
Organochlorines and organophosphours pesticides,petroluem hydrocarbons,polychlorinated biphenyls and trace metal monitoring of nile river in egypt

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Egypt is a typical third world country as well as being mainly an agriculturaleconomy. It has relied heavily on pesticides to fight pests harmful, mainly, to cotton,maize, corn, sugarcane and rice as well as many different varieties of vegetable and fruitcrops.It is well recognized that the industrial activities over a long period of time haveenhanced the levels of pollutants in the environment. As a result of the modernagricultural practices, River Nile receives municipal, industrial and agricultural wastesalong its course.In Egypt, the continuing discharge of many industrial wastes as well asagrochemical in water streams might increase the level of pesticides, PCBs, petroleumhydrocarbon and heavy metals in River Nile and subsequently in surface and groundwater. In Egypt there are no regular monitoring programmes concerning theidentification and determination of different pollutants in the environment, althoughEgypt is the largest pesticide market in Arabian countries and the fourth largest importerof pesticides among developing countries.Scope and Objective of Study:The objectives of this study are to evaluate the levels of various chemicalpollutants such as highly toxic heavy metals, organochlorine and organophosphoruspesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons and aliphatichydrocarbons in aquatic environment (sediment, water and fish) at El Menofiyagovernorate, Egypt. Samples were taken from El-Sarsawia, El-Bagoria, Bahr Shebincanals, in addition to three drainage canal sites El-Embaby, El-Menofi and Miet-Rabihadrain.The obtained results could summarize in the following points:1. Pesticide residuesA. Organochlorine pesticidesA.1. Organochlorine pesticide residues in water· The highest mean amounts of β -HCH, heptachlor epoxide and endrin were1.668, 2.098 and 4.66 ng l-1, respectively in water samples from El-SarsawiacanalThe highest average amounts of aldrin and endosulfan were 2.149 and 5.746 ng l-1, respectively, which were found in El-Embaby drain.· The highest average amount of γ -HCH (1.815 ng l-1), heptachlor (1.232 ng l-1),dielddrin (1.199 ng l-1) and γ -chlordan (1.569 ng l-1) were found in water sampletaken from El-Menofi drain, El-Embaby drain, Bahr Shebin canal and MietRabiha drain, respectively.· The highest average amount of DDT and its metabolites p,p'-DDE (15.106 ng l-1), p,p'-DDD (8.150 ng l-1) were found in El-Menofi drain and p,p'-DDT (0.894ng l-1) was found in Miet Rabiha drain,

respectively, in water sample. The data showed that the concentration of pesticides residue in the analysed samples followed the following descending order p,p' -DDE > p,p' -DDD > endosulfan > endrin > heptachlor epoxide > aldrin > γ -HCH > β -HCH > γ -chlordane > heptachlor > p,p' -DDT.

A.2. Organochlorine pesticide residues in sediment: The highest average concentration of α -HCH (21.234 ng g⁻¹) was found in sediment sample of El-Bagoria canal. The highest average residue level of β -HCH (7.815 ng g⁻¹) was found in El-Embaby drain. In addition, the highest amount of γ -HCH (57.471 ng g⁻¹ in El-Menofi drain), δ -HCH (27.08 ng g⁻¹ in Miet-Rabiha drain), heptachlor (16.56 ng g⁻¹ in El-Menofi drain), heptachlorepoide (66.010 ng g⁻¹ in Miet-Rabiha drain) and endosulfan (32.942 ng g⁻¹ in El-Menofi drain) were detected in sediment samples. DDT and its metabolites p,p' -DDD, p,p' -DDE, p,p' -DDT (mean concentrations 29.79, 32.506 and 11.067 ng g⁻¹, respectively, in El-Menofi drain) were detected at high levels in sediment sample. Metabolic transformation of DDT under oxidative conditions leads to p,p' -DDE, whereas under anaerobic conditions p,p' -DDD is formed. The data showed that sediment samples had higher concentrations of pesticide residues than water and fish samples.

A.3. Organochlorine pesticide residues in fish: The p,p' -DDE residues were the most abundant residues in fish, and were detected in most samples at relatively higher concentration compared to other residues. The highest average concentration of p,p' -DDE was found in fish samples from El-Bagoria canal (5.957 ng g⁻¹). α -HCH residues were only found in fish samples from El-Sarsawia canal and El-Embaby drain at the average concentration of 0.837 and 2.404 ng g⁻¹, respectively. The highest average concentration of heptachlor (2.88 ng g⁻¹) and heptachlorepoide (4.541 ng g⁻¹) were found in fish samples collected from Miet Rabiha drain. While the highest average concentration of aldrin (1.122 ng g⁻¹), dieldrin (2.123 ng g⁻¹) and γ -chlordane (1.650 ng g⁻¹) were found in fish samples collected from El-Bagoria canal. In addition, the highest mean concentration of endrin (1.75 ng g⁻¹) and endosulfan (3.836 ng g⁻¹) were found in fish samples collected from El-Embaby drain. The data showed that the mean values of DDT, dieldrin and γ -HCH found in this study were therefore below the Philippines maximum permissible limits set for surface water and below the limit set by EU for drinking water. The residue levels of organochlorine pesticides in all analyzed fish in this investigation are considerably lower than the tolerance levels set by the National Academy of Sciences and National Academy of Engineering (NAS-NAE, 1972) and WHO maximum acceptable limits (WHO, 1996).

