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Organophosphorus Pesticides Residues in Fish Samples from the River Nile Tributaries in Egypt

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Abstract The concentration of organophosphorus pesticides in fish samples from different tributaries of the Nile River in Egypt was monitored. Fish samples were collected from El Menofiya, canal water supplies (El-Sarsawia, El-Bagoria and Bahr Shebin), in addition to El-Embaby, El-Menofi and Miet Rabiha drainage canals each 2 month during periods of 16 month, June 2007–Septemper 2008. Chloropyrifos, cadusafos, diazinon, prothiphos and malathion were detected in fish tissues samples at level below the maximum residue limit. The highest average amount of chlorpyrifos (9.38 ng g^{-1}) and malathion (8.31 ng g^{-1}) were detected in El-Embaby drain. Prothiphos 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}.

Keywords Organophosphorus · Residues · Fish

A large number of pesticides have been used in Egypt for agricultural and public health purposes. Drainage water from the pesticides treated land is pumped into several major drains that finally discharged their waters into the River Nile or lakes. Therefore, the human population is exposed to pesticides both through the drinking water and via the food supply. Pollution with these materials is a serious problem facing the world. However, its risk is increasing in the third world countries due to lack of regulations, lack of awareness among consumers, lack of research and lack of efficient monitoring programmes dealing with the incidence of these hazardous materials in foods. In an effort to substitute the persistent organochlorine pesticides (OCPs), agricultural sectors have shifted towards organophosphorus (OPs) pesticides. However, OPs pesticides are generally much more toxic to vertebrates compared to other classes of insecticides even though they rapidly degrade in the environment (Chambers et al. 2001). Medical reports assert that liver and kidney diseases have increased in the past few years in Egypt. However, the widespread use of pesticides during the last 20 years in Egypt has created serious problems following chronic exposure to trace residues. In Egypt there are no regular monitoring programmes concerning the identification and determination of different pollutants in the environment, although Egypt is the largest pesticide market in Arabian countries and the fourth largest importer of pesticides among developing countries (Yamashita et al. 2000). A few studies were carried out to measure the concentration of OCPs in the aquatic environment. Particularly, this study was designed to evaluate the levels of OPs pesticides in fish samples collected from different tributaries of the Nile River at El Menofiya governorate, Egypt.

Materials and Methods

All solvents were Pesticide Residue grade and were purchased from Alliance Bio, USA. Charcoal-celite chromatographic mixture, one part (by weight) charcoal decolorizing powder, neutral, BDH, is combined with four parts celite 545 diatomaceous earth, not acid-washed and mixed well. Sodium sulfate anhydrate were analytical

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grade, and purchased from El Naser Pharmaceutical Chemical Co., Egypt. OPs compound tested in this study were dichlorvos, ethoprophos, cadusafos, diazinon, chlorpyrifos-methyl, pirimiphos-methyl, chlorpyrifos, parathion-methyl, pirimiphos-ethyl, malathion, prothiphos, profenofos, fenamiphos, azinphos-methyl and purchased from Dr. Ehrenstorfer, Augsburg in Germany with purities larger than 98.5%. Before use all, the glassware was wash with tap water and detergent, hot water, distilled water, and rinsed with acetone then with n-hexane. All glassware used had glass or Teflon stoppers. Fish samples were collected each 2 month, during the period from June 2007 to September 2008 from six sites. The sampled site for the study was selected in El-Menofiya governorate. Samples were taken from El-Sarsawia, El-Bagoria, Bahr Shebin canals, in addition to three drainage canal sites El-Embaby, El-Menofi and Miet Rabiha drain. Some fishermen in El Menofiya governorate depend on theses canals for fishing and small-scale fish culture. Healthy and vigorous fish (*Tilapia Nilotica*) were caught by fishermen about 2–2.5 kg from the different sites. They were transport without sexing to the laboratory. The soft parts of fish samples be removed and a muscle tissue sample (10 g) was taken from the dorsal muscle in aluminum foil and kept in deep freezer until analysis. Fish sample (10 g of wet weight) was placed in ceramic mortar, anhydrous sodium sulfate (20 g) was added, and the mixture was well homogenized. The mixture was transferred to 500 mL conical flask and homogenized with 100 mL of chloroform + acetone (1:1 v/v). The homogenate was shaken for 3 h and filtered. The filtrate was evaporated to dryness using rotary evaporator. Fish extract was cleaned up using charcoal-celite column (Fillion et al. 1995). The column was prepared as follow: a small amount of acetonitrile was added to the column then one gram of sodium sulfate was added. Break the tip of the column, and slurry 2.0 g of charcoal-celite (1:4 w/w) mixture in 10 mL acetonitrile was added into the column. The acetonitrile was drained just to the top of the charcoal-celite, and then cap the tip and 0.5 g of sodium sulfate was added to the top of the column. The column was conditioned with 10 mL acetonitrile-toluene (3:1 v/v) before use. The extract was dissolved in 1 mL of acetonitrile and quantitatively transferred to the top of the column and eluted with 50 mL acetonitrile-toluene (3:1 v/v). The elute was concentrated using a rotary vacuum evaporator adjusted at 35°C and evaporated until the volume reached 2–3 mL. The final extract was transferred quantitatively by rinsing with aliquot of the organic solvent into a concentrator tube and evaporated to dryness. The residue was dissolved in 2 mL of ethyl acetate and transferred into autosampler vial for GC–FPD analysis. The same volume of solvents and anhydrous sodium sulfate, which used in extraction of OPs pesticides from fish samples were subjected to the same procedures as the examined samples to detect any possible traces of the studies pesticides and its value was subtracted from the results. The extract was concentrated and injected into a gas liquid chromatography equipped with a flam photometric detector GC/FPD. GC analysis was conducted on a PAS-1701 (Agilent, Folsom, CA) fused silica capillary column of 30 m length, 0.32 mm id., and 0.25 μm film thicknesses. The oven temperature was programmed from an initial temperature 160 (2 min hold) to 210°C at a rate of 5°C min^{-1} and was maintained at 210°C for 3 min and raised to 240°C at rate of 5°C min^{-1} and was maintained at 240°C for 1 min and raised to 270°C at a rate of 20°C min^{-1} and was maintained at 270°C for 10 min. Injector and detector temperature were maintained at 240 and 260°C, respectively. Nitrogen was used as a carrier at flow rate of 3 mL/min. The hydrogen and air flow rate were 75 and 100 mL/min, respectively. Peak was identified by comparison of sample retention time value with those of the corresponding of pure standard compounds. Method sensitivity and recovery were determined by using samples spiked with the tested pesticides. Before analysis, relevant standards were run to check column performance, peak height, resolution, and limits of detection. Peak was identified by comparison of sample retention time value with those of the corresponding of pure standard compounds. With each set of samples to be analysed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. The average recovery percentages of OPs pesticides for fortified samples at different levels were determined and calculated for all tested compounds in each aquatic system compartment (Table 1).

