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Assessment of Organochlorine pesticides and heavy metals in groundwater in Belbis region, El-Sharqia, Egypt

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ABSTRACT **: In Egypt, the shortage of freshwater resources and their pollution constitutes a growing concern. Due to the uncensored use of pesticides in the agricultural regions of Egypt, the contamination risks of ground water increase periodically in planting seasons. Therefore, the present work aims to monitor the occurrence of organochlorine pesticides (OCPs) residues and heavy metals in five ground water samples collected from agricultural area with long-term pesticide application history in Belbis region, El-Sharqia, Egypt. Water samples were processed using a solid-phase extraction technique and gas chromatograph equipped with mass spectrometry (GC-MS). Results revealed that, the concentrations of OCPs in groundwater are in the limits except only 0.65 µg/L of p,p'-DDT recorded in ground water at Hassan Bieh village location, Belbis region, El-Sharqia, Egypt. Levels of iron and manganese in (Elnoba and Awlad Mahnaa) ground water samples were found to be much higher than the limits of Egyptian quality standards. The other elements in this study were found in the limits. The turbidity in 3 site (Hassan Beih, Elnoba and Awlad Mahnaa) villages has high values (4.7, 28.4 and 4.4), respectively. TDS values in two sites (Hassan Beih and Awlad Mahnaa) villages showing values above the 1000 mg/L limit.**

KEYWORDS: Assessment; Organochlorine pesticides; Heavy metals; Ground water; Belbis region, El-Sharqia, Egypt.

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I. INTRODUCTION

Persistent organic pollutants (POPs) are toxic and bioaccumulative chemicals that have long-range atmospheric transport potential. One class of organic pollutants which has rightly gained greater attention in environmental studies is the organochlorine pesticides (OCPs) [1]. They are highly persistent and toxic in nature, and some of them has been suspected to be carcinogenic. Organochlorine pesticides (OCPs) are typical persistent organic pollutants (POPs) that are widely used as broad-spectrum insecticides and are successfully used in agricultural pest control. OCPs have attracted global attention because of their resistance to environmental degradation, toxicity, and bioaccumulation potential [2]. OCPs are synthetic chemicals comprising a variety of compounds containing carbon, hydrogen, and chlorine; they are widely used around the world [3]. In Egypt, large amounts of OCPs were used for agricultural purposes during the last decades. The OCPs residues are still detectable in water due to their long persistence in the environment. Although, Egypt is the largest pesticide market in Arabian countries and the fourth largest importer of pesticides among developing countries [4], there are no regular monitoring programs in Egypt for identification and determination of pesticides in the environment [5]. The quantities of pesticides used in Egypt based on Environmental Affairs agency, Egypt; January 2009, is about 600 ton/annually in agricultural and pests control in Egyptian aquatic environment [6].

Hexachlorocyclohexane (HCH) is a fully chlorinated alicyclic compound. The most common isomers are α, β and δ-HCH. The γ-isomer known as Lindane is one normally used as an agricultural pesticide. HCH is a reasonably stable compound and only under alkaline condition decomposes to yield trichlorobenzene. It is considered as one of the less persistence organochlorine pesticide. DDT is generally used against a wide variety of agricultural and forest pests and against insect pests including vectors such as mosquito and tse-tse fly. In the environment, DDT can be degraded by solar radiation or metabolised in organisms. Heptachlor is the common name for 1,4,5,6,7,8,8-heptachloro-3a,4,7,7atetrahydro-4,7-methane-1H-indane. It is generally used as insecticide and also occurs technically as chlorodane. In the environment, it is degraded or metabolized and is more commonly found as its epoxide form; Heptachlorepoxide (UNEP, 1990).

OCPS are usually determined using gas chromatographic techniques, with electron capture (ECD) [7, 8] and mass spectrometry detector (MS) [9]. However, a wide variety of sample pretreatment methods have been developed and applied for extraction of OCPs from water samples such as the classical solvent extraction (LLE) [10] and solid-phase extraction (SPE) [9].

As monitoring of pesticide water pollution is an substantial source of information describing the current state of environmental pollution and reflecting the effectiveness of environmental legislation policies. So the aim of this study was to monitoring the presence of OCPs in different types of water samples collected from Belbis region, El-Sharqia governorate, Egypt. To the best of our knowledge, the evaluation of the distribution of heavy metals in water also recommended in this work.

