



Research Journal of
**Environmental
Sciences**

ISSN 1819-3412



Academic
Journals Inc.

www.academicjournals.com

Evaluation of Pesticide Residues in Saudi Arabia Ground Water

M.H. El-Saeid, A.M. Al-Turki, M.I. Al-Wable and G. Abdel-Nasser

Department of Soil Science, College of Food and Agricultural Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia

Corresponding Author: M.H. El-Saeid, Department of Soil Science, College of Food and Agricultural Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia Tel: 00966-14673418/00966509828168 Fax: 00966-14678440

ABSTRACT

The objective of present study is to demonstrate the practical applicability of Microwave-Assisted Extraction (MAE) and Gas Chromatography-Mass Spectrometry (GC-MS) for the surveying and determining pesticide residues in ground water samples. A survey, undertaken in Saudi Arabia, has shown the presence of organochlorine, organophosphorous, carbamates and pyrethroids pesticides in the ground water samples. Fifteen regions were selected at Central, East, North and South of Saudi Arabia to perform the survey process of pesticide residues in ground water. The MAE followed by GC-MS was used for the extraction and determination of the pesticides residues. The pesticide residues of DDE, DDT, dimethoate, toxaphen chloroneb, methomyl, promoxenyl, bendiocarb, promoxenyl, bendiocarb and cypermethrin were detected in ground water samples. The most detected pesticides in water samples were Dimethoate (86.66% of total regions), Methomyl (53.3% of all regions) and Chloroneb (20% of all regions). All the pesticide residues extracted by MAE method were recovered in good yields and detection limits ranged from 0.0001 to 0.003 mg L⁻¹. Dimethoate was detected at high concentration in water samples collected from Mezahemya (0.418 mg L⁻¹), Chloroneb (0.114 mg L⁻¹) in Al-hassa and Bendiocarb (0.181 mg L⁻¹) in Abha. It was concluded the MAE and GC-MS techniques were accurate, reliable, less time consuming and cost effective in the analysis of different ground water samples and are recommended for the monitoring of pesticides with a broad range of physico-chemical properties in ground water. The present results are alarming for the health of the human beings in the studied regions.

Key words: Groundwater, microwave extraction, pesticide residues, organochlorines, organophosphorus, GC-MS

INTRODUCTION

Several hundred pesticides of different chemical nature are currently used for agricultural purposes all over the world. Because of their widespread use, they are detected in various environmental matrices, such as soil, water and air. Pesticides are divided into many classes, of which the most important are organochlorine and organophosphorous compounds. Organochlorine pesticides are known to resist biodegradation and therefore, they can be concentrated through food chains and produce a significant magnification of the original concentration at the end of the chain (Iwata *et al.*, 1994; Sankararamakrishnan *et al.*, 2005).

Recently, many investigators reported that the persistence of different pesticides left residual amounts in ground water of many areas with different levels (Matin *et al.*, 1998; Leonard, 1990; Legrand *et al.*, 1991; Hernandez *et al.*, 1993; El-Kabbany *et al.*, 2000; Kashyap *et al.*, 2002; Shukla *et al.*, 2006; Maloschik *et al.*, 2007).

Monitoring of pesticide residues in water collected from Kafr El-Zayat Governorate, Egypt. Water samples and groundwater samples had the highest residues of HCHs and DDTs, followed by Nile River water and then tap water. However, the organochlorine pesticide residues were found at concentrations below the maximum allowable limits set by the World Health Organization for drinking water (Dogheim *et al.*, 1996).

Contamination of ground water resources by pesticides has brought increased environmental concern (Papadopoulou-Mourkidou *et al.*, 2004). The problem has become more prominent in countries where ground water aquifers constitute the main drinking water resources for rural and adjacent urban areas (Spliid and Koppen, 1998; Tuxen *et al.*, 2000).

