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Case study

Monitoring of the pesticide levels in some water supplies and agricultural land, in El-Haram, Giza (A.R.E.)

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Abstract

Monitoring of pesticide residues were conducted at different locations in the El-Haram region Giza, Egypt. The water samples were collected from El-Haram Giza, canal water supplies (El-Zomor, Abd-el-aal land and seaside and El-Mansorya), in addition to El-Moheet drainage water. The soil samples were collected from the arable land that surrounds water canals. Water samples were obtained by solid phase extraction (SPE) and soil samples by gel permeation chromatography (GPC). The combination of gas chromatography and mass spectroscopy with different ionization techniques was used for determination and identification of the pesticides, which were quantitatively determined as $\mu g\ l^{-1}$ levels in environmental samples. The residues of pesticides were varied between different locations. Also, organochlorine pesticide residues in El-Moheet drainage water were relatively higher than in the canal water. The concentrations of organophosphrous compounds (chlorpyrifos, dimethoate and parathion) seem to be low in water as compared to soil samples. Most findings were less than 1 $\mu g\ g^{-1}$, which is considered a low-level finding. Sixteen organochlorine pesticides were detected in most of the water samples and the percent of positive samples followed the order drins > total BHC > total DDT > endosulfan > heptachlor epoxid > heptachlor. Pentachlorophenol (PCP) was detected only in El-Zomor and Abd-el-aal canal water. Results obtained confirm the presence of different pesticide residues representing different chemical classes in the canal waters. This means that the discharging of wastes in to the water supplies must be controlled. Drainage water was highly polluted and

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contains much more pesticide residues than different canal waters.

Keywords: Monitoring; Pesticides; Water supplies; Drainage water; Agricultural land

1. Introduction

Environmental pollution by pesticides is a major environmental concern. Several hundred pesticides of diverse chemical nature are widely used for agricultural purposes. The pesticides reach adjacent vegetation, wildlife soil and waters.

According to what was known in the last few years about the contamination of water supplies [1,2], it is therefore highly important to monitor the irrigation water supplies and the arable land that surrounds water canals. This is a particularly acute problem in areas used for agricultural purposes adjoining large urban areas in El-Haram-Giza.

A number of studies assessed the River Nile and drinking water pollution by pesticides and heavy metals [2]: the water pollution by organic chemicals in an open delta lake and sediments in Egypt [3] and the monitoring of drinking water pollution by heavy metals and certain anion content in Mahmoudieh canal in Alexandria region, Egypt [4].

The objective of this work is to monitor the rate of pesticide pollution in El-Haram Giza water supplies. These water canals are subjected to different sources of pollution, which affect the physical, chemical, as well as its biological characteristics, and subsequently its quality as a source of irrigated fruit and vegetable fields.

2. Materials and methods

2.1. Sampling sites

Water and soil samples were collected during a period of 2 months, April and May 1996, as shown on the map (Fig. 1). The sampled site for the study in El-Haram Giza region was selected because of its nearness to large urban areas. Approximately three quarters of the study sites are used as water canals with which to irrigate fruit and vegetable gardens. Farmers at such sites always use these waters for domestic as well as agricultural purposes.

2.2. Water samples

Five-liter water samples were collected from the surface to a depth at the bottom of canal (1–2 m) near the plant's water intake points.

Water samples were taken from El-Zomor, Abd-el-aal (land and sea side) and Kafer-Hakim (El-Mansorya) canals, in addition to two drainage sites. The first was from the main ditch supplying the faculty's farm (Faculty of Agriculture, Cairo University); the second was from the El-Moheet drain (El-Maryotia).