II. MATERIALS AND METHODS

Apparatus

Chromatographic analysis was performed on an Agilent Technologies (7890A) gas chromatography–mass spectrometry analysis (GC-MS) system equipped with (5975C) agilent inert XL EI MSD with Triple-Axis Detector (TAD), Inert electron ionization (EI) source with High Performance Turbo pump. Inductively coupled plasma mass (ICP – MASS) Agilent 7700 (USA). MILLIPORE direct Q -3 UV lamp and sterilized by autoclave (Raypa AES 75) at 121° for 20 minutes. The pH were measured at the sampling time by using a pH meter model HANNA HI 98190 (Rumani). Waterproof Portable Dissolved Oxygen meter (DO) (Hanna Model HI98193, Rumani), Turbidimeter (HACH Model 2100N, USA) , and Conductivity meter -Total Dissolved solids (EC/TDS SCHOTT-Glas-Mains Model CG853 P, Germany), respectively. Samples are placed in folders Ice (Ice Box) and transported to the laboratory. Water samples from different sources were collected. Sampling sites along with their coordinates are indicated as follows.

Study area

A large-scale monitoring study was conducted on OCPs residue levels in five ground water samples collected from the ground water wells of Belbis region, El-Sharqia governorate, Egypt (Fig. 1) (Table 1). To avoid the negative effects of continuous pesticide application year-round, the sampling time was set for February 20 and 21, 2018, when the vegetables had been harvested and pesticide usage had ceased.

Sample collection

The volume of water samples ranging from (4-5 liter) were collected in drip-free borosilicate amber glass bottles for OCPs analysis and immediately transported to the laboratory and stored in amber glass flasks at −4 °C until analysis. Before sampling, containers were washed by deionized water (distilled water). Water samples were filtered through 0.45 μm fiber glass filters to remove sand and debris (WHATMAN) [11].

Chemicals and reagent

A mixture of standard solution of 19 types of OCPs used in this study was obtained from AccuStandard, Inc (New Heaven, USA) containing: aldrin, dieldrin, α-endosulfan, β-endosulfan, endosulfan sulfate, α-hexachlorocyclohexane (α-HCH), β-hexachlorocyclohexane (β-HCH), δ-hexachlorocyclohexane (δ-HCH), γ-hexachlorocyclohexane (γ-HCH), α-chlordane, γ-chlordane, *p,p′*-dichlorodiphenyltrichloroethane (*p,p′*-DDT), *p,p′*-dichlorodiphenyldichloroethylene (*p,p′*-DDE), *p,p′*-dichlorodiphenyldichloroethane (*p,p′*-DDD), endrin, endrin aldehyde, heptachlor, heptachlor epoxide and methoxychlor. Their detailed information's were shown in Table 2. Several types of solvents had been used for the extraction of the samples by Dionex AutoTrace (280).

HPLC grade solvents such as (dichloromethane, ethyl acetate and methanol) purchased from (Sigma Aldrich). Hydrochloric acid and sodium sulfate were obtained from (Merck). The water used for samples was purified using a Milli-Q purification system (Millipore, USA),and SolEx (C-18) Extraction Columns (1000 mg/6 mL) were obtained from (Thermo Scientific Dionex). High purity helium and nitrogen were made by high purity helium generator and nitrogen generator respectively[12].

Preparation of standard solution

The stock solution of OCPs consists of 19 kind of pesticides dissolved in ethyl acetate with 0.5 mg/ml concentration stored at ambient temperature. Then, working solution were prepared from the stock solution with almost concentration equal 0.0005 mg/ml and therefore standard calibration curves were made with concentrations ranging from 0.001 to 0.5 ng/µL in ethyl acetate and stored in a freezer at -4C .

Analytical procedures

Extraction of OCPs

The nineteen OCPs were extracted from surface drinking water using a Thermo Scientific Dionex AutoTrace 280 Solid Phase Extraction (SPE) Instrument (AT 280) according to (Zhang, Perati, and Verma). Dionex AT 280 6 mL SPE Cartridge System were sequentially washed with 5 mL of ethyl acetate followed by 5 mL dichloromethane, then 10 mL of methanol and 10 mL of deionized water at a 5 mL/min flow rate. Dechlorinate water sample (1.0 L) with 50 mg/L sodium sulfite followed by adjusting water sample to pH=2.0 with HCl. Then, load six 1.0 L water samples onto the cartridges using solid-phase extraction (SPE) the Dionex AT 280 at a constant flow rate of 10 mL/min. Then, dry cartridge with nitrogen gas for 5 min. Manually rinse sample container with 20 mL ethyl acetate and 20 mL dichloromethane to collect then elute with ethyl acetate and dichloromethane with 5.0 mL for each one into 40 mL tubes at a speed of 5 mL/min. After the extraction, 1.0 g of anhydrous sodium sulfate was added to the sample bottle to remove any residual water and the bottle was rinsed three times with approximately 4.0 mL of dichloromethane. Concentrate each extract to 1.0 mL using a slow flow of nitrogen stream in a water bath using evaporation apparatus (Turbo-Vap—Zymark Turbo Vap(R), LV evaporator (Caliper Life Sciences, USA) before injecting into GC-MS.