Pesticide residues reach the aquatic environment through direct runoff, leaching, careless disposal of empty containers, equipment washings, etc. (Milidas, 1994). Surface water contamination may have eco-toxicological effects for aquatic flora and fauna as well as for human health if used for public consumption (Forney and Davis, 1981; Mulla and Mian, 1981; Leonard, 1988; Miyamoto *et al.*, 1990). Wide use of pesticides could lead to extensive pollution of the environment and constitutes a potential and/or deliberate risk to human health because some of this pesticide classified as a probable human carcinogen (Eskenazi *et al.*, 1999; Clegg and van Gemert, 1999; Brock *et al.*, 2000). The present study aims to demonstrate the practical applicability of MAE and Gas Chromatography-Mass Spectrometry (GC-MS) for the surveying and determination of pesticide residues in groundwater samples collected from fifteen regions selected around the Saudi Arabia.

MATERIALS and METHODS

Chemicals and reagents: Pesticide standards (DDE, DDT, Dimethoate, Toxaphen Chloroneb, Methomyl, Promoxenyl, Bendiocarb, Promoxenyl, Bendiocarb and Cypermethrin) were provided by Chem Service Inc, USA. All pesticide standards were of 98.9-99.8% purity. All the solvents (Hexan and Acetone) were residue analysis grade and stock working solutions of pesticides were prepared in acetone.

Groundwater sampling collection: Fifteen regions were selected at Central, East, North and South of Saudi Arabia scale (Tabouk, Jouf, Hail, Qasseem, Qatif, Al-Hasa, Taif, Wadi Al-Dawaser, Abha, Gazan, Dereiah, Deirab, Hardh, Kharj and Mezahmiah) to perform the survey process of pesticide residues (Fig. 1) (Al-Turki *et al.*, 2009). Water samples were collected from three locations for each region during 2007 (one sample for each location). The Water samples were prepared and then the pesticides were extracted by MAE technique and determined with GC-MS method. The present study was carried out during the year of 2008 in Labs of the Soil Sciences Department, King Saud University, Saudi Arabia.

Preparation of spiked groundwater samples: Spiked water samples were prepared by adding an appropriate volume of spiking solution to 10 mL of water were spiked with a stock solution of the pesticides (5 mg L^{-1}) prepared in Acetone. The spiked samples were prepared just before analysis, waiting approximately 30 min until solvent evaporation. Water samples were extracted by MAE technique. The main purpose of this step is to calculate the average of the recovery per cent of investigated pesticides by extraction and determination techniques.



Fig. 1: Water sampling sites in Saudi Arabia

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

Extraction of Pesticide Residue by MAE: EPA Method 3540C (USEPA, 1996) and CEM application note No. E003 (CEM Corporation, 1994) was modified and used during conducting of the present study (El-Saeid *et al.*, 2010). A Microwave Assisted Extraction (MAE) system model MES-1000 (CEM Corporation, Matthews, NC, USA) with Lined Extraction Vessels (LEV) was used. Preliminary studies were performed to evaluate MAE efficiency by the effects of temperature, microwave power, extraction time and solvent volume, to extract different groups of pesticide residues from water samples. For this purpose, 10 mL of water was potted in a tetrafluoromethaxil (TFM) microwave extraction vessel with addition of 1 mL of an aqueous spiking solution containing mixture of the pesticide standard solution. Water samples were equilibrated by shaking for 1 h before microwave extraction. Finally, all samples extracted under different conditions to obtain the optimal MAE conditions with this procedure. Finally the optimum Extraction conditions with highly recovery were conducted with 10 mL water samples. Samples extraction solvent was 35 mL of Acetone and Hexane mixture in ratio of (3:2), pressure was 80 psi; microwave power was 60%, temperature was 120°C and time of extraction was 20 min. After extraction, water extracts were filtered and evaporated to dryness; the residue was re-dissolved and directly analyzed by Gas Chromatography Mass Spectrometer (GC-MS) and clean chromatograms were obtained without any additional cleanup step.

Gas Chromatography Mass Selective (GC-MS) 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} to 240 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 plotting peak area versus ppm concentration. The result was expressed in percentage recovery of pesticide (El-Saeid *et al.*, 2010).

Quality assurance/quality control: Recoveries were determined for all samples by spiking with the mix of pesticide standards prior to extraction. Analytical method recoveries for the given set of pesticides were also determined by repeating the whole analytical procedure with the reference soil enriched by the standard mix of pesticides of the known concentration.