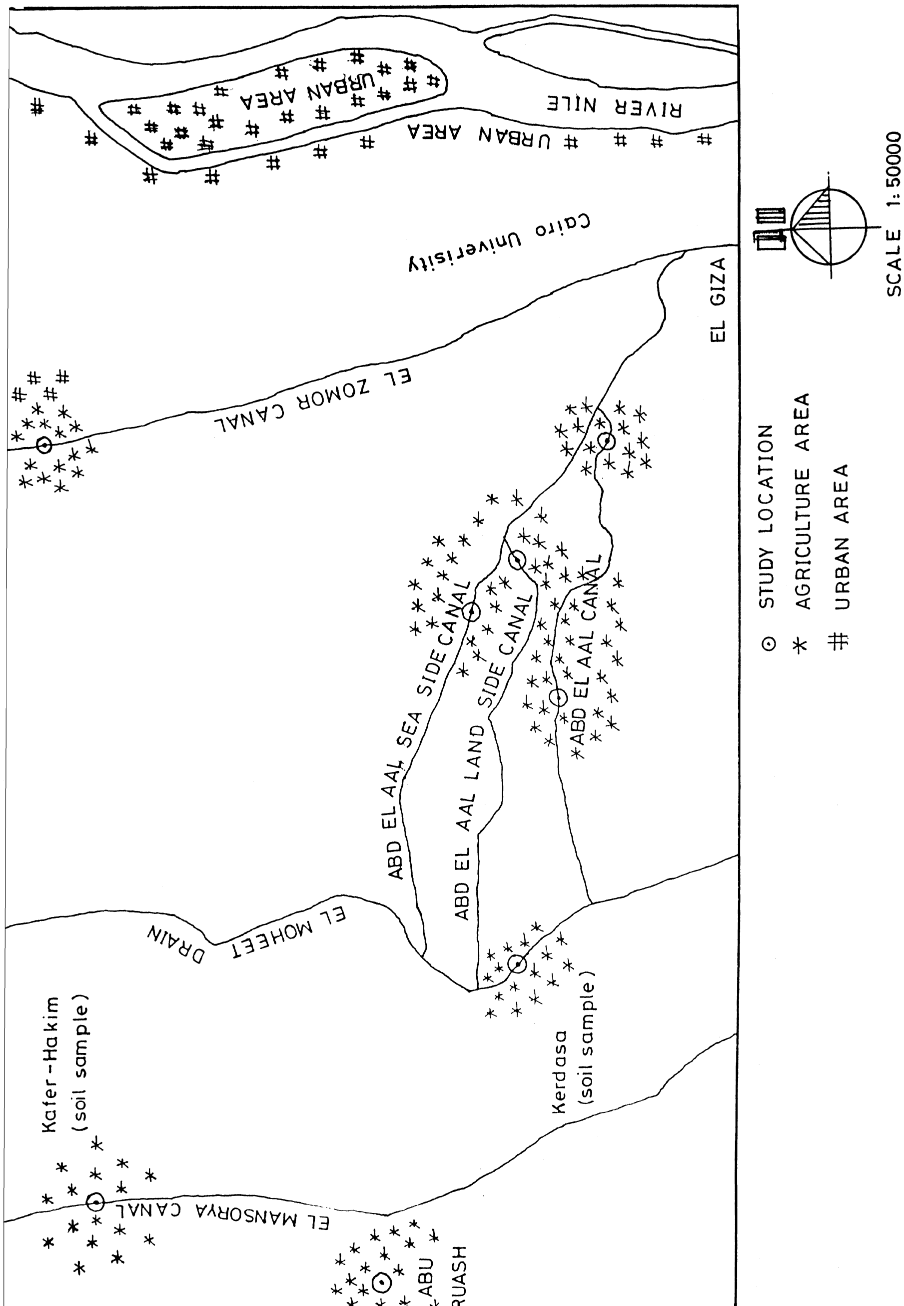

Fig. 1. Locations of investigated water and soil samples in Giza, Egypt.

Water physical and chemical characteristics (temperature, pH, total soluble salts, dissolved O_2 and redox potential) were recorded at the sampling sites. Water samples were collected in a glass bottles and transferred immediately to the laboratory for analysis. The samples were stored at 10°C for no more than 10 days before analysis. Five hundred milliliters of water samples were cleaned by removal of any floating or insoluble materials.

Solid-phase extraction (SPE) experiment was carried out for pre-concentration, clean-up and preparation of water samples. A C_{18} polar plus and two eluents, methanol and ethyl acetate, were used. This extraction procedure using the C-18 cartridge is a well established technique applicable to different classes of pesticides [5]. Samples were passed through the SPE cartridges at 3–5 ml m^{-1}, suction continued for 30 min to dry out the packing material, the cartridges were disconnected and the absorbed pesticides were eluted with methanol–ethyl acetate (1:1 v/v) in glass test tubes. The extract was then stored until chromatographic analysis.

