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Monitoring of Pesticide Residues in Saudi Arabia Agricultural Soils

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ABSTRACT

The objective of our study was to monitor the multiple pesticide residues in soil samples collected from 15 regions around the Saudi Arabia. Fifteen regions were selected at Central (Dereiah, Deirab, Kharj, Mezahmiah and Qaseem); East (Qatif, Al-Hasa and Haradh); West (Taif); North (Tabouk, Jouf and Hail) and South (Abha, Gizan, Wadi Al-Dwaser) of Saudi Arabia to perform the survey process of pesticide residues. Soil samples were collected from nine sites for each region from surface layer (0-30 cm depth) and sub-surface layer (30-60 cm depth). A simple Microwave-Assisted Extraction (MAE) technique and gas chromatography with mass spectrometer detector were modified and applied as extraction and analytical techniques, respectively. The major groups of pesticides tested were Organochlorines (OCPs), Organophosphorus (OPPs), Carbamates, Pyrethroids (PYR) and Herbicides in different soil samples. The overall data showed that the highest concentration of pesticide residues was differed according to the pesticide type, soil layer and regions. Twelve pesticide residues were detected in soil samples collected from different regions and ranged as follows; Dimethoate (0.007-0.700 mg kg⁻¹); Chloroneb (0.011-0.4 mg kg⁻¹); Methomyl (0.018-0.405 mg kg⁻¹); Oxamyl (0.014-0.150 mg kg⁻¹); Toxaphen (0.006-0.162 mg kg⁻¹); pp-DDT (0.080-0.575 mg kg⁻¹); pp-DDE (0.1-0.525 mg kg⁻¹); Monocrotophos (0.021-0.047 mg kg⁻¹); Chlorpyrifos (0.12-0.24 mg kg⁻¹); Diazinon (0.024 mg kg⁻¹); Cypermethrin (0.012-0.205 mg kg⁻¹) and Lindane (0.290-394 mg kg⁻¹). The results indicated that Dimethoate, Chloroneb, Methomyl, Oxamyl and Toxaphen were the more contamination sources in the studied regions. Also, Gizan region was more contaminated with pesticide residues followed by Wadi Al-Dwaser and Abha regions.

Key words: Extraction, residues, GC-MS, survey, soil, DDT, MAE

INTRODUCTION

Historically, as an agricultural terms, a persistent pesticide was considered to be remaining in the soil in significant quantities after application until the next growing seasons (Sun and Lee, 2003; Gong *et al.*, 2004; Craven and Hoy, 2005). Pesticides have been used in agriculture for decades and they are distributed widely across the globe, even in pristine regions. This results in wide concentration levels of their residues in the soils and the environment. They are among the hazardous contaminants and can persist in soils for decades even after being banned (Goncalves *et al.*, 2006; Hussen *et al.*, 2007; Oldal *et al.*, 2006; Shegunova *et al.*, 2007). The common use of pesticides can cause pollution for the environment and became a potential and/or

deliberate risk to human health due to their potential carcinogenic effects (El-Saeid, 1999; Brock *et al.*, 2000).

Organochlorine Pesticides (OCPs) have been a major environmental issue, attracting both scientific and public concern because of their nature of toxicity, persistence, health problems and endocrine disrupting effects (Wang *et al.*, 2008). It has also a great concern due to their high bioaccumulation potential, ubiquity, persistence in the environment, deleterious effect and high toxicity to non-target organisms (Jones and de Voogt, 1999; Hao *et al.*, 2008). Recent investigations showed that the persistence of DDTs and HCHs has left considerable amount of residues in soils for many areas (Zhang *et al.*, 2006; Wang *et al.*, 2007; Cai *et al.*, 2008). The OCPs residues in soils showed a temporal and spatial changes in the world (Skrbic and Durisic-Mladenovic, 2007) because the residue level of OCPs depends on the balance of inputs and disappearance (such as decomposition, leaching and volatilization). Their concentration in the environment are affected by many factors including application history and agricultural practices (Wang *et al.*, 2006) and nature and persistence of the pesticides. For several years, organophosphorus pesticides (OPPs) and pyrethroid pesticides (PYR) are widely used in agriculture, especially in the developing countries. Although, the use of OPP and PYR pesticides increase crop production, their usage have a great deal to the environment (Wang *et al.*, 2008).

