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Characteristic levels of some pesticides and heavy metals in imported fish

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Imported fish samples of sardine and mackerel were collected from the Egyptian governorates. Some pesticides were found at high frequency (e.g. dimethoate, 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (*p,p'*-DDA), lindane, endrin, heptachlor and malathion). However, a lower frequency was found with aldrin, β-benzene hexachlor (β-BHC) and methyl parathion. Although some pesticides were at relatively high concentrations, mean concentrations were below the permissible levels proposed by the FAO. Imported sardine and mackerel had higher levels of lead and chromium than the permissible limits proposed by FAO. However, other metals (cadmium, copper, iron, manganese and zinc) were found at levels lower than the proposed permissible limits. Copyright © 1996 Published by Elsevier Science Ltd

INTRODUCTION

Pesticides and heavy metals constitute a major group of potential environmental hazards to man. Pesticides have been routinely used in most countries of the world to control harmful pests. Therefore, high levels of these chemicals may be causing contamination in both irrigation and drainage water. On the other hand, contamination with pesticides may be introduced into natural water sources via direct application for control of aquatic weeds and/or indirectly by drainage from agricultural lands. These will mainly contaminate fishing areas; consequently, fish may be affected. The stability of certain pesticides, particularly the chlorinated hydrocarbons, and the fact that residues can remain in foods, increases the human health hazard. Studies carried out to detect the pesticide residues in fish indicated that organochlorines were the main pesticides found. DDT predominated, as reported by Dogheim *et al.* (1990), Sharaf (1984) and Hamza & Michael (1979), who found averages of 4.17, 0.061 and 0.114 ppm, respectively. Abou-Donia (1990) reported lindane at a mean level of 0.59 ppm. However, Dogheim *et al.* (1990), Sharaf (1984) and Hamza & Michael (1979) reported mean levels of lindane of 0.20, 0.035 and 0.033 ppm, respectively. The other organochlorine pesticides detected were β-BHC (mean 0.435 ppm) and gamma-chlordane (mean 0.059 ppm), which were found by Abou-Donia (1990), while Dogheim *et al.* (1990) detected heptachlor (mean 0.56 ppm) and heptachlor epoxide (0.14 ppm). Other studies in developed countries indicated that the organochlorine pesticides were the main pesticides detectable in fish. Cocchieri & Arnese (1988) reported lindane, heptachlor and endosulfan concentration ranges of 0.005–0.008, ND (not detected)–0.005 and ND–0.008 ppm, respectively, in fish samples collected from four rivers in Italy.

Heavy metals that may contaminate different foods constitute serious health hazards depending on their relative levels. Some of these metals, such as cadmium and mercury, injure the kidney and cause symptoms of chronic toxicity, including impaired kidney function, poor reproductive capacity, hypertension, tumours and hepatic dysfunction (Luckey & Venugopal, 1977). Moreover, lead causes renal failure and liver damage (Emmerson, 1973; Luckey & Venugopal, 1977). Some other metals (chromium, zinc and copper) cause nephritis, anuria and extensive lesions in the kidney (Luckey & Venugopal, 1977). The presence of metals in the environment is partially due to natural processes such as volcanic activity and erosion, but is mostly the result of industrial wastes (PNUE, 1984).

Fish are often at the top of the aquatic food chain and may concentrate large amounts of some metals. Accumulation patterns of contaminants in fish depend both on uptake and elimination rates (Hakanson, 1984). Studies indicate that fish accumulate such metals from the water. Lowe *et al.* (1985) found that fresh water fish collected from rivers in the USA had mean levels of cadmium as follows: in 1978, 0.04 ppm; in 1979, range 0.01–0.41 ppm; in 1980, 0.03 ppm; and in 1981, range 0.01–0.35 ppm. These levels were below the legal limits (0.5 ppm) recommended by FAO (1983). On the other hand, lead was detected at mean levels of 0.19 ppm in