2.3. Soil samples

Fresh soil samples (0–30 cm, root zone), were collected from the arable land that surrounds the water canals. Soil samples were air-dried and passed through a 2-mm sieve. Fifty grams of three dried soil samples were weighted and transferred to 500-ml conical flasks, 100 ml methanol and an amount of water equivalent to this natural content in the soil were added and the mixture shaken overnight. The extract was saturated with NaCl (15 g) and diluted with 100 ml cyclohexane and shaken for 30 min.The organic phase was separated into a 250-ml flask and dried with anhydrous sodium sulfate. The evaporated residue of the organic phase (5 ml) was cleaned up by gel permeation chromatography (GPC) on a Bio-Beeds S-X_8 polystyrene gel, using a mixture of ethylacetate/cyclohexane (1:1 v/v) as an eluent. The extract was taken through 0.45 μm filtrate into the GPC glass. Fractions of GPC 0–100 ml was pre run 20 min, 100–200 ml analytical fraction 20 min, 200–275 ml post run 15 min. Then the concentrated fraction of the pesticides was ready for chromatographic analysis. GPC was a very suitable means for the removal of high molecular organic material of the spiked extracts such as humine substances, pigments, high molecular oils and high molecular hydrocarbons [6].

3. GC–MS parameters

All mass spectrometric measurements were performed with a Hewlett Packard HP5970 MSD combined with a PH5890 gas chromatograph fitted with a 25 m × 0.2 mm i.d. × 0.33 μm HP-5 capillary column. All gas chromatographic and mass spectrometric parameters were described earlier [6].

Quantification was carried out by the use of a computer integrator. Identification of the unknown peaks in the samples' chromatograms was managed by comparing unknown pesticide spectrum with those of spectral library and the relative retention time

(RRT) of the unknown peaks to the RRTs of the reference standards. This is to confirm the identity of the pesticides found, (Fig. 2).

Determination of pesticides and pesticide residues were carried out mainly at the Institute for Ecological Chemistry and Waste Analysis, T.U. Brauschweig, Germany, 1996.

Dissolved oxygen was measured with a polarographic oxygen electrode system (WTWOX191/E090). pH was measured with a glass electrode (ingold 104573002, WTW pH 90).