The Microwave Assisted Extraction (MAE) techniques were used by Ganzler *et al.* (1986), to extract anti-nutritive compounds from various plant materials. Since then, microwave methodologies have been adapted for other scientific applications, including the extraction of pesticides (Prados-Rosales *et al.*, 2002; Fuentes *et al.*, 2006; Sporning *et al.*, 2005; Tavares *et al.*, 2005). There are many advantages of MAE procedures such as reduced solvent usage and shorter analysis time. There are the possibilities of new applications of MAE and several publications have describing the extraction methodologies (Barriada-Pereira *et al.*, 2003; Sun and Lee, 2003; Fuentes *et al.*, 2006; Yuan *et al.*, 2006; CEM Corporation, 2000).

The aims of the present study are to demonstrate the practical applicability of MAE in combination to gas chromatography-mass spectrometry (GC-MS) for the surveying and determining of pesticide residues in different soil samples collected from Saudi Arabia.

MATERIALS AND METHODS

Chemicals and reagents: Pesticide standards (Dimethoate, Chloroneb, Methomyl, Oxamyl, Toxaphen, DDT, DDE, Monocrotophos, Chlorpyrifos, Diazinon, Cypermethrin and Lindane,) were provided in the year of 2007 by Chemservice, USA. All pesticide standards were of 98-99% purity. Hexane and Acetone used for residues analysis were analytical reagent grade. The pesticides stock and working solutions were prepared in acetone.

Soil sampling collection: Total of fifteen regions (Table 1) were selected at Central (Dereiah, Deirab, Kharj, Mezahmiah and Qaseem); East (Qatif, Al-Hasa and Haradh); West (Taif); North (Tabouk, Jouf and Hail) and South (Abha, Gizan, Wadi Al-Dwaser) of Saudi Arabia to explore pesticide residues in soils (Fig. 1). Soil samples were collected from three locations for each region. For each location, three sites were selected to collect the soil samples from surface layer (0-30 cm depth) and sub-surface layer (30-60 cm depth). The soil samples were placed in clean plastic sheet and mixed up carefully on the site with a small shovel. Approximately, one kg portion of each sample was collected. The soil samples were air dried and sieved through a 2.0 mm sieve and then were prepared to extract the pesticides residues (Al-Turki *et al.*, 2009).

Table 1: List of regions for soil sampling sites in Saudi Arabia

No.	Regions	Area	No. of collected samples
1	Qasseem	Central	18
2	Deirab		18
3	Deriyah		18
4	Kharj		18
5	Mezahmiyah		18
6	Qatif	Eastern	18
7	Al-Hasa		18
8	Haradh		18
9	Taif	Western	18
10	Tabuk	Nourthern	18
11	Jouf		18
12	Hail		18
13	Abha	Southern	18
14	Gizan		18
15	Wadi Al-Dwaser		18



Fig. 1: Soil sampling sites in Saudi Arabia

Preparation of spiked soil samples: Spiked soil samples were prepared by adding an appropriate volume of spiking solution (5 mg L⁻¹ of pesticides in acetone) to five grams of soil. The spiked samples were prepared just before analysis, waiting approximately 30 min until solvent evaporation. Soil sample was extracted with both Microwave-Assisted Extraction, MAE (Ganzler *et al.*, 1986) and Soxhlet extraction techniques (Singh *et al.*, 2007; Carvalho *et al.*, 2008; Schreck *et al.*, 2008). The main purpose of this step is to determine the average recovery percent of investigated pesticides by both extraction techniques.

Minimum detection limit (MDL): To determine the MDL and perform the GC-MS quantification using a four-point calibration curve plotting peak area versus mg L⁻¹ concentration of 12 pesticides using the dilution levels ranged from 0.0001 to 5.00 mg L⁻¹.

