



Monitoring of Organophosphorus and Organochlorine Pesticides Residues in Freshwater of Suez Canal Region, Egypt by Gas Chromatography

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Abstract

Water is very essential for the human, animal and agriculture existence. Water supplies are exposed to contamination by different sources from industrial, pharmaceutical, agricultural and natural origins. Traditionally, analytical methods based on gas chromatography or liquid chromatography were used to monitor water quality. The objective of this research was to monitor some OPPs and OCPs pesticides residues in Ismailia freshwater canal in the three governorates (Ismailia, Port Said and Suez) over a period started from May 2008 to January 2011 by GC using flame photometric detector (FPD) for OPPs and electron capture detector for OCPs pesticides. No OCPs pesticides residues were found in freshwater at quantification level of the GC method, however OPPs pesticides methamidophos (1.97 ngL⁻¹) and ethoprophos (1.73 ngL⁻¹) were detected in freshwater samples collected from Port Said governorate in February 2009.

Keywords: Pesticides; Freshwater; Suez Canal Region.

Received on: 13.10. 2018

Revised on: 19. 11. 2018

Accepted on: 25. 11. 2018

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1. Introduction

The use of pesticides has greatly increased with the development of intensive agricultural practices, a consequence, the number of organic compounds being detected in surface or groundwater has raised concern about raw water contamination. These pollutants, present in water resources at low concentrations, can affect ecosystems and impact drinking water supplies. Ismailia freshwater canal is mainly affected by inputs of agricultural pollutants and to a lesser extent by urban and industrial activities. As water drains from the canal catchments area it could transport residues of a variety of toxic chemical products, some of which could cause ecological damage.

The complex matter of pesticide trace analysis can be afforded by developing / using multi-component methods able to determine as many as possible pesticides and pesticide metabolites having a broad range of polarity and structural properties in a wide array of sample matrices at the required sensitivity limit. Today, gas chromatography (GC) still remains the most popular technique for accomplishing multi-component methods, as demonstrated by an effective identification /confirmation tool. The literature survey revealed that Gas chromatography (GC) and GC-MS has traditionally been the methods of choice for the analysis of organophosphorus pesticides (OPPs) in water samples (Serrano et al., 2012; Akdoğan et al., 2011; Fang et al., 2012; Samadi et al., 2012; Yang et al.,

2011; Camino-Sánchez et al.,2011; Alves et al., 2011; Portolés et al.,2011; Toledano et al.,2010; Jurzik et al., 2010; Huang et al., 2010; López-Blanco et al.,2005)and for analysis of organochlorine pesticides (OCPs) (Beamer et al., 2012; Dasgupta et al.,2011; He et al., 2011; Mawussi et al., 2009; Kumari et al., 2008; Brondi et al., 2005; Wasswa et al., 2011; Chen et al., 2011; Jan et al., 2009; Portolés et al., 2010; Tahboub et al., 2005). The objective of this research was to monitor some OPPs and OCPs pesticides residues in Ismailia freshwater canal samples by GC using flame photometric detector (FPD) for OPPs and electron capture detector for OCPs pesticides.

2. Experimental

2.1. Materials and Reagents

The authentic standards of thirteen OPPs pesticides standards (Dichlorovos, methamidophos, ethoprophos, dimethoate, chloropyrifos-me, malathion, chlorpyrifos, phenthoate,prothiophos, profenophos, ethion, triazophos and azinophos-ethyl)and thirteen OCPs (α , β and Δ – benzenehexachloride (BHC), heptachlor, aldrine, heptachlor epoxide, γ -chlordane, endosulfan, dieldrin, p,p'-Dichlorodiphenyl dichloro-ethylene (p,p' DDE), endrin, p,p' Dichlorodiphenyldichloroethane (p,p' DDD), p,p'-Dichlorodiphenyltrichloroethane (p,p' DDT)), were purchased from Accustandards Co. (New Haven, Connecticut, USA). Florisil (BDH, 60-100 U.S. mesh, England) activated at 130 oC for 16 hours before use. Methanol and acetonitrile were (BDH, Poole, UK). Sodium Chloride and anhydrous sodium sulphate (ADWIC, Egypt), n-hexane, chloroform, dichloromethane were analytical grade.

2.2. GC method

The Gas Liquid Chromatography Processes for OPPs and OCPs were conducted in the "Central Agricultural Pesticides Laboratory", Ministry of Agriculture and Land Reclamation, located in Dokki, Cairo as follows:

2.2.1. GC for organophosphorus pesticides

A Hewlett Packard, model HP 6890 gas liquid chromatograph equipped with flame photometric detector (FPD) was used to monitor residues of OPPs. The column was DB-5 (30 m length, 0.32 mm i.d. x 0.52 μ m film thickness). Injector

temperature was held at 225 °C and detector temperature was held at 280 °C. Nitrogen was used as a carrier gas running at a flow rate of 3 mL min⁻¹. Column temperature program was as follows: initial temperature 90 °C held for 2 min., elevated at a rate of 20 °C min⁻¹. The final temperature was 150 °C, then raised at a rate of 6 °C min⁻¹. The final temperature was 270 °C for 15 min.