Quantitative determination

Quantitative analysis of OCPs was performed on an Agilent Technologies (7890A) GC system equipped with (5975C) agilent inert XL EI MSD with Triple-Axis Detector (TAD) Inert electron ionization (EI) source with High Performance Turbo pump. Separation was performed on HP-5 MS column (5% Phenyl Methyl Silox) (30 m length × 0.25 mm internal diameter ×0.25 µm film thickness) with helium as carrier gas of 99.9999% purity was used at a flow rate of 1 mL/min. The GC temperature conditions were as follows: the column oven temperature was programmed as follows; the oven temperature was programmed from an initial temperature 40 °C (1 min hold) to 160 °C (3 min hold) at a rate of 20 °C/min, then further increased to 250 °C at a rate of 3 °C/min and a ramp increase to 300 °C at 20 °C/min. Transfer line temperature was set at 280°C and the source temperature at 230°C. The injector temperature, 250 °C; The mass spectrometer was operated in the electron impact mode (EI). Electron multiplier voltage was set at 2000 V. The three replicates of each sample were injected to calculate the mean concentration. Injection volume was 2 µL of the extracted or standard solutions was introduced into the GC system via split less mode of injection, throughout the whole experiment [13].

Quality assurance and quality control

The quality of OPCs (aldrin, dieldrin, α-endosulfan, β-endosulfan, endosulfan sulfate, α-HCH, β-HCH, δ-HCH, γ-HCH, α-chlordane, γ-chlordane, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, endrin, endrin aldehyde, heptachlor, heptachlor epoxide and methoxychlor) were assured through the analysis of solvent blanks, procedure blanks and triplicate samples. All blanks were below the limits of detection (LOD). The LOD were set to be triple the standard deviation of the blank. The LOD of target OCPs was found to be 0.5 µg/L and limits of quantification (LOQ) was found to be 1.5 µg/L. The calibration curves had acceptable degree of linearity (correlation coefficients**,** $R^2 >$ 0.987) for all the compounds in the GC-MS. Sample of each series was analyzed in triplicates.

III. RESULTS AND DISCUSSION

In addition to illustrating the results of OPCs in different ground water samples, physicochemical properties like (pH, conductivity, turbidity, total dissolved solids TDS) will be mentioned according to Egyptian water quality standards. Variation in the physicochemical parameters, among the sampled sites, is shown in Table 3.

According to Egyptian water quality standards, water with TDS values in excess of 1000 mg/L, is categorized as poor quality [14]. In this study, TDS values ranged between 480 and 1570 mg/L, with almost 40% of the sites (Hassan Beih and Awlad Mahnaa) villages showing values above the 1000 mg/L limit. The high TDS values might be a consequence of the salts in the soil resulting from the continuous dissolution and erosion of rocks. Also, the high level of ground water caused by the absence of good drainage after the irrigation process in addition to dissolved salts added through irrigation and fertilization water [15]. Also, the turbidity in 3 site (Hassan Beih, Elnoba and Awlad Mahnaa) villages has high values (4.7, 28.4 and 4.4), respectively due to the bacteriological materials and colloidal present in water. The temperature, dissolved oxygen (DO), pH and electrical conductivity (EC), are agree with the limits of Egyptian water quality standards.

The results of the concentration of the heavy metals for all the measured groundwater samples were given in Table 4. Level of iron in (Arab Elbayadeen, Elnoba and Awlad Mahnaa) ground water samples were found to be much higher than the limits of Egyptian quality standards and the level of manganese in (Elnoba and Awlad Mahnaa) ground water samples were found to be much higher than the limits of Egyptian quality standards. The other elements in this study were found in the limits.

Monitoring of OCPs

The analytical parameters of OCPs and maximum residue limits of these pesticides are shown in Table 5.