Extraction of pesticide residue by MAE: The proposed EPA Method 3540C (USEPA, 1996) and CEM application note No. E003 (CEM Corporation, 2000) was modified and used during conducting of the present study. A microwave assisted extraction (MAE) system MES-1000, CEM Corporation, Matthews, NC, USA with Lined Extraction Vessels (LEV).

In the preliminary studies, the effects of temperature, microwave power, extraction time and solvent volume were tested (Table 1), to extract different groups of pesticide residues from soil samples. For this purpose, 5.0 g of soil was weighed in a tetrafluoromethaxil (TFM) microwave extraction vessel with addition of 1 mL of an aqueous spiking solution containing mixture of the pesticide standard solution. Soil samples were equilibrated by shaking for 1 h before microwave extraction. Finally, all samples extracted under different conditions as will show in the results to obtain the optimal MAE conditions with this procedure. Finally the optimum extraction conditions with acceptable recovery rate was mixture of 5.0 g soil samples with extraction solvent of (Acetone: Hexane, 3:2 on v/v base), 80 psi pressure, 60% microwave power, 120°C temperature and 20 min extraction time. After extraction, soil extracts were filtered and evaporated to dryness; then the residue was re-dissolved and directly analyzed by gas chromatography mass spectrometer (GC-MS). By this procedure, clean chromatograms were obtained without any additional cleanup step.

Gas Chromatography-Mass Spectrometer (GC-MS) analysis: The extracts of pesticide residues in soil samples extracted by MAE technique were performed and analyzed by a HP 5890 series II plus GC coupled to an HP 5972 Mass Selective Detector. The GC columns were a DB-5 fused silica capillary column (30 m×0.32 mm ID, 1 µm film thickness; J and W Scientific, Folsom, CA). One microliter of the extract was injected split-less injector at 250°C temperature, on the GC-MS for analysis. The temperature program for the GC was as follows: isothermal for 1 min at 100°C, increased at a rate of 10°C min⁻¹ up to 240°C and isothermal for 15 min. Helium was used as a carrier gas (1.2 mL min⁻¹). Quantification was performed using a four-point calibration curve plotted peak area versus mg L⁻¹ concentration. The results were expressed in percentage recovery of the pesticides.

Quality control: Recoveries were determined for all samples by spiking with the mix of pesticide standards prior to extraction. Recoveries were higher than 98% for all samples and the recovery factors were not applied to any of the data. Analytical method recoveries for the given set of pesticides were also determined by repeating the whole analytical procedure with the reference soil

Table 2: Pesticide recovery ± RSD, (%) of spiked soil samples extracted by MAE and determined with GC-MS

Pesticides	Recovery±RSD (%)
Dimethoate	99.64±1.67
Chloroneb	99.28±1.22
Methomyl	98.56±2.07
Oxamyl	98.70±2.48
Toxaphen	99.04±1.47
pp-DDT	102.44±1.55
pp-DDE	101.67±2.26
Monocrotophos	98.14±2.00
Chlorpyrifos	98.00±2.29
Diazinon	98.00±2.25
Cypermethrin	98.45±1.68
Lindane	101.55±1.22

enriched by the standard mixture of the pesticides of the known concentration. They ranged from 98 to 102.44% for all tested compounds as showed in (Table 2). Reproducibility was calculated based on the replicate analyses, with relative standard deviation (RSD,%) less than 2.48%. All laboratory blanks were below the detection limits.

RESULTS AND DISCUSSION

Average pesticide residue concentrations in different regions of Saudi Arabia agricultural soils from surface (0-30 cm) and subsurface (30-60 cm) layers are summarized in Table 3 and 4. The collected soil samples represent five areas as shown in Table 1. The highest concentration of pesticide residues was differed according the pesticide type. The highest concentrations in surface layer were 0.7 mg kg⁻¹ for Dimethoate at Abha. In subsurface layer, the highest concentration was 0.575 mg kg⁻¹ for pp-DDT at Wadi Al-Dwaser (Table 4).

The present results indicated that soil surface layer as general has higher concentrations than soil subsurface layer (Ahmed *et al.*, 1998). Also Gizan region was more contaminated with pesticide residues (5 pesticide residues) followed by Wadi Al-Dwaser and Abha regions (3 pesticide residues for each). Other regions have one or two pesticide residues only.