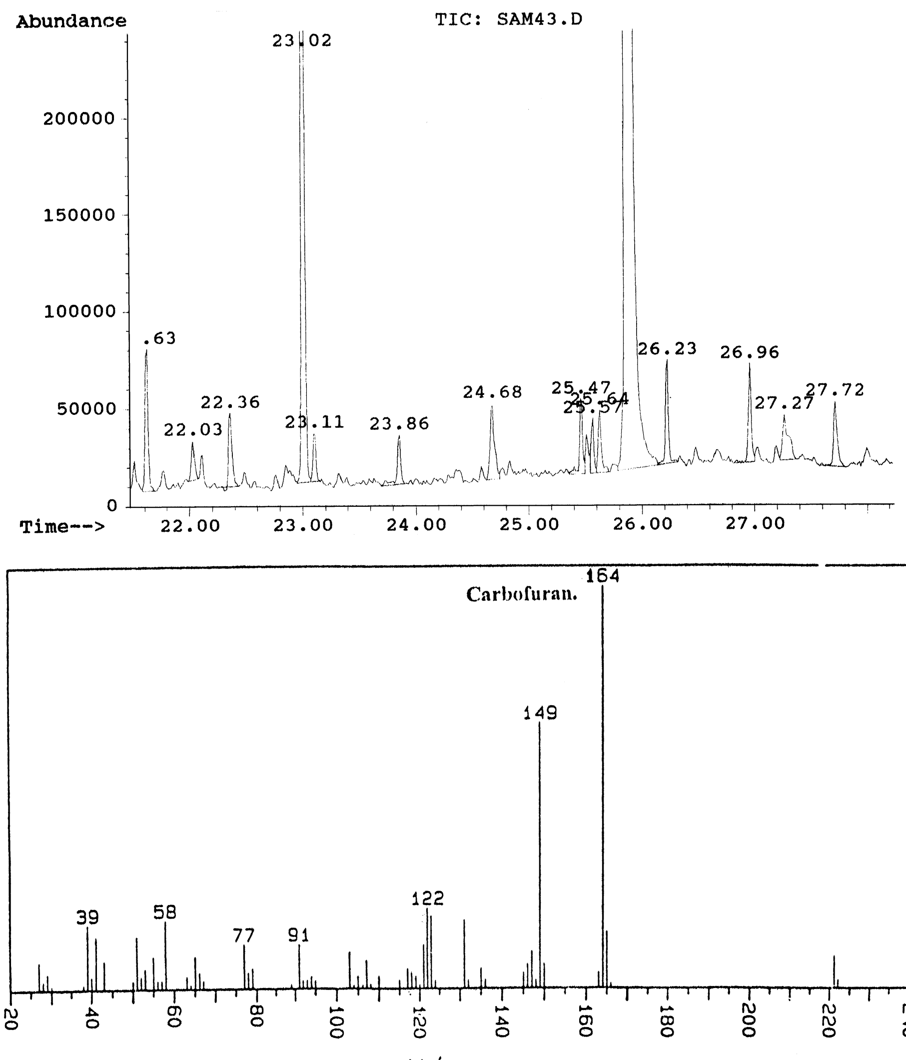

Fig. 2. GC and mass spectrum of Abd-el-aal (seaside) soil sample.

The total soluble salts content (TSS) was calculated from specific conductivity according to the method stated by El-Nomrosy [1].

4. Results and discussion

Water and soil characteristics at the different sampling sites are summarized in Tables 1 and 2. The oxygen content (parts per million) in the water samples depends on a number of physical, chemical, biological and microbiological processes. The analysis of dissolved oxygen (DO) is a key test in water pollution and water treatment process control [7]. The DO levels (Table 1) exhibit fluctuation, so the lowest DO values were in El-Moheet drain. Also, lateral and spatial changes in the DO levels were observed depending on industrial, human and thermal activity at certain points along the sites. It was found also that drainage water samples had higher content of total soluble salts (total concentration of ionized substances in water (858 ppm).

The pH of the water at the sampling sites ranged from 7.2 to 8.3. The presence of high concentrations of plant biomass such as algae and plant material in the Moheet drain is characterized by relatively high percentage of carbohydrate contents.

The presence or absence of particulate matter, soluble salts, etc. in water, should be reported when measuring pesticide residues in water since adsorption and other factors may have a greater effect on the, measurement than solubility of the pesticides in water.

Table 2 shows that the soils studied from El-Maryotia (Kerdasa) and Kafer-Hakim sites are sandy with low clay fraction but with high organic carbon contents. Organic carbon is frequently cited as being highly sorptive [8] and could be responsible for the difficulty in extraction of some kinds of pesticides in the soils examined. Ideally, pesticide monitoring should survey all pesticides in all samples. Detectable pesticides are given in Table 3. It indicates the presence of aldicarb, chlorpyrifos and total BHC = (alpha, gamma, beta and delta BHC) in three different sites of soil (Abd-el-aal, land and seasides and El-Maryotia). Abd-el-aal seaside had the highest residues value. The results indicate the presence of at least eight compounds in the soils. Eight in El-Maryotia (Kerdasa), seven in Abd-el-aal (seaside) and five in El-Zommor and Kafer-Hakim could be detected (Table 3).

Table 1
Water characteristics

Water sample	Water temperature (°C)	Water pH	Total soluble salts (ppm)	Dissolved O_2 (ppm)
El-Zomor Canal	20.7	8.0	333	1.4
Abd-el-aal (landside canal)	19.1	7.5	398	1.3
Abd-el-aal (seaside canal)	21.0	8.3	448	2.8
El-Moheet drain (El-Maryotia)	23.3	7.2	858	1.0
El-Mansorya Canal (Kafer-Hakim)	18.2	7.8	736	3.6