1978–1979 and 0.17 ppm in 1980–1981; these levels were below the FAO, 1983 legal limits (2.0 ppm). Copper in fish was also detected by Lowe *et al.* (1985) who reported that, with the exception of the level detected in 1979 (mean 38.8 ppm), the other levels (mean 0.86 ppm in 1978 and 0.68 ppm in 1980) were below the permissible levels recommended by FAO, 1983 (20.0 ppm). Zinc levels were also detected in fish; Wiener & Giesy (1979) found that levels ranged from 42 to 582 ppm. On the other hand, Eisenberg & Topping (1986) reported that chromium was found in fish samples at levels from 0.1 to 1.9 ppm. Iron was also found in fish (Harms, 1975). Ramos *et al.* (1979), Luckas (1987) and Barak & Mason (1990) reported that fish samples contained iron at levels below the permissible levels.

In Egypt, fish are liable to be contaminated by pesticides and heavy metals. This study was conducted to reveal and draw attention to the great problem of environmental pollution, in particular by pollutant residues in fish in the Great Cairo market.

MATERIALS AND METHODS

Materials

Sample collection

Fifty composed imported fish samples (sardine and mackerel) were collected randomly from Great Cairo governorates to assess the levels of some organochlorine and organophosphorus pesticides as well as some metals.

Standards

Standards of lindane, β-BHC, endrin, *p,p'*-DDA, dieldrin, heptachlor, aldrin, 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (*p,p'*-DDT), malathion, dimethoate, methyl parathion, silicron and endosulfan were provided by the Environmental Protection Agency (EPA). Heavy metal standard solutions (lead, chromium, cadmium, zinc, manganese, copper and iron) were bought from Merck (Darmstadt, Germany).

Methods

Determination of pesticide residues

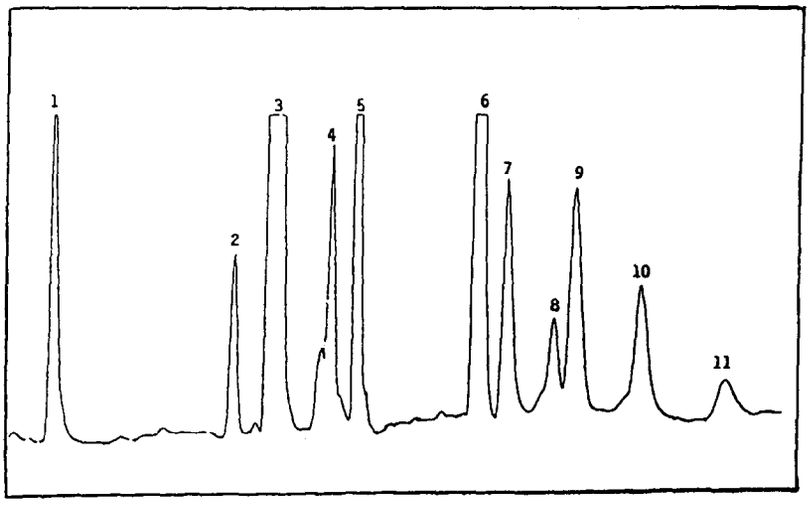
Residues of pesticides in the fish samples were determined according to the methods of the AOAC (1980) and the US Department of Health (1978). The separation was based on gas chromatography (Hewlett-Packard, Model 5890 A) with a ^{63}Ni electron capture detector (ECD) and a mass selective detector. The apparatus was also equipped with an HP-3392A integrator. An HP-101 (methyl silicon fluid) capillary column (25 m × 0.2 mm × 0.2 μm film thickness) was used to determine the types of pesticide detected. The temperature programme used to detect pesticide residues (except silicron and endosulfan) was as follows: initial temperature, 80 °C; initial time, 2 min; rate, 3 °C min^{-1}; final temperature, 160 °C; final time, 2 min; rate A, 5 °C min^{-1}; final temperature A, 220 °C; final time A, 40 min; injection temperature, 220 °C; detector temperature, 300 °C. To detect and determine silicron and endosulfan, isothermal programming was applied as follows: oven temperature, 220 °C; injection temperature, 230 °C; detector temperature, 300 °C. Chromatograms of the mixed standard pesticides are shown in Fig. 1.