RESULTS AND DISCUSSION

Pesticide recovery of spiked ground water samples: The recovery percent of targeted pesticides tested in water sample ranged from 96.23 to 102.44% for all tested compounds as shown in Table 1. Reproducibility was calculated based on the replicate analyses, with relative standard deviation (RSD, %) less than 2.63%. All laboratory blanks were below the detection limit.

Pesticide residues in water samples: The pesticide residues studied are found frequently in the environment and groundwater. Microwave Solvent Extraction (MSE) with GC-MS technique was modified and developed to obtain the optimum conditions to extract and determined the pesticide residues in ground water samples collected from the mentioned 15 regions with short time, with high recovery %. MDL, extraction- determination times, averages of residues. Table 2 showing the results of mean concentration of different pesticide residues (mg L^{-1}) in the 15 regions. The results

Table 1: Pesticide recovery and Relative Standard Deviation (RSD) and Minimum Detection Limit (MDL) of spiked groundwater samples extracted by MAE and determined with GC-MS

Pesticides	Recovery% ±RSD	MDL (mg L ⁻¹)
Dimethoate	99.23±2.47	0.002
Chloroneb	99.67 ±1.22	0.003
Methomyl	98.56±2.07	0.002
Promoxenyl	96.23±2.63	0.001
Toxaphene	99.04±1.47	0.001
pp-DDT	102.44±1.55	0.0001
pp-DDE	101.67±2.26	0.0001
Bendiocarb	96.29±2.43	0.002
Cypermethrin	98.45±1.68	0.002

Table 2: Pesticide residues concentration and standard deviation (inside parentheses), mg L⁻¹ of tested groundwater samples

Region	Dimethoate	Chloroneb	Methomyl	Promoxenyl	Toxaphen	pp-DDT	pp-DDE	Bendiocarb	Cypermethrin
Tabouk	0.020 (0.0046)				0.008 (0.0012)				
Jouf	0.040 (0.020)								
Hail	0.011 (0.009)							0.021 (0.019)	
Qassim	0.045 (0.049)		0.020 (0.031)						
Qatif	0.028 (0.045)								
Alhassa	0.006 (0.003)	0.114 (0.0985)	0.097 (0.0306)						
Taif	0.078 (0.1233)	0.011 (0.0139)	0.093 (0.0542)	0.074 (0.1264)					
Wadi	0.008						0.0057 (0.0098)		
Al-Dawaser	(0.011)								
Abha			0.057 (0.0482)					0.181 (0.1626)	
Gazan	0.043 (0.0153)					0.107 (0.055)	0.090 (0.0608)		0.037 (0.0208)
Deriah	0.015 (0.0141)		0.018 (0.0144)						
Deirab	0.005 (0.0021)		0.004 (0.0025)						
Haradh	0.007 (0.0046)		0.007 (0.0051)		0.022 (0.012)				
Kharj		0.003 (0.0025)	0.004 (0.0015)						
Mezahmiah	0.418 (0.720)								

showed that, four pesticide residues were detected in water samples collected from Gazan (Dimethoate, pp-DDT, pp-DDE and Cypermethrin) and Taif (Dimethoate, Chloroneb, Methomyl and Promoxenyl), but 3 pesticide was detected in Al-Ahssa (Dimethoate, Chloroneb and Methomyl) and Haradh (Dimethoate, Methomyl and Toxaphen). Meanwhile, two pesticide residues were

found in seven regions and only one pesticide residue was found in four regions. Many investigators reported the persistence of different pesticides left residual amounts in ground water for many areas with different levels (Matin *et al.*, 1998; Leonard, 1990; Legrand *et al.*, 1991; Hernandez *et al.*, 1993; El-Kabbany *et al.*, 2000; Shukla *et al.*, 2006; Maloschik *et al.*, 2007).

The most detected pesticides in water samples were Dimethoate (86.66% of total regions), Methomyl (53.3% of all regions) and Chloroneb (20% of all regions). On the other hand, the lowest detected pesticides were Toxaphen, pp-DDE and Cypermethrin (13.33% for each) and Promoxenyl, Bendiocarb and pp-DDT (6.66% for each). Dimethoate was detected at high concentration in water samples collected from Mezahemya (0.418 mg L^{-1}), Chloroneb (0.114 mg L^{-1}) in Alhassa and Bendiocarb (0.181 mg L^{-1}) in Abha. Therefore, residues may have been originated from earlier applications given the reported high persistence in soil and then ground water. All pesticides detected in the water samples had different concentrations of residues as reported and agreement by Kashyap *et al.* (2002), Sankararamakrishnan *et al.* (2005) and Shukla *et al.* (2006).