Twelve pesticide residues were detected in soil samples collected from different regions as follows; Dimethoate (15 region); Chloroneb (12 regions); Methomyl (11 regions); Oxamyl and Toxaphen (8 regions); pp-DDT and pp-DDE (4 regions); Cypermethrin (3 regions); Monocrotophos (2 regions); Chlorpyrifos, Diazinon and Lindane (one region). Therefore, the results indicated that Dimethoate, Chloroneb, Methomyl, Oxamyl and Toxaphen were the more contamination sources in the studied regions.

The most important notice in the results of soil analysis was the detection of the residue of pp-DDT and one of their derivatives pp-DDE. Both pesticide residues were detected in 4 regions. The concentration of pp-DDT was found to be higher than that of pp-DDE in soil samples from all regions, because DDE is one of the primary metabolites of DDT. All detected pesticide residues in our study were higher than pesticide residues detected in other studies. These results may be due to the extensive use of organochlorine insecticides and their long resistance in the investigated regions (Harner *et al.*, 1999; Ribes and Grimalt, 2002; Zhang *et al.*, 2005, 2006; Wang *et al.*, 2007, 2008; Shegunova *et al.*, 2007; Li *et al.*, 2008).

Table 3: Average pesticide residue concentrations (mg kg⁻¹) in soil samples collected from surface layer (0-30 cm) of different Saudi Arabia regions

Pesticides	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Dimethoate	0.115	0.131	0.110	0.156	0.297	0.250	0.090	0.034	0.168	0.053	0.245	0.456	0.700	0.390	0.240
Chloroneb	0.095	0.043	ND*	0.021	ND	ND	0.165	0.136	0.240	0.033	ND	0.126	0.145	0.400	0.203
Methomyl	0.160	0.068	0.205	0.045	ND	0.145	0.099	0.206	ND	0.063	0.120	0.018	ND	0.405	ND
Oxamyl	0.017	ND	ND	0.048	ND	0.115	0.120	ND	0.090	0.057	0.065	ND	ND	0.150	ND
Toxaphen	0.069	ND	0.014	ND	ND	0.125	0.160	0.036	0.034	0.037	0.068	ND	ND	ND	ND
pp-DDT	ND	ND	ND	ND	ND	0.055	0.092	ND	ND	ND	ND	ND	ND	0.285	0.190
pp-DDE	ND	ND	ND	ND	ND	0.135	0.111	ND	ND	ND	ND	ND	ND	0.140	0.210
Monocrotophos	ND	ND	ND	ND	ND	ND	ND	ND	0.021	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.240	ND	ND
Diazinon	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cypermethrin	ND	ND	ND	ND	ND	ND	ND	ND	0.205	0.014	ND	0.165	ND	ND	ND
Lindane	ND	ND	ND	ND	0.394	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

*ND not detected

Table 4: Average pesticide residue concentrations (mg kg⁻¹) in soil samples collected from subsurface layer (30-60 cm) of different Saudi Arabia regions

Pesticides	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Dimethoate	0.110	0.011	0.010	0.011	0.027	0.115	0.135	0.061	0.145	0.007	0.079	0.061	0.475	0.320	0.110
Chloroneb	0.038	0.021	0.011	0.011	ND	ND	0.075	0.056	0.140	0.011	ND	0.060	0.120	0.240	0.113
Methomyl	0.100	0.025	0.110	0.030	ND	0.065	0.059	0.126	ND	0.035	0.040	0.092	ND	0.245	ND
Oxamyl	0.014	ND	ND	0.030	ND	0.050	0.100	ND	0.029	0.038	0.025	ND	ND	0.075	ND
Toxaphen	0.016	ND	0.006	ND	ND	0.080	0.120	0.162	0.021	0.010	0.023	ND	ND	ND	ND
pp-DDT	ND	ND	ND	ND	ND	0.080	0.102	ND	ND	ND	ND	ND	ND	0.178	0.575
pp-DDE	ND	ND	ND	ND	ND	0.100	0.141	ND	ND	ND	ND	ND	ND	0.131	0.525
Monocrotophos	ND	0.047	ND	ND	ND	ND	ND	ND	0.024	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.120	ND	ND
Diazinon	ND	ND	0.024	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cypermethrin	ND	ND	ND	ND	ND	ND	ND	ND	0.120	0.012	ND	0.160	ND	ND	ND
Lindane	ND	ND	ND	ND	0.290	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

