

Monitoring of Organophosphorous Pesticides Residues in Water from the Nile River Tributaries, Egypt

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Abstract The levels of 14 organophosphorus pesticides in water samples from different tributaries of the Nile River in Egypt were monitored. water 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 two month during periods of 16 month, June 2007-September 2008. the water samples were extracted with methylene chloride and analyzed using a gas chromatography fitted with an flame photometric detector. In all water sample analyzed only chlorpyrifos-methyl (41.53ng L^{-1}) and prothiphos (30.03ng L^{-1}) were detected in only one water samples collected from El-Embaby drain.

Keywords: organophosphorus, pesticide residues, water, Egypt, Nile River

1. Introduction

Organophosphorous (OPs) compound consist of a group of roughly 250 chemicals manufactured all over the world. Approximately 140 of these compounds are pesticide, and the remaining are mainly industrial chemicals used as flame retardants, plasticizers and industrial hydraulic fluids and solvents [1]. Ops pesticides are generally among the most acutely toxic of all pesticides to vertebrate animals. They are also unstable and therefore break down relatively quickly in the environment [2]. The persistence of these compounds in the marine environment depends on the different degradation pathways including chemical, photochemical and biological processes. Hydrogen ion concentration, temperature, salinity, and microorganisms affect their persistence in the marine environment [1]. The principal route of degradation in the environment seems to be hydrolysis.

OPs pesticides have been used for agricultural purposes for at least 50 years. Since the organochlorine pesticides (OCPs) have been withdrawn from registered use because of the mounting evidence of their toxicity, persistence, and bioaccumulation in the environment, the OP pesticides are currently the largest and most versatile class in use. These compounds can be as toxic as or even more toxic to humans and to aquatic life than any other kind of pesticide [3]. Their propensity for relatively short persistence, due to chemical and biological degradation, favours their usage.

Although many OP pesticides are short-lived or are metabolized by the animals that ingest them, some are persistent and when applied in large amounts pervade the environment. Once a pesticide has been introduced into

the environment, its chemical and physical properties determine its fate: where it goes and how long it persists. Each pesticide has its own unique set of properties. Pesticides that break down quickly do not offer much opportunity for exposure. The degradation rate of a pesticide depends on the pesticides chemistry, as well as environmental factors, such as temperature, rainfall, and soil pH [4].

Pesticides are designed to be effective for a finite period to control pests and then breakdown to non-toxic substances. Pesticides mobility depends on its water solubility, solubility in fat, adsorption to soil, and its tendency to vaporize. A pesticide that is adsorbed to or taken up into a plant is less likely to become a vapor, be washed off onto the soil, or be transferred to the skin if the plant is touched. Pesticides that strongly adsorb to soil are not very mobile in water that infiltrates toward groundwater, or water that runs off into surface water, such as a pond, lake or stream. Pesticides strongly adsorbed to soil may still enter the surface water if there is soil erosion. Pesticides strongly adsorbed onto soil do not volatilize easily. When a pesticide is applied, much of it reaches the soil. Water of streams and rivers, lakes and underground aquifers become contaminated from direct application, drift, run-off from treated areas, or waste materials.

The aim of this study was to determine the identity and concentrations of 14 OPs pesticides in water samples collected from different tributaries of the Nile River at El-Menofiya governorate, Egypt.

2. Materials and Methods

2.1. Analytical Standards and Reagents

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%. 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 grade, and purchased from El Naser Pharmaceutical Chemical Co., Egypt.

2.2. Cleaning of Glassware

Before use all, the glassware was wash with tap water and detergent, hot water, distilled water, and rinsed with acetone then with methylene chloride.

2.3. Sampling Site

Water samples were collected each two month, during the period from June2007 to September 2008 from six sites. The sampled site for the study was selected in El-Menofiya governorate (Figure 1). 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. Three of the study sites are used as water canals with which to irrigate fruit and vegetable gardens. One of this sites (El-Bagoria) are at the inlet of Menof water purification station. Farmer at such sites always uses these waters for domestic as well as agricultural purposes.

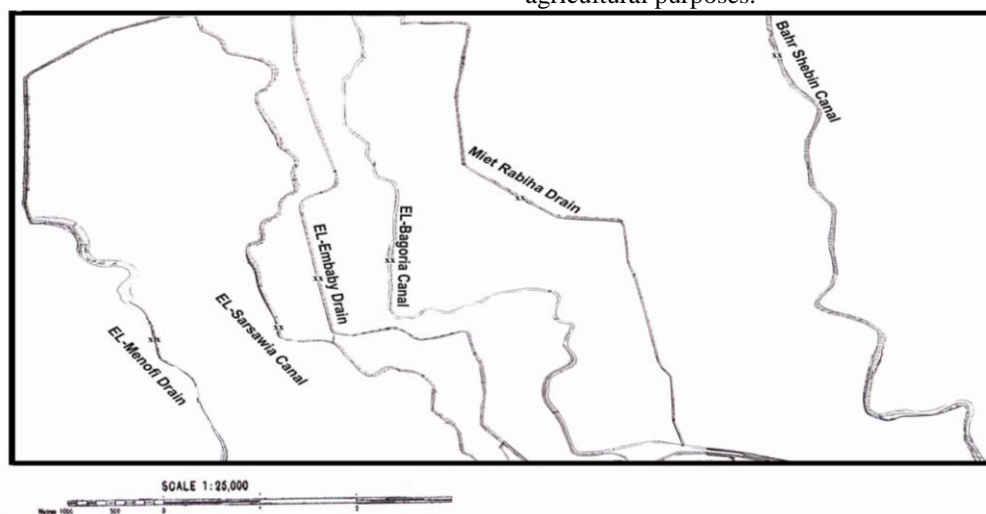


Figure 1. Location of sampling sites at El-Menofiya Governorate, Egypt

2.4. Sampling

Water samples (2.5-L) were collected in glass bottles at the water surface and 50cm below water level. The bottles were covered with screw caps and the samples were immediately transported to the laboratory for analysis. Water samples were filtered to remove sand and debris.