Determination of heavy metals

Heavy metals were extracted from the fish samples according to the method of the AOAC (1980). The sample extracts were determined using a Perkin Elmer (2380) atomic absorption spectrophotometer. The maximum absorbance was obtained by adjusting the cathode lamps at specific slit and wavelengths as shown in Table 1.

RESULTS AND DISCUSSION

Composed fish samples (imported sardine and mackerel) were collected from Egyptian governorates (Great Cairo) to examine the levels of contamination by some types of pesticides and heavy metals (Tables 2–4 and Figs 2 and 3).



No. of peak	Pesticide type	Retention time (min)
1	lindane	25.970
2	β-BHC	36.301
3	endrin	38.486
4	malathion	41.738
5	*p,p'*-DDA	43.151
6	dimethoate	50.051
7	dieldrin	51.703
8	heptachlor	54.436
9	parathion methyl	55.664
10	aldrin	59.482
11	*p,p'*-DDT	64.391

Fig. 1. Identification of some pesticides separated by gas chromatography.

Table 1. Wavelengths (nm) and slit width (nm) for determination of heavy metals

Metal	Wavelength (nm)	Slit width (nm)
Cadmium (Cd)	228.8	0.7
Copper (Cu)	324.8	0.7
Ferrous iron (Fe)	248.3	0.2
Manganese (Mn)	279.5	0.2
Lead (Pb)	217.0	0.7
Zinc (Zn)	319.9	0.7
Chromium (Cr)	425.4	0.2

Table 2 and Fig. 2 show that among the 25 samples of mackerel, most contain dimethoate (92%), followed by *p,p'*-DDA, lindane, endrin, heptachlor and malathion, with frequencies of 56%, 44%, 40%, 36% and 36%, respectively. Lower frequencies were found for aldrin (8%), β-BHC (4%) and methyl parathion (4%). However, *p,p'*-DDT, silicron and endosulfan were not detected in any sample. Concerning the detected amounts of pesticide residues, different trends were recorded. The highest mean residue concentrations were for dimethoate, malathion, lindane, aldrin, heptachlor and *p,p'*-DDA, i.e. 0.1060, 0.1023, 0.0635, 0.0284, 0.0275 and 0.0223 ppm, respectively. The other mackerel samples examined were found to contain dieldrin (0.005 ppm), β-BHC (0.003 ppm), methyl parathion (0.003 ppm) and endrin (0.001 ppm). These pesticide levels are below the maximum acceptable limits proposed by FAO (1983), which are 5.0 ppm for DDT and 0.3 ppm for other pesticides.

Table 3 and Fig. 2 indicate that the majority of sardine samples contain dimethoate (80%), followed by endrin, dieldrin, malathion and methyl parathion (70% of the samples for every pesticide). The other pesticides, i.e. lindane *p,p'*-DDA, β-BHC, heptachlor, aldrin and *p,p'*-DDT, showed frequencies of 60%, 60%, 50%, 50%, 40% and 40%, respectively. However, silicron and endosulfan were not detected in the samples. Some pesticides were found in some samples at concentrations