*ND not detected

The highest concentration of pesticide residues in surface layer was found in southern part of Saudi Arabia. The concentrations were 0.443 mg kg⁻¹ for Dimethoate; 0.249 mg kg⁻¹ for Chloroneb; 0.405 mg kg⁻¹ for Methomyl; 0.150 mg kg⁻¹ for Oxamyl; 0.238 mg kg⁻¹ for pp-DDT; 0.175 mg kg⁻¹ for pp-DDE and 0.240 mg kg⁻¹ for Chlorpyrifose. But the highest value of Cypermethrin (0.205 mg kg⁻¹) was at Western region and Lindane (0.394 mg kg⁻¹) at Central region. For subsurface layer, the highest values were found in southern region (0.302 mg kg⁻¹ for Dimethoate; 0.158 mg kg⁻¹ for Chloroneb; 0.245 mg kg⁻¹ for Methomyl; 0.075 mg kg⁻¹ for Oxamyl; 0.377 mg kg⁻¹ for pp-DDT; 0.328 mg kg⁻¹ for pp-DDE and 0.120 mg kg⁻¹ for Chlorpyrifos). The highest values of Monocrotophos (0.047 mg kg⁻¹); Diazinon (0.024 mg kg⁻¹); Lindane (0.290 mg kg⁻¹) were detected in central region. Toxaphen (0.121 mg kg⁻¹) was detected in highest value in eastern region.

The general distribution of studied pesticides reflects the agricultural use of these pesticides in all region overall Saudi Arabia. Some of these pesticides were never used in these regions, other were used in small or large quantities, such as in southern region.

Organochlorine Pesticides (OCPs) attracted wide concern for decades because of their nature of persistence, biomagnification and high toxicity to non-target organisms (Nakata *et al.*, 2002). Some of OCPs are even identified as endocrine disrupting pesticides by USEPA (1998). OCPs were well documented in urban and suburban soils (Ma *et al.*, 2003; Zhu *et al.*, 2005, Zhang *et al.*, 2005; Li *et al.*, 2006, 2008). The chemical properties of organochlorine pesticides such as low water and high fat solubility, stability to photo-oxidation and low vapour pressure are the main factors not only in the efficacy of these compounds as pesticides but also in their persistence in the environment.

According to the environmental quality standard for soils (Wang *et al.*, 2008), the quality of soil was classified as having little pollution (below 0.05 mg kg⁻¹), slight pollution (between 0.05-0.5 mg kg⁻¹), moderate pollution (between 0.5-1.0 mg kg⁻¹) and heavy pollution (>1.0 mg kg⁻¹). When compared the levels of present study could be defined as having slight pollution in most regions and moderate pollution in few regions (Table 3, 4).

CONCLUSION

Most of the compounds studied were recovered in good yields with Relative Standard Deviations (RSDs) below 2.48%. The averages of MDL ranged from 0.0001 to 0.004 mg L⁻¹ for MAE. The MAE modified method was successfully applied to the extraction of 12 pesticide residues namely, Dimethoate, Chloroneb, Methomyl, Oxamyl, Toxaphen, DDT, DDE, Monocrotophos, Chlorpyrifos, Diazinon, Cypermethrin and Lindane from soils which was considered an appropriate index to establishing its applications. Further characterization of pesticide residues in soil and their mobility and transport in soil profile would be useful. Also, the interaction between pesticide residues and soil properties will be good point to study. The present results indicated that soil surface layer as general has higher concentrations than soil subsurface layer. Also, Gizan region was more contaminated with pesticide residues followed by Wadi Al-Dawaser and Abha regions. MAE and GC-MS techniques were accurate, reliable and less time consuming in the analysis of different surface and sub-surface layer soil samples and are recommended for the monitoring of pesticides with a broad range of physico-chemical properties in soils.

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