Table 2
Soil characteristics

Soil sample	Particle size distribution (%)			Organic C (%)	N (%)	pH in $CaCl_2$
	Clay	Silt	Sand			
El-Zomor (Giza)	37	37	26	3.6	0.3	8.0
Abd-el-aal (Giza) (land side)	36	37	27	3.2	0.22	7.8
Abd-el-aal (Giza) (sea side)	35	38	27	3.0	0.21	7.5
El-Maryotia	25	35	40	6.4	0.8	7.2
Kafer-Hakim	20	23	47	5.1	0.13	7.4

There are many factors that play an important role in the persistence and degradation of pesticides in soil [9]. The persistence of organic chemicals in soil is related to the interacting effects of the chemical and soil environmental factors. Carbaryl and total BHC were present in El-Zomor and Kafer-Hakim, carbofuran was found in Giza soils (Abd-el-aal and El-Zomor) Fig. 2. Diazinon was found in El-Haram soils (El-Maryotia Kerdasa and Kafer-Hakim). Before comparing results of different monitoring studies, it is very important to know which kind of pesticides is accepted for use in a special site, e.g. chlorpyriphos were established for citrus fruits and grapes (El-Maryotia), pirimiphos-methyl on orange and tomatoes (El-Zomor), malathion for wheat and chlorpropham and dizinon for potatoes (El-Maryotia and Kafer-Hakim). When chlorpyrifos was applied as termiticidal soil, nearly 70% of the initial chlorpyrifos remained in the soil after 18 months [9].

Most findings of pesticide residues in the different soil sites were less than 1 $\mu g/g^{-1}$, which is considered a low-level finding.

The level of pesticides in canal and drainage water at all locations are presented in Table 3. The data show that the residues of pesticides varied between different locations, e.g., organochlorine pesticide residue levels detected in El-Moheet drainage water was the highest residues values, as shown in Table 3, while drainage water has been exposed to much industrial and sewage pollution.

Table 3 confirms the presence of organochlorine compounds in the canal water (El-Zomor, Abd-el-aal and El-Mansorya) with low concentration. That must direct our attention to stop discharging the wastes into the water supplies.

These data in Table 3 indicate that ‘‘drins’’ (aldrin + endrin + dieldrin + pentachloronisole + pentachlorobenzene) are the most commonly found organochlorine pesticides and usually in the highest concentrations ranging between 37.4 (in El-Mansorya), 18.5.6 (in Abd-el-aal seaside) and 280.7 (in El-Moheet drain) $\mu g\ kg^{-1}$, respectively. Although the concentration of the total DDT (P, P-DDE, P, P-DDD and P, P DDT) is well below the guideline limit (between 2.3 and 10.3 $\mu g\ l^{-1}$ in all canal waters, while El-Moheet drainge water had the highest concentration, 61.0 $\mu g\ l^{-1}$). The distribution of organochlorine pesticides in the Egyptian aquatic ecosystem (El-Malek, El-Saleh and Manzala Lake) was studied [10]. Data showed that the total DDT followed

Table 3
Pesticides detected in water and soil samples — limit of detection as mean values ($\mu g\ l^{-1}$ or $\mu g\ kg^{-1}$ — ppp)
Drins = aldrin, endrin, dieldrin, pentachloroanisole and pentachlorobenzene; total DDT = P,P-DDE, P,P-DDD and P, P-DDT; total BHC = alpha, gamma, beta and delta BHC; ND = not detected; PCP = pentachlorophenol.

Sample pesticide	El-Zomor Giza		Abd-el–aal (land side)		Abd-el–aal (seaside)		El-Moheet drain (El-Maryotia)		Kafer-Hakim (El-Mansorya)	
	Water	Soil	Water	Soil	Water	Soil	Water	Soil	Water	Soil
Chlorpyrifos	14.5	17.0	13.4	16.0	ND	23.0	15.8	18.6	ND	ND
Dimethoate	ND	ND	ND	ND	ND	9.0	12.4	32.0	ND	ND
Parathion	ND	ND	ND	1.5	ND	2.3	10.8	26.2	ND	1.2
Carbofuran	16.0	25.8	12.0	18.8	21.0	35.2	ND	ND	ND	ND
Diazinon	ND	ND	ND	ND	ND	ND	ND	14.3	ND	20.8
Aldicarb	8.9	