Ground water samples taken from the studied region (Belbis, El-Sharqia, Egypt) at five sites were analyzed. The residual concentration of OCPs monitored and determined in collected groundwater samples. The results in Table 5 showed that the absence of several OCPs residues (aldrin, dieldrin, α-endosulfan, β-endosulfan, endosulfan sulfate, α-HCH, β-HCH, δ-HCH, γ-HCH, α-chlordane, γ-chlordane, *p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD, endrin, endrin aldehyde, heptachlor, heptachlor epoxide and methoxychlor) in the five sampling times. It is surprising to note that Belbis region, various OCPs were not detected although major industrial and agricultural activities are concentrated there. This could be due to the pesticides evaporation in tropical countries (Egypt), pesticide residues dilution or adsorption.

DDT is generally used against a wide variety of agricultural and forest pests and against insect pests including vectors such as mosquito and tse-tse fly. In the environment, DDT can be degraded by solar radiation or metabolised in organisms. This proves the presence of only 0.65 µg/L of *p,p′*-DDT recorded in ground water at Hassan Bieh village location, Belbis region, El-Sharqia, Egypt (Table 5).

Ground water is the principle source of fresh water for rural and industrial region. In Belbis region the sources of drinking water are drilled wells located mainly within agricultural area and rarely in the household. Considerable amount of pollution with organochlorine pesticides were detected in this area. Moreover, a high incidence of pollution of water intake by these pesticides (particularly DDT) was observed.

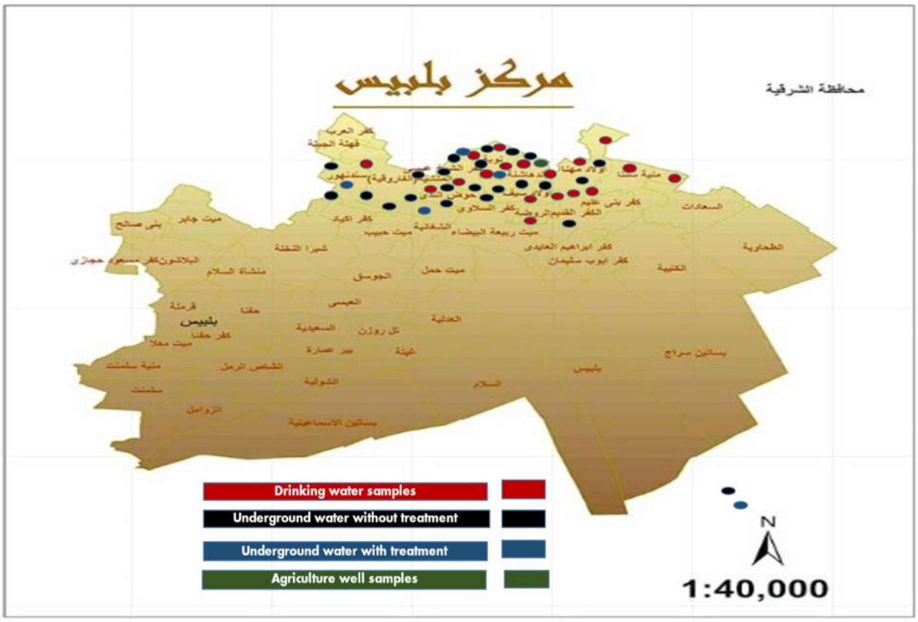

Fig. 1. Map of Belbis region showing sites of water sampling.

Table 1. Location and anthropogenic use of water at the studied sites.

Sampling sites	Depth (m)	pH	GPS coordinates	
			Longitude	**Latitude**
Arab elbaydeen Village	35	7.42	31°54′47″	30°49 ′ 02 ″
Hassan Beih Village	40	7.5	31°54 ′ 69 ″	30°48 ′ 60 ″
Sendnhor Village	40	7.5	31°50 ′ 55 ″	30°48 ′ 39 ″
Elnoba Village	40	6.6	31°55 ′ 65 ″	30°48 ′ 10 ″
Awlad Mahnaa Village	40	7	31°58 ′ 81 ″	30°47 ′ 68 ″

Table 2. Description of analytes in OCPs standards :