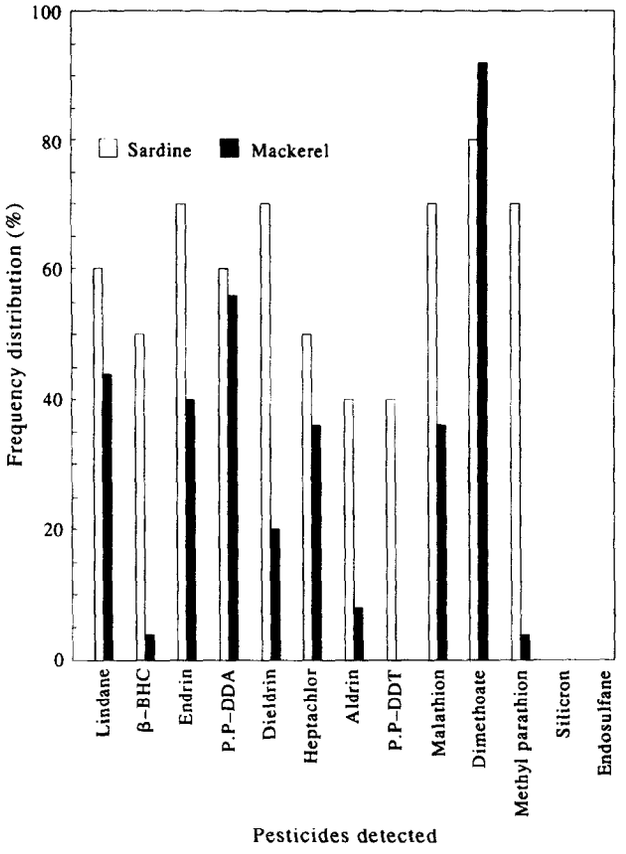


Fig. 2. Frequency distribution of pesticide residues in imported fish samples of mackerel and sardine from Great Cairo.

higher than the maximum acceptable limits proposed by FAO (1983), i.e. lindane, β-BHC, dieldrin, malathion and dimethoate, with concentrations of 1.43, 2.44, 0.732, 1.13 and 1.04 ppm, respectively.

From the above results it can be concluded that, although the incidences of pesticides were relatively high, mean concentrations were below the permissible levels proposed by FAO (1983). On the other hand, the organochlorine pesticides were predominant in the fish

Table 2. The distribution concentrations (ppm) of pesticide residues detected in imported mackerel samples collected from Great Cairo governorates

Pesticides detected	Concentrations of pesticide residues (ppm)		Frequency of positive samples		Permissible limits (ppm) (FAO, 1983)
	Range	Mean ± SD	No.	%	
Lindane	ND–0.299	0.0635 ± 0.09	11	44	0.3
β-BHC	ND–0.0697	0.0003 ± 0.01	1	4	0.3
Endrin	ND–0.0015	0.0001 ± 0.01	10	40	0.3
p,p'-DDT	ND	—	—	—	0.5
p,p'-DDA	ND–0.216	0.0223 ± 0.04	14	56	—
Aldrin	ND–0.626	0.0284 ± 0.12	2	8	0.3
Dieldrin	ND–0.0390	0.005 ± 0.01	5	20	—
Heptachlor	ND–0.145	0.0275 ± 0.04	9	36	0.3
Malathion	ND–1.13	0.102 ± 0.24	9	36	—
Dimethoate	ND–1.28	0.106 ± 0.30	23	92	—
Methyl parathion	ND–0.085	0.003 ± 0.01	1	4	—
Silicron	ND	—	—	—	—
Endosulfan	ND	—	—	—	—

ND, not detected.

Table 3. The distribution concentrations (ppm) of pesticide residues detected in imported sardine samples collected from Great Cairo governorates

Pesticides detected	Concentrations of pesticide residues (ppm)		Frequency of positive samples		Permissible limits (ppm) (FAO, 1983)
	Range	Mean ± SD	No.	%	
Lindane	ND–1.43	0.404 ± 0.53	30	60	0.3
β-BHC	ND–2.44	0.397 ± 0.73	25	50	0.3
Endrin	ND–0.0712	0.0086 ± 0.02	35	70	0.3
p,p'-DDT	ND–0.0209	0.0075 + 0.01	20	40	0.5
p,p'-DDA	ND–0.280	0.0777 ± 0.09	30	60	—
Aldrin	ND–0.323	0.0859 ± 0.12	20	40	0.3
Dieldrin	ND–0.732	0.182 ± 0.24	35	70	—
Heptachlor	ND–0.218	0.0465 ± 0.07	25	50	0.3
Malathion	ND–1.13	0.257 ± 0.36	35	70	—
Dimethoate	ND–1.044	0.293 ± 0.32	40	80	—
Methyl parathion	ND–0.141	0.0582 ± 0.05	35	70	—
Silicron	ND	—	—	—	—
Endosulfan	ND	—	—	—	—

ND, not detected.

samples, but in low concentrations, which might be attributed to the association of organochlorine pesticide residues with the fat phase in fish. However, some types of organophosphorus pesticides were found.

