3}	4.02×10^{-3}	3.1×10^{-3}
	Total	7.61×10^{-3}	1.09×10^{-2}	4.25×10^{-3}	6.08×10^{-3}
	Daily exposure	7.61×10^{-3}		3.93×10^{-2}	
	St. range of hazard	0.11−0.16			
Cr	Ingestion of sediment	3.08×10^{-3}	4.11×10^{-2}	1.47×10^{-3}	1.96×10^{-2}
	Dermal contact	5.55×10^{-3}	4.28×10^{-2}	2.64×10^{-2}	2.04×10^{-2}
	Total	8.63×10^{-3}	8.39×10^{-2}	2.79×10^{-2}	3.99×10^{-2}
	Daily exposure	8.61×10^{-2}		0. 259	
Hg	Ingestion of sediment	7.95×10^{-4}	1.06×10^{-3}	4.5×10^{-5}	6×10^{-4}
	Dermal contact	1.43×10^{-3}	1.1×10^{-3}	8.1×10^{-4}	6.24×10^{-4}
	Total	1.51×10^{-3}	2.16×10^{-3}	8.55×10^{-4}	1.22×10^{-3}
	Daily exposure	1.4×10^{-2}		7.9×10^{-3}	

Table 8. Margin of exposure.

Metal	RFD (mg kg^{-1} day^{-1})	Species	MOE
Cd	1.0×10^{-3}	*Siganus rivulatus*	1.22
		Sargus sargus	0.77
Pb	7.1×10^{-4}	*Siganus rivulatus*	7.62
		Sargus sargus	5.27
Hg*	1.0×10^{-4}	*Siganus rivulatus*	3.2
		Sargus sargus	0.96

*The US EPA [55] recommends analysing for total mercury and making a conservative assumption that all mercury is present as methylmercury.

The margin of exposure, MOE, to evaluate the yearly, species-specific, non-carcinogenic risk from consumption of fish contaminated with individual compounds is obtained from the following equation:

$$\mathrm{MOE} = \frac{\mathrm{MCC} \times \mathrm{CR}}{\mathrm{BW} \times \mathrm{RFD}},$$

where MCC is the species-specific mean chemical concentration (mg kg^{-1}); CR is the consumption rate (assumed to be 0.032 kg day^{-1}); BW is the body weight (assumed to be 70 kg); and RFD is the reference dose for the specific compound (mg kg^{-1} day^{-1}). An MOE greater than 1 indicates exposure to a dose greater than the safe daily dose for chronic non-carcinogenic effects [54] (table 8).

4. Conclusion

This study was carried out to provide information on heavy-metal concentrations in different fish species and sediments from El-Mex Bay. Based on the samples collected, the metal concentrations found in the edible parts of *Siganus rivulatus* and *Sargus sargus* are not heavily burdened with metals. Although the concentrations are below the limit values for fish, a potential danger may emerge in the future depending on the domestic waste waters and the agricultural and industrial activities in this region. Although fish livers are very seldom consumed, they represent good biomonitors of metals present in the surrounding environment. The concentrations of heavy metals in surface sediments in both fractions (total and labile) may be of anthropogenic origin. In future, the Bay may receive a huge amount of heavy metals, due to industrial development in this region, besides domestic and agricultural wastes.

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