2.5. Extraction and Purification

A measured volume (1-L) of the sample was transferred in a 2-L separatory funnel and was extracted twice with 100ml of methylene chloride. The combined extracts were dried over anhydrous sodium sulfate and evaporated to dryness in a rotating evaporator.

Water extract was cleaned up using charcoal-celite column [5]. 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 2.0g of charcoal-celite (1:4 w/w) mixture in 10ml acetonitrile was added into the column. The acetonitrile was drained just to the top of the charcoal-celite, and then cap the tip and 0.5g of sodium sulfate was added to the top of the column. The column was conditioned with 10ml acetonitrile-toluene (3:1 v/v) before use. The extract was dissolved in 1ml of acetonitrile and quantitatively transferred to the top of the column and eluted with 50ml 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 2-3ml. 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 2ml of ethyl acetate and transferred into auto-sampler vial for gas chromatographic analysis.

2.6. Preparation of Blank Solution

The same volume of solvents and anhydrous sodium sulfate, which used in extraction of OPs pesticides from water samples were subjected to the same procedures as the examined samples to detect any possible traces of the studied pesticides and its value was subtracted from the results.

2.7. Instrumental Determination

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 30m length, 0.32mm 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 3min and

raised to 240 °C at rate of 5 °C min⁻¹ and was maintained at 240 °C for 1min and raised to 270 °C at a rate of 20 °C min⁻¹ and was maintained at 270 °C for 10min. Injector and detector temperature were maintained at 240 and 260 °C, respectively. Nitrogen was used as a carrier at flow rate of 3ml/min. the hydrogen and air flow rate were 75 and 100ml/min, respectively. Peak was identified by comparison of sample retention time value with those of the corresponding of pure standard compounds.

2.8. Recovery Assays

The average recovery percentages of OPs pesticides for fortified samples at different levels were determined and calculated for all tested compounds in water (Table 1).

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

Pesticide Name	Recovery	RSD	LOD(ng L^{-1})
Dichlorvos	88	7	0.05
Ethoprophos	86	5	0.05
Cadusafos	85	7	0.02
Diazinon	83	7	0.06
Chlorpyrifos-methyl	87	6	0.03
Pirimiphos-methyl	89	5	0.03
Chlorpyrifos	78	8	0.02
Methyl-parathion	91	4	0.07
Pirimiphos-ethyl	96	4	0.02
Malathion	90	3	0.01
Prothiphos	87	6	0.04
Profenophos	89	5	0.04
Fenamiphos	87	10	0.04
Azinphos-methyl	86	3	0.02

2.9. Statistical analysis

All statistical analysis was done using the statistical package for social sciences (SPSS 16.0) program.

3. Results and Discussion

Method sensitivity and recovery were determined by using samples spiked with the tested pesticides. The data in Table 1 shows the fortified results of OPs Pesticides in water samples. The mean recoveries in water samples for OPs pesticides were ranged from 78% to 96%, with RSD of 3-10%. Recovery rates and their relative standard deviation were acceptable. The LODs for OPs pesticides were ranged from 0.02ng L⁻¹ to 0.07ng L⁻¹ in water, ensuring LOD values significantly lower than the MRLs. These results demonstrate the good performance of the method. 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.

There are many factors which may affect the contamination levels of OPs in drainage water such as the presences of most minerals and salts [6], photosensitizers, temperature, pH, radiation, metal cations [7,8], as well as micro-organisms [9]. In all water sample analyzed only chlorpyrifos-methyl and prothiphos were detected in only one water samples collected from El-Embaby drain Table 2. In this concern Dogheim et al. reported that no OPs pesticide residues detected in water samples collected from Kafr El-Zayat Governorate [10]. OPs pesticides are quickly degradable in aquatic environment where the alkaline media accelerates their degradation [11]. However, 3,5,6-trichloro-2-pyridinol which is the major metabolite of chlorpyrifos, is more likely to leach to ground water under normal use. Domagalski et al., reported that diazinon was found to be the highest concentrations of OPs pesticides detected at San Joaquin River in California [12]. The chronic ambient water quality criteria recommended by US EPA for freshwater are 43ng/L for diazinon, 10ng/L for azinphos-methyl, 41ng/L for chlorpyrifos, 100ng/L for malathion and 13ng/L for parathion [13].

Table 2. Concentration (ng L^{-1}) of organophosphorus pesticides in water samples

Pesticides Name	El-Sarsawia canal	El-Bagoria canal	Bahr Shebin canal	El-Embaby drain	El-Menofi drain	Meit-Rabiha drain
	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max	Min-Max
	Mean n=8	Mean n=8	Mean n=8	Mean n=8	Mean n=8	Mean n=8
Dichlorvos	ND	ND	ND	ND	ND	ND
Ethoprophos	ND	ND	ND	ND	ND	ND
Cadusafos	ND	ND	ND	ND	ND	ND
Diazinon	ND	ND	ND	ND	ND	ND
Chlorpyrifos-methyl	ND	ND	ND	ND	ND	ND
Pirimiphos-methyl	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND-41.53 41.53	ND	ND
Methyl-parathion	ND	ND	ND	ND	ND	ND
Pirimiphos-ethyl	ND	ND	ND	ND	ND	ND
Malathion	ND	ND	ND	ND	ND	ND
Prothiphos	ND	ND	ND	ND-30.03 30.03	ND	ND
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

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