2.2.2. GC for organochlorine pesticides

A Hewlett Packard gas liquid chromatograph equipped with 63Ni electron capture detector (ECD) was used to monitor residues of OCPs. A capillary column PAS-5 (25 m, i.d. 0.32 mm, 0.52 mm film thickness) was used. Injector temperature was held at 225 °C. The temperature program was as follows: initial temperature 90 °C held for 10 min., then the temperature was raised at a rate of 6 °C min⁻¹. The final temperature was 270 °C and held for 25 min. Nitrogen was used as a carrier gas and make up gas running at a flow rate of 3 mL min⁻¹.

2.3. Standard solutions and calibration

Stock standard solutions of the selected OCPs and OPPs pesticides were prepared separately by dissolving 1 mg of each compound in 10 mL hexane: acetone mixture (9:1). These stock solutions were stored at 4°C, protected from light.

2.3.1. Calibration of GC method

The standard solutions were prepared by further dilutions of the stock standard solutions with hexane to reach the concentration range of 0.01-10 mgL⁻¹ for the studied OPPs and OCPs pesticides. All the standard solutions were stored at 4 °C in the dark.

2.4. Sampling

Water samples from both freshwater and drinking water reservoir tanks were collected 15-20 centimeter depth at the selected sites in Ismailia, Port Said and Suez. The samples were collected bimonthly in 1-L capacity, glass, with TFE-lined screw capped bottles. Sampling bottles were rinsed three times with tap water, once with chromic acid, three times with organic-free water, twice with washing acetone, once with special grade acetone, twice with pesticide grade hexane and dry (uncapped) in a hot air oven at 360 °C. Sampling bottles were washed three times with the sample then samples collected and preserved in cool ice boxes throughout the field trip and during transportation to the laboratory. 17 samples were collected from each site during the research period.

2.5. Sample preparation

Sample was shaken and accurately 1L was transferred to a 2 L separatory funnel, then 10 mL of saturated sodium chloride was added. Sample bottle was rinsed with 60 mL of 15% methylene chloride in hexane and the solvent was poured to the separatory funnel. The sample was shaken vigorously for 5 min and was allowed to separate for 10 min. Organic layer was filtered through anhydrous sodium sulfate while the aqueous phase was returned back to the sampling bottle. The same procedure repeated three times. The organic solvent was evaporated and the residues were dissolved in 50 mL of chloroform. Sample clean-up done by transferring the extract to florisil columns, each containing 4 inches of florisil and 1 inch of anhydrous sodium sulfate. The columns eluted with 200 mL 15% methylene chloride in hexane. The collected solutions evaporated at 40 °C to dryness, and the residues brought-up in 10 mL acetone prior to analysis.

3 μ L of the extracted solution were injected into GC-FPD, GC-ECD. Identification of the unknown peaks in the samples chromatograms was managed by comparison of sample retention time (Rt) with that of the corresponding pure standard compounds for GC method.

3. Results and discussion

The pesticides studied in this chapter include several types of compounds (OPPs and OCPs pesticides), so it is not possible to detect all the elements simultaneously in one GC run, so it was necessary to use more than one kind of detector to achieve selective and/or highly sensitive detection of these compounds. The determination of sulfur or phosphorus containing compounds is the job of the flame photometric detector (FPD), which is the detector of choice for separation of the studied OPPs, Fig. 1 represents complete separation of OPPs standards (Dichlorovos , methamidophos , ethoprophos , dimethoate, chlorpyrifos-me, malathion, chlorpyrifos, phenthoate, prothiophos, profenophos, ethion, triazophos and azinophos-ethyl pesticides). Electron Capture Detector or GC-ECD is a technique used to analyze halogenated compounds and is primarily used in the environmental, forensic and pharmaceutical analysis. Within an ECD, when certain molecules pass by the detector, they capture some of the electrons in the

sample and this reduces the current measured. The compensation for this reduction is recorded as a positive peak. ECD is used for the determination of OCPs and gives complete separation with reasonable retention time and selectivity for α -BHC β -BHC and Δ - BHC, heptachlor, aldrine, heptachlor epoxide, γ -chlordane, endosulfan, dieldrin, p,p' DDE, endrin, p,p' DDD and p,p' DDT (Fig. 2).

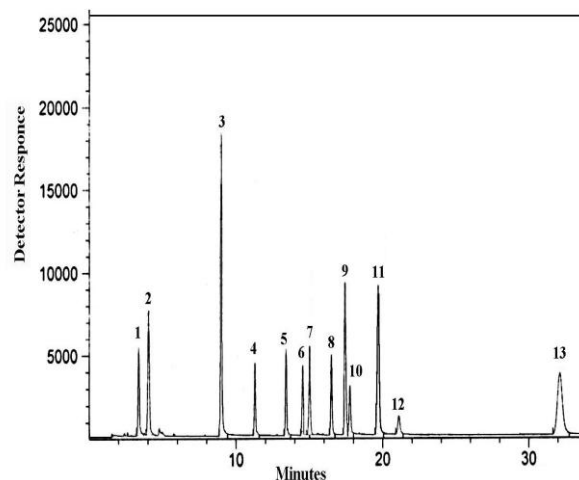


Fig. 1: GC/ FPD chromatogram of 1) Dichlorovos , 2) methamidophos, 3) ethoprophos , 4) dimethoate, 5) chlorpyrifos-me, 6) malathion, 7) chlorpyrifos, 8) phenthoate, 9) prothiophos, 10) profenophos, 11) ethion, 12) triazophos and 13) azinophos-ethyl pesticides.