Other studies have been carried out in Egypt to detect pesticides in fish collected from different locations. It was found that the organochlorines were the main pesticides found in fish samples. DDT and its derivatives predominated, as reported by Hamza & Micheal (1979), Sharaf (1984), Abou-Donia (1990) and Dogheim *et al.* (1990), who found averages of 0.114, 0.061, 0.291 and 4.17 ppm, respectively. Lindane (mean 0.59 ppm), β-BHC (mean 0.435 ppm) and chlordane (mean 0.059 ppm) were also detected by Abou-Donia (1990), while Dogheim *et al.* (1990) detected lindane (mean 0.07 ppm), heptachlor and heptachlor epoxide (means 0.56 and 0.14 ppm), aldrin and dieldrin (means 0.59 and 0.61 ppm) and endrin (mean 0.70 ppm). It is worthy of note that, in studies in developed countries, the organochlorines were also the main pesticides detected in fish. Stout (1980), Falandysz (1986) and Cocchieri & Arnese (1988) reported that DDT predominated and showed 0.18, 2.6 and a range of 0.018–0.153 ppm, respectively. Stout (1980) also surveyed residues of endrin and dieldrin in the Northwestern Atlantic Ocean and Northern Gulf of Mexico, reporting mean values of 0.008 and 0.007 ppm, respectively.

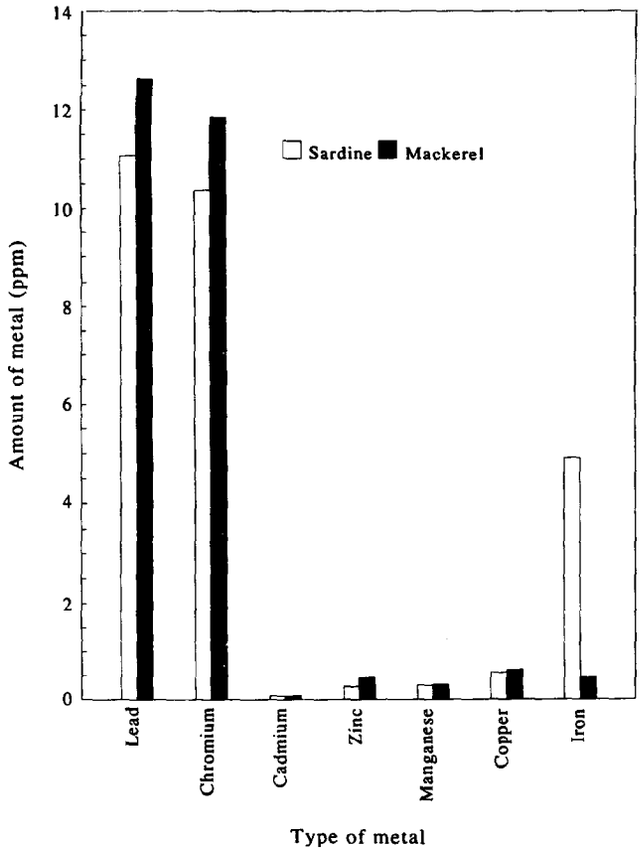


Fig. 3. Concentration of some heavy metals in imported mackerel and sardine fish samples collected from Great Cairo.

The imported fish samples were also examined for the incidence of some heavy metals (Pb, Cr, Cd, Zn, Mn, Cu and Fe). The results obtained (Table 4 and Fig. 3) indicate that lead was the major contaminant in fish samples, with mean levels of 12.6 and 11.1 ppm in mackerel and sardine, respectively. Table 4 shows also that the metal chromium is at high levels (11.8 ppm in mackerel and 10.4 ppm in sardine). Cadmium was found at mean levels of 0.086 ppm in sardine and 0.077 ppm in mackerel, which are comparatively much lower than levels of the other detected metals. The mean concentrations of zinc were 0.450 ppm in mackerel and 0.262 ppm in sardine. Manganese was also detected in fish samples, which showed mean levels of 0.308 and 0.289 ppm in mackerel and sardine, respectively. The samples contained copper 0.622 ppm and 0.561 ppm, respectively, in mackerel and sardine. Iron was found at mean levels of 5.09 ppm in mackerel and 4.91 ppm in sardine.