B. Organophosphorus pesticides

B.1. Organophosphorus pesticide residues in water: In all water sample analyzed only chlorpyrifos-methyl and prothiphos were detected in only one water samples collected from El-Embaby drain.

B.2. Organophosphorus pesticide residues in sediment: Compound identified included profenophos, prothiphos, chlorpyrifos and diazinon. Profenophos were detected at the level of 63.37 ng g⁻¹ (dry weight basis) in one sediment sample collected from El-Menofi drain and at the level of 13.43 ng g⁻¹ (dry weight basis) in one sediment sample collected from Miet-Rabiha drain. Chlorpyrifos, prothiphos and diazinon were found only in one sediment samples collected from Bahr Shebin canal at the levels of 33.79, 36.84 and 7.80 ng g⁻¹ (dry weight basis), respectively.

3. Organophosphorus pesticide residues in fish: Chlorpyrifos, cadusafos, diazinon, prothiphos and malathion were detected in fish.

tissues samples. Chlorpyrifos was detected in samples collected from El-Sarsawia canal, and El-Embaby, El-Menofi and Miet-Rabiha drain. The highest amount of chlorpyrifos (9.38 ng g⁻¹ fresh weight basis) was detected in El-Embaby drain. Prothipfos were found in tissues collected from El-Sarsawia canal and Miet-Rabiha drain at mean concentration of 4.91 and 6.55 ng g⁻¹, respectively. Diazinon was only found in one fish sample that collected from El-Menofi drain at the level of 9.23 ng g⁻¹. Malathion was detected in samples from El-Embaby and El-Menofi drain at average concentration of 8.31 and 1.47 ng g⁻¹, respectively.

3. Polychlorinated Biphenyls residues

A. Polychlorinated Biphenyls residues in water. The data showed that most of PCB congeners were detected in water samples, except for PCB congeners no 192 and 194. The highest concentration of total PCBs in water samples was 67.89 ng L⁻¹, which was found in Bahr Shebin canal. Among the congeners, PCB no 44 and 152 represented the most abundant congeners in water samples. The congener patterns are dominated by tetra-, penta- and hexachlorobiphenyl, including the highly persistent and hydrophobic 152. The levels of PCBs in water samples are considered to be high and exceed the permissible levels for drinking water recommended by EPA.

B. Polychlorinated Biphenyls residues in sediment. The data showed that, most of PCB congeners were detected in sediment samples. The highest concentration of total PCBs in sediment samples was 108.118 ng g⁻¹ dry weight basis, which was found in El-Embaby drain. Among the congeners, PCB no 44 and 152 represented the most abundant congeners in sediment samples.

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145. The data showed that the residue levels of PCBs in sediment followed in the order, El-Embaby drain > Meit-Rabiha drain > El-Sarsawia canal > Bahr Shebin canal > El-Bagoria canal > El-Menofi drain.

C. Polychlorinated Biphenyls residues in fish. The data showed that the concentration levels of total PCB congeners in fish samples ranged from 11.036 to 69.367 ng g⁻¹ fresh weight at Bahr Shebin canal and El-Bagoria canal, respectively. Also, the result illustrated that the most abundant PCBs congeners in fish samples was PCB congener no 70 which represented 62.5, 87.5, 37.5, 50, 50 and 25% in sample collected from El-Sarsawia canal, El-Bagoria canal, Bahr Shebin canal, El-Embaby drain, El-Menofi drain and Miet Rabiha drain, respectively. The residue levels of PCBs in all analyzed fish in this investigation are considerably lower than the tolerance levels set by National Academy of Sciences and National Academy of Engineering (NAS-NAE, 1972), FDA, and Egyptian standard.

4. Petroleum Hydrocarbon

4.1. Polycyclic aromatic hydrocarbon

A. Polycyclic aromatic hydrocarbon in water. The total concentrations of 13 PAH in water samples ranged from 226.9 ng L⁻¹ at El-Sarsawia canal to 1492.2 ng L⁻¹ at El Menofi drain. The highest concentration of total PAHs was observed at El-Menofi drain which obviously related to combustion of fossil material followed by atmospheric fallout, sewage outfalls and industrial and agricultural waste water discharge, which were observed during the sampling. Naphthalene was found only in water samples collected from El-Sarsawia canal and El-Embaby drain with an average concentration of 17.2 and 22.7 ng/L, respectively. The highest mean levels of acenaphthene (96.6 ng/L), acenaphthylene (117.4 ng/L), fluorene (100.15 ng/L), anthracene (69.66 ng/L) and pyrene (71.3 ng/L) were recorded in El-Menofi drain.