Table 1 Recovery percentage, relative standard deviation and method detection limits of organophosphorus pesticides

Pesticide name	Recovery	RSD	LOD (ng g^{-1})
Dichlorvos	89	8	0.03
Ethoprophos	80	13	0.05
Cadusafos	85	4	0.06
Diazinon	84	9	0.06
Chlorpyrifos-methyl	83	7	0.07
Pirimiphos-methyl	79	5	0.02
Chlorpyrifos	78	5	0.06
Methyl-parathion	91	14	0.07
Pirimiphos-ethyl	91	6	0.07
Malathion	89	8	0.05
Prothiphos	83	6	0.05
Profenophos	89	5	0.04
Fenamiphos	85	10	0.06
Azinphos-methyl	88	8	0.04

Table 2 Concentration (ng g^{-1} fresh weight) of organophosphorus pesticides in fish samples

Pesticides name	El-Sarsawia canal Min–Max Mean n = 8	El-Bagoria canal Min–Max Mean n = 8	Bahr Shebin canal Min–Max Mean n = 8	El-Embaby drain Min–Max Mean n = 8	El-Menofi drain Min–Max Mean n = 8	Meit-Rabiha drain Min–Max Mean n = 8
Dichlorvos	ND	ND	ND	ND	ND	ND
Ethoprophos	ND	ND	ND	ND	ND	ND
Cadusafos	ND-3.35 3.21	ND	ND	ND	ND-5.42 5.42	ND
Diazinon	ND	ND	ND	ND	ND-9.23 9.23	ND
Chlorpyrifos-methyl	ND	ND	ND	ND	ND	ND
Pirimiphos-methyl	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND-3.06 2.37	ND	ND	ND-18.33 9.38	ND-8.15 4.10	ND-2.813 2.813
Methyl-parathion	ND	ND	ND	ND	ND	ND
Pirimiphos-ethyl	ND	ND	ND	ND	ND	ND
Malathion	ND	ND	ND	ND-12.60 8.31	ND-1.47 1.47	ND
Prothiphos	ND-4.91 4.91	ND	ND	ND	ND	ND-9.53 6.55
Profenophos	ND	ND	ND	ND	ND	ND
Fenamiphos	ND	ND	ND	ND	ND	ND
Azinphos-methyl	ND	ND	ND	ND	ND	ND

n number of sample, *ND* Not Detectable

Data were statistically evaluated by one-way analysis of variance (ANOVA). Determination the differences among means were carried out by using the least significant differences (LSD) test. All statistical analysis was done using the statistical package for social sciences (SPSS 16.0) program.

Results and Discussion

There are many factors which may affect the contamination levels of OPs in drainage water such as the presences of most minerals and salts (Schlauch 1989), photosensitizers, temperature, pH, radiation, metal cations (Meikle and Youngson 1970), as well as micro-organisms (Haven and Rase 1990). Chloropyrifos, cadusafos, diazinon, prothiphos and malathion were detected in fish tissues samples (Table 2). 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}) was detected in El-Embaby drain. Prothiphos 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. The presence of chloropyrifos, cadusafos, diazinon, prothiphos and malathion, in fish samples from the studying area could be attributed to the intense agricultural activity in the area (cotton, maize and potatoes planted) and chemical application for control of agricultural pests. The contamination of fish and other aquatic organisms by OPs pesticides and their oxidation products was shown to be very low (Tsuda et al. 1997). The discharge and runoff of most minerals and salts promote photodecomposition of dissolved compounds (Schlauch 1989). Similarly, the chemical manufacturing effluent may be exposed to degradation in the environment resulting in formation of smaller molecular entities through biotransformation, hydrolysis, photolysis and elimination as a result of mineralization. The component in the waste effluents can also undergo photodegradation if they are exposed to natural sunlight. They can also undergo indirect photodegradation when one or more of the chemical components (sensitizers) present in the waste effluent. Degradation is done with different mechanisms such as photoionization and electron transfer (Schlauch 1989, Lymann et al. 1990).

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