Table 4. The distribution concentrations (ppm) of some heavy metals in imported fish samples (sardine and mackerel) collected from Great Cairo governorates

Heavy metals	Sardine		Mackerel		Permissible limits (ppm) (FAO, 1983)
	Range	Mean ± SD	Range	Mean ± SD	
Lead (Pb)	0.920–25.7	11.1 ± 7.8	0.700–28.7	12.6 ± 9.6	0.5
Chromium (Cr)	0.500–18.9	10.4 ± 5.3	3.00–20.4	11.8 ± 5.1	—
Cadmium (Cd)	0.004–0.184	0.086 ± 0.1	0.004–0.224	0.077 ± 0.1	0.5
Zinc (Zn)	0.006–3.48	0.262 ± 0.7	0.004–3.87	0.450 ± 1.0	40.0
Manganese (Mn)	0.010–1.06	0.289 ± 0.3	0.006–1.08	0.308 ± 0.3	—
Copper (Cu)	0.064–1.30	0.561 ± 0.3	0.014–1.35	0.622 ± 0.3	30.0
Iron (Fe)	0.240–16.6	4.91 ± 4.2	0.820–12.6	0.450 ± 1.0	—

Data summarized in Table 4 and Fig. 3 show that mackerel had comparatively higher mean levels of lead, chromium, zinc, manganese, copper and iron and lower mean levels of cadmium than sardine samples. The mean concentrations of lead in this study were 12.6 and 11.1 ppm in mackerel and sardine, respectively, which are higher than the permissible limits proposed by FAO, 1983 (2.0 ppm) and far higher than the levels reported from other investigations. Szefer & Falandysz (1983) reported a mean level of lead of 0.09 ppm in herring and sprat samples. On the other hand, Lowe *et al.* (1985) reported a mean concentration of lead of 6.73 ppm in fish in 1979, lower than the levels recorded in the current study. In this study, chromium was found at levels higher than those recorded by Eisenberg & Topping (1986) and Ramelow *et al.* (1989) (0.1–1.9 ppm and 0.15–5.5 ppm, respectively). On the other hand, cadmium levels in the fish samples in the current study were below the permissible levels proposed by FAO (1983) but similar to those obtained by Szefer & Falandysz (1983), who found that the levels detected in samples of cod and sprats ranged from 0.002 to 0.019 ppm. The levels of zinc in the current study were below the legal limits (50.0 ppm) and lower than those recorded by Szefer & Falandysz (1983), who found that the level of zinc in samples taken from the Southern Baltic was 12.6 ppm. On the other hand, the levels of manganese in the present study were lower than those detected by Szefer & Falandysz (1983) and Falandysz & Lorence (1984), who found mean levels 0.40 and 0.45 ppm, respectively. Mean concentrations of copper in this study were below the legal limits (20.0 ppm). However, it was found at levels higher than those reported by Szefer & Falandysz (1983), who showed that the averages of the metal were 0.18, 0.38 and 0.40 ppm for cod, herring and sprat samples, respectively. Levels of iron were below the permissible limits and lower than the levels detected in fish samples collected by Szefer & Falandysz (1983), who found a mean level of 13.5 ppm.

It can be concluded that the imported fish samples in the current study had high levels of lead and chromium. This may be attributed to the high levels of such pollutants in the fishing area which accumulated in the fish. Accumulation patterns of metals in fish are dependent on uptake and elimination rates. The uptake of metals is influenced by species of fish and various environmental factors such as pH and temperature (Hakanson, 1984). The elimination of metal is an active biochemical and physiological process, dependent on growth, salinity, age, sex, position relative to shoreline, water depth, and pollutant interactions (Phillips, 1980).

Overall, the imported fish samples contained residues of pesticides and some dangerous heavy metals such as lead and chromium. Accordingly consumption of Egyptian fish may be safer than consumption of imported fish.

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