The water health standards (Drinking use) report the Minimum Concentration Level (MCL) of pesticide (0.1 mg L^{-1}) for the single compound, but (0.5 mg L^{-1}) for a group of pesticide. Four regions, Dereyah, Deirab, Haradh and Kharj registered as lower of detected pesticide than MCL. Meanwhile, the rest of regions under investigation were higher than the MCL.

The studies performed to evaluate pesticide exposure in groundwater showed that some of the monitored pesticides were present at different concentration levels. The implementation of multiresidue methods and also automated techniques such as MAE-GC/MS to improve analytical conditions would be desirable.

The pesticides, which have been detected, were higher than the qualitative target set by EPA and EU (European Union, 2004). This is due to possible transfer of pesticides from agricultural and health protection activities carried out and in near regions.

These results are alarming for the health of the human beings in the studied regions. Though, this study was done only for a short period and for some regions of Saudi Arabia, the results obtained can be used to design an Integrated Management Program to control the concentration of pesticide residues in groundwater.

CONCLUSION

The present study clearly demonstrates that agricultural practices in the agricultural area of the selected regions have degraded the quality of groundwater. The study also provides a clear example that MAE followed by GC-MS techniques can be used as a routine way for the determination of pesticide pollution in groundwater. The results of the current study suggest that contamination by pesticides in the 15 studied areas is not as severe as might be anticipated. However, this study was limited to samples collected from a small number of farms in only one phase of the growing season. At the same time, the significance of the presence of Dimethoate, carbamates and DDTs in water in close proximity to human and animal populations should not be discounted. Further residue studies in other agricultural areas of Saudi Arabia are needed in order to assess the levels of pesticide residues in ground water and living organisms in same areas.

ACKNOWLEDGMENT

Authors thank the deanship of scientific research at King Saud University for financial support through Project # DSR-AR-2-(14).

REFERENCES

- Al-Turki, A.M., G. Abdel-Nasser, M.I. Al-Wabel and M.H. El-Saeid, 2009. Evaluation of pollutants in agricultural soils in Saudi Arabia. Financial Supported from Deanship of Scientific Research, King Saud University. Two Parts, pp: 649.
- Brock, T.C.M., R.P.A. van Wijngaarden and G.J. van Geest, 2000. Ecological Risk of Pesticides in Freshwater Ecosystems. Part 2: Insecticides. Green World Research, Wageningen, The Netherlands.
- CEM Corporation, 1994. Chlorinated Pesticide Residues Recovery Using Microwave Extraction. CEM Corporation, Matthews, NC., USA.
- Clegg, D.J. and M. van Gemert, 1999. Determination of the reference dose for chlorpyrifos. *J. Toxicol. Environ. Health B Crit. Rev.*, 2: 211-255.
- Dogheim, S.M., El-Z. Mohamed, S.A. Gad Alla, S. EL-Saied, S.Y. Emel, A.M. Mohsen and S.M. Fahmy, 1996. Monitoring of pesticide residues in human milk, soil, water and food samples collected from Kafr El-Zayat Governorate. *J. AOAC Int.*, 79: 111-116.
- El-Kabbany, S., M.M. Rashed and M.A. Zayed, 2000. Monitoring of the pesticide levels in some water supplies and agricultural land, in El-Haram, Giza (A.R.E). *J. Hazardous Mater.*, 72: 11-21.
- El-Saeid, M.H., M.I. Al-Wabel, G. Abdel-Nasser, A.M. Al-Turki and A.G. Al-Ghamdi, 2010. One-step extraction of multiresidue pesticides in soil by microwave-assisted extraction technique. *J. Applied Sci.*, 10: 1775-1780.
- Eskenazi, B., A. Bradman and R. Castorina, 1999. Exposures of children to organophosphate pesticides and their potential adverse health effects. *Environ Health Perspectives*, 107: 409-419.
- European Union, 2004. Corrigendum to regulation (EC) No 850/2004 of the European parliament and of the council of 29 April 2004 on persistent organic pollution and amending directive 79/117/EEC. *Official J. Eur. Union*, L229: 5-22.
- Forney, D.R. and D.E. Davis, 1981. Effects of low concentrations of herbicides on submerged aquatic plants. *Weed Sci.*, 29: 677-685.
- Hernandez, F., I. Morell, J. Beltran and F.J. Lopez, 1993. Multi-residue procedure for the analysis of pesticides in groundwater: application to samples from the Comunidad Valenciana, Spain. *Chromatographia*, 37: 303-312.
- Iwata, H., S. Tanabe, N. Sakai, A. Nishimura and R. Tatsukawa, 1994. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania and their implications for global redistribution from lower latitudes. *Environ. Pollut.*, 85: 15-33.
- Kashyap, R., V.K. Bhatnagar and H.N. Saiyed, 2002. Integrated pest management and residue levels of dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) in water samples from rural areas in Gujarat State, India. *Arch. Environ. Health Int J.*, 57: 337-339.
- Legrand, M.P., E. Costentin and A. Bruchet, 1991. Occurance of 38 pesticides in various French surface and ground waters. *Environ. Technol.*, 12: 985-996.
- Leonard, R., 1988. Herbicides in Surface Water. In: *Environmental Chemistry of Herbicides*, Grover, R. (Ed.). Vol. 1. CRC Press, Boca Raton, FL., pp: 45-87.
- Leonard, R.A., 1990. Movement of Pesticides in to Surface Waters. In: *Pesticides in the Soil Environment: Processes, Impacts and Modeling*, Cheng, H.H. (Ed.). SSSA, Madison, WI., pp: 303-349.
- Maloschik, E., A. Ernst, G. Hegedus, B. Darvas and A. Szekacs, 2007. Monitoring water-polluting pesticides in Hungary. *Microchemical J.*, 85: 88-97.