Analyte	CAS Number	Target Concentration
Aldrin	309-00-2	0.5 mg/mL
Dieldrin	60-57-1	0.5 mg/mL
α-endosulfan	959-98-8	0.5 mg/mL
β-endosulfan,	33213-65-9	0.5 mg/mL
Endosulfan sulfate	1031-07-8	0.5 mg/mL
α-HCH	319-84-6	0.5 mg/mL
β- HCH	319-85-7	0.5 mg/mL
δ- HCH	58-89-9	0.5 mg/mL
γ- HCH	319-86-8	0.5 mg/mL
α-chlordane	5103-71-9	0.5 mg/mL
γ-chlordane	5103-74-2	0.5 mg/mL
p,p′-DDD	72-54-8	0.5 mg/mL
p,p′-DDE	72-55-9	0.5 mg/mL
p,p′-DDT	50-29-3	0.5 mg/mL
Endrin	72-20-8	0.5 mg/mL
Endrin aldehyde	7421-93-4	0.5 mg/mL
Heptachlor	76-44-8	0.5 mg/mL
Heptachlor epoxide	1024-57-3	0.5 mg/mL
Methoxychlor	72-43-5	0.5 mg/mL

Table 3. Physicochemical and statistical results at the study area.

Sample site / Parameters	Arab Elbaydeen Village	Hassan Bieh Village	Sendnhor Village	Elnoba Village	Awlad Mahnaa Village	Egyptian standards 190/2007
Temperature (T, °C)	27.5	26.8	27.9	28	26.5	8-28
Dissolved oxygen (DO, mg/L)	1.15	1.84	1.67	1.64	1.24	≤5-6
Conductivity (EC, µS/cm)	838	1400	923	1470	1960	≤ 2000
Turbidity (NTU)	1.4	4.7	0.77	28.4	4.4	≤ 2
pH (Unit)	7.42	7.5	7.5	6.6	7	6.5-8.5
Total dissolved solids (TDS, mg/L)	480	1210	706	831	1570	≤ 1000

Table 4. Mean concentration of detected heavy metals (mg/L) at 5 sampling sites.

Sample site / Parameters	Arab Elbaydeen Village	Hassan Bieh Village	Sendnhor Village	Elnoba Village	Awlad Mahnaa Village	Maximum limit (µg/l)
Iron (Fe)	0.4	Nil	Nil	2.4	1.03	0.3
Lead (Pb)	Nil	Nil	Nil	0.002	Nil	0.01
Cadmium (Cd)	Nil	Nil	Nil	0.00009	Nil	0.05
Nickel (Ni)	Nil	Nil	Nil	0.01	Nil	0.02
Manganese (Mn)	0.004	Nil	Nil	1.3	1.6	0.4
Zinc (Zn)	0.015	Nil	Nil	0.1	0.013	3

Concentration in µg/L, precision in %RSD Calibration curves with five point concentrations, using Accu-standard ICP Multi element calibration solutions, were: for Fe from 1.0 to 10 mg/L ; for other elements (Pb-Cd-Ni -Zn) from 1.0 to 100 µg/L

Table 5. OCPs levels (µg/l) in Belbis region, El-Sharqia, Egypt groundwater samples .

Sample site / Parameters	Arab Elbaydeen Village	Hassan Bieh Village	Sendnhor Village	Elnoba Village	Awlad Mahnaa Village
Aldrin	ND	ND	ND	ND	ND
Dieldrin	ND	ND	ND	ND	ND
α-endosulfan	ND	ND	ND	ND	ND
β-endosulfan,	ND	ND	ND	ND	ND
Endosulfan sulfate	ND	ND	ND	ND	ND
α-HCH	ND	ND	ND	ND	ND
β- HCH	ND	ND	ND	ND	ND
δ- HCH	ND	ND	ND	ND	ND
γ- HCH	ND	ND	ND	ND	ND
α-chlordane	ND	ND	ND	ND	ND
γ-chlordane	ND	ND	ND	ND	ND
p,p'-DDD	ND	ND	ND	ND	ND
p,p'-DDE	ND	ND	ND	ND	ND
p,p'-DDT	ND	0.65	ND	ND	ND
Endrin	ND	ND	ND	ND	ND
Endrin aldehyde	ND	ND	ND	ND	ND
Heptachlor	ND	ND	ND	ND	ND
Heptachlor epoxide	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND

The quantities of pesticides used in Egypt based on Environmental Affairs agency, Egypt; January 2009, is about 600 ton/annually.

V –CONCLUION

The results of the OCPs in the ground water will be used to establish the environmental Guid levels for various OCPs and heavy metals and other physico and chemical parameters in Egypt. All the chemical pollutants in the ground water wells are within the Egyptian and the WHO guide. The use of water obtained from these wells must undergo some measures to limit the possible chemical hazard. This study has highlighted the need for further research, in order to determine the permitted levels of OCPs in groundwater as well as to identify areas of potential toxicity and the drinking water quality.

CONFLICTS OF INTERESTS

The authors confirm that this article content has no conflict of interest.

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