While the highest average concentrations of phenanthrene (100 ng/L), fluoranthene (50.86 ng/L), chrysene (27.5 ng/L), - - - - -

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dibenzo[a,h]anthracene (15.6 ng/L) and benzo[g,h,i]perylene (11.04 ng/L) were recorded in water samples collected from El-Embaby drain. Benzo[a]pyrene was detected in most samples from all location sites and its mean concentration ranged from 2.88 to 16.96 ng L⁻¹. The highest concentration was found in El-Embaby drain. Meanwhile, the detected concentration was below the permissible limits (700 ng L⁻¹) according to Egyptian guidelines. The highest mean concentration of benzo[b]fluoranthene (29.63 ng/L) was found in water samples collected from Bahr Shebin canal. In terms of individual PAH composition in surface water, the samples were dominated by three-ring PAHs. In general the residue levels of PAHs in water samples collected from 6 sites tend to be in the order: El-Menofi drain > El-Embaby drain > Miet-Rabiha drain > Bahr Shebin canal > El-Bagoria canal > El-Sarsawia canal.

B. Polycyclic aromatic hydrocarbon in sediment. The total concentration of 13 PAH in sediment ranged from 1197.79 ng g⁻¹ dry weight at Bahr Shebin canal to 2701.55 ng g⁻¹ dry weight at El-Embaby drain. The highest mean concentrations of acenaphthene (35.18 ng g⁻¹), acenaphthylene (32.18 ng g⁻¹), phenanthrene (139.5 ng g⁻¹), anthracene (127.5 ng g⁻¹), pyrene (89 ng g⁻¹), chrysene (87.60 ng g⁻¹) and benzo[b]fluoranthene (78.76 ng g⁻¹) were present in sediment samples collected from El-Embaby drain. The highest average concentrations of naphthalene (16 ng g⁻¹), fluorene (66 ng g⁻¹) and dibenzo[a,b]anthracene (229 ng g⁻¹) were found in sediment samples collected from El-Menofi drain. The highest mean concentrations of fluoranthene (131.6 ng g⁻¹) and benzo[a]pyrene (95.80 ng g⁻¹) were recorded in sediment samples collected from El-Sarsawia canal. Benzo[g,h,i]perylene was recorded the highest average level (119.6 ng g⁻¹) in sediment samples of Miet Rabiha drain.

C. Polycyclic aromatic hydrocarbon in fish. The total concentrations of PAH in fish samples in the same location were determined at 371.68 ng g⁻¹ wet weight in El-Sarsawia canal to 2019.25 ng g⁻¹ wet weight in Bahr Shebin canal with differences between location site. - - - - -

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The concentration of PAHs detected in fish samples were higher than those detected in water samples from the same sampling location site. The highest concentration of total PAHs was observed at Bahr Shebin canal which is surrounded by densely populated and urban area with an intense industrial and agricultural activity. The highest mean concentrations of acenaphthene (10.07 ng g⁻¹), anthracene (23.51 ng g⁻¹), fluoranthene (173.2 ng g⁻¹), pyrene (114.18 ng g⁻¹), chrysene (19.57 ng g⁻¹) and benzo[a]pyrene (16.60 ng g⁻¹) were present in fish samples collected from Bahr Shebin canal. While the highest average concentrations of naphthalene (7.35 ng g⁻¹), acenaphthylene (31.58 ng g⁻¹) and phenanthrene (49.50 ng g⁻¹) were found in fish samples collected from El-Menofi drain. The highest mean concentrations of benzo[b]fluoranthene (32.88 ng g⁻¹) and dibenzo[a,b]anthracene (72.27 ng g⁻¹) were recorded in fish samples collected from Miet-Rabiha drain. The highest mean concentration of fluorene (8.13 ng g⁻¹) was recorded in El-Sarsawia canal. Benzo[g,h,i]perylene was only found in one fish sample collected from Bahr Shebin canal at concentration of 9.10 ng g⁻¹ wet weight. The data showed that the residue

levels of PAHs in fish samples collected from 6 sites tend to be in the order: Bahr Shebin canal > El-Menofi drain > El-Embaby drain > Miet-Rabiha drain > El-Bagoria canal > El-Sarsawia canal. Similar to sediments PAH in the fish were mostly dominated by the high molecular weight PAHs (4-6-rings). The data showed that in water, sediment and fish samples the simultaneous occurrence of isomer ratios 1, in all studied location except in fish sample collected phenanthrene / anthracene from El-Bagoria canal and in water sample collected from El-Menofi drain, which indicates that the polycyclic aromatic hydrocarbon are of pyrolytic (combustion) origin at most stations. - - - - -

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4.2. Aliphatic hydrocarbon

A. Aliphatic hydrocarbon in water. The total concentration of the fourteen aliphatic hydrocarbons in water samples ranged from 804.9 ng/L at El-Bagoria canal to 1741.81 ng/L at Meit-Rabih drain. The highest levels of aliphatic hydrocarbons were found at Miet-Rabiha drain due to direct spillage of industrial, agricultural and domestic wastes into the drain.