- Matin, M.A., M.A. Malek, M.R. Amin, S. Rahman and J. Khatoon *et al.*, 1998. Organochlorine insecticide residues in surface and underground water from different region of Bangladesh. *Agric. Ecosyst. Environ.*, 69: 11-15.
- Milidas, G.E., 1994. Determination of pesticide residues in natural water of in Greece. *Bull. Environ. Contam Toxicol.*, 52: 25-30.
- Miyamoto, J., N. Mikami and Y. Takimoto, 1990. The Fate of Pesticides in Aquatic Ecosystems. In: *Environmental Fate of Pesticides*, Hutson, D.H. and T.R. Roberts (Eds.). John Wiley and Sons, New York, pp: 123-147.
- Mulla, M. and L. Mian, 1981. Biological and environmental impacts of insecticides malathion and parathion on non-target biota in aquatic ecosystem. *Residue Rev.*, 78: 100-135.
- Papadopoulou-Mourkidou, E., D.G. Karpouzas, J. Patsias, A. Kotopoulou, A. Milothridou, K. Kintzikoglou and P. Vlachou, 2004. The potential of pesticides to contaminate the groundwater resources of the Axios river basin in Macedonia, Northern Greece: Part I. Monitoring study in the north part of the basin. *Sci. Total Environ.*, 321: 127-146.
- Sankararamakrishnan, N., A.K. Sharma and R. Sanghi, 2005. Organochlorine and organophosphorous pesticide residues in ground water and surface waters of Kanpur, Uttar Pradesh, India. *Environ. Int.*, 31: 113-120.
- Shukla, G., A. Kumar, M. Bhanti, P.E. Joseph and A. Taneja, 2006. Organochlorine pesticide contamination of ground water in the city of Hyderabad. *Environ. Int.*, 32: 244-247.
- Spliid, N.H. and B. Koppen, 1998. Occurrence of pesticides in danish shallow ground water. *Chemosphere*, 37: 1307-1316.
- Tuxen, N., P.L. Tuchsén, K. Rugge, H.J. Albrechtren and P.L. Bjerg, 2000. Fate of seven pesticides in an aerobic aquifer studied in column experiments. *Chemosphere*, 41: 1485-1494.
- USEPA., 1996. Method 3540C. U.S. Environmental Protection Agency, Washington, DC.