Although the traditional liquid- liquid extraction (LLE) requires the handling of a large volume of chlorinated solvents and tends to be difficult to automate, the nature of the environmental sample can determine the choice between LLE and SPE methods. The analysis of wastewater and surface water requires the treatment of the total sample, including pesticides adsorbed on fine materials. LLE should be then preferred since the total sample can be handled without filtration.

Many solvents were used for extracting OPPs and OCPs pesticides, such as chloroform, n-hexane, dichloromethane, and ethyl acetate. It was found that mixture of dichloromethane in n-hexane is a better extraction solvent than the others. Also the ratio of dichloromethane to n-hexane was studied and the better recovery percent for the analyzed pesticides was found to be 15% dichloromethane in n-hexane.

The LLE is followed by clean up on florisil column which is composed of a hard powdered

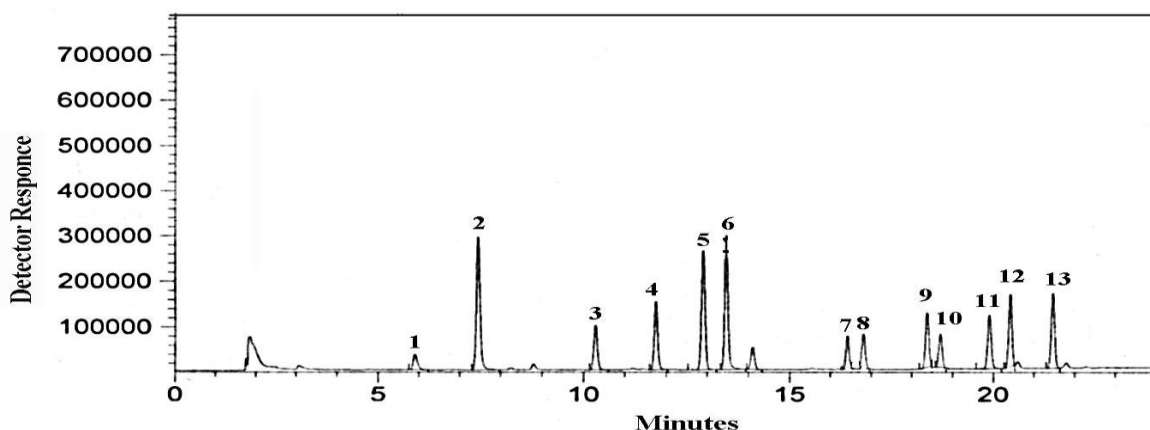


Fig. 2: GC/ ECD chromatogram of 1) α -BHC , 2) γ -BHC 3) Δ -BHC, 4) heptachlor, 5) aldrine, 6) heptachlor epoxide, 7) γ -chlordane, 8) endosulfan, 9) dieldrin, 10) p,p' DDE, 11) endrin, 12) p,p' DDD and 13) p,p' DDT.

magnesia-silica gel, It is often referred to as "activated magnesium silicate" and anhydrous sodium sulfate. As a highly selective adsorbent frequently employed in cleanup of pesticide residues and purification of chlorine-containing pesticides.

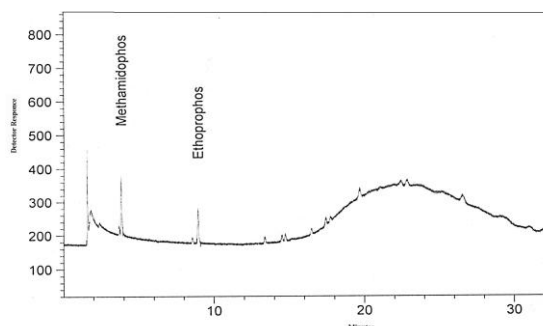


Fig. 3: GC/FPD chromatogram of freshwater sample collected from Port Said governorate in February 2009

The described GC method has been successfully employed to determine the most utilized OPPs and OCPs pesticides in freshwater and drinking water in the three governorates (Ismailia, Port Said and Suez) over a period started from May 2008 to January 2011. No OCPs pesticides residues were found in freshwater at quantification level of the GC method, however OPPs pesticides methamidophos (1.97 ngL^{-1}) and ethoprophos (1.73 ngL^{-1}) were detected in freshwater samples collected from Port Said governorate in February 2009 (Fig.3).

4. Conclusion

The performed GC method using two types of detectors FPD and ECD with simple liquid-liquid extraction conjunction offers a simple and sensitive approach for the simultaneous determination of OPPs and OCPs, which may be present in surface water samples due to excessive and misused handling of pesticides in Egypt.

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