B. Aliphatic hydrocarbon in sediment. The total concentration of 14 aliphatic hydrocarbons in sediment samples ranged from 1227.9 ng g⁻¹ dry weight at El-Sarsawia canal to 2860.70 ng g⁻¹ dry weight at El-Embaby drain. The residue levels of aliphatic hydrocarbon also varied between different location sites with highest concentration values in samples collected from the drainage canals, while the drainage canals have been exposed to much industrial and sewage pollution.

C. Aliphatic hydrocarbon in fish. The total concentrations of aliphatic hydrocarbons in fish samples in the same location were ranged from 1051.20 ng g⁻¹ wet weight in El-Bagoria canal to 1975.72 ng g⁻¹ wet weight in Miet-Rabiha drain with differences between location sites. The highest concentration of total aliphatic hydrocarbon was observed at Miet-Rabiha drain which obviously related to sewage outfalls and industrial and agricultural waste water discharge, which were observed during the sampling.

5. Heavy metal

A. Heavy metal in water. According to the data, iron has the highest concentration, followed by lead, zinc, cadmium and copper. The mean concentration of iron ranged from 52.132 µg/L in water samples collected from Bahr Shebin canal to 152.26 µg/L in water samples collected from El-Bagoria canal. The mean lead concentration ranged from 8.678 to 21.948 µg/L, in water samples collected from El-Sarsawia canal and El Embaby drain, respectively. - - - - -

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The copper and cadmium mean concentrations ranged from 0.67 and 0.500 to 4.908 and 5.650 µg/L, respectively, in water samples collected from Bahr-Shebin canal and El-Embaby drain, respectively. The highest mean concentration of zinc (7.086 µg/L) was found in water samples collected from El-Embaby drain, while the lowest mean concentration (2.678 µg/L) was found in water samples collected from El-Bagoria canal. The water samples from all location sites are polluted by lead according to EPA. Iron and copper values are within the allowable limits according to WHO, (1993), US-EPA, (2001) and Egyptian chemical standard, (1994). Water samples collected from El-Embaby drain is considered as polluted water by cadmium according to WHO and EU.

B. Heavy metal in sediment. Iron was the dominant metal measured in the sediment samples from the entire sampling location site and cadmium presented the lowest levels. The mean concentration of iron ranged from 4551 to 4955 µg/g,

in sediment samples collected from El-Embaby and El-Menofi drain, respectively. The average concentration of lead ranged from 17.12 to 46.42 µg/g in sediment collected from El-Bagoria canal and Miet Rabiha drain, respectively. Copper mean concentration varied from 14.48 to 36.04 µg/g in sediment samples collected from El-Bagoria canal to El-Menofi drain, respectively, while the mean concentration of cadmium ranged from 0.830 to 1.630 µg/g in sediment samples collected from El-Bagoria canal and El-Sarsawia canal, respectively. In addition, the average concentration of zinc in sediment samples collected from all the sampling location varied from 2.092 to 19.31 µg/g at Bahr Shebin canal and El Embaby drain, respectively. In the present investigation, the high concentrations of metals were found in sediment samples collected from the drainage canal, and is referred to some waste effluents discharge from human activities, agricultural run off and from the atmospheric input. The mean concentrations of Cd, Cu, Pb and Zn in sediment samples in this study are less than the probable effect concentrations recorded by MacDonald et al., 2000- - - - -

-----SUMMARY150C. Heavy metal in fish. Iron concentration was highest in fish samples analyzed in this study. Mean metal content in the fish samples in all location sites followed the profile: iron > zinc > lead > copper > cadmium. The highest mean concentration of lead (1.864 µg/g), copper (1.495 µg/g) and cadmium (1.840 µg/g) were found in fish samples collected from El-Embaby drain. While the highest mean concentration of iron (108.26 µg/g) and zinc (24.35 µg/g) were present in fish samples collected from Miet Rabiha drain. Also, the highest concentrations of the metals were found in fish samples that collected from the drainage canal. Lead and cadmium were found in higher concentration than those recommended for fish; other heavy metals were almost found at the concentration to those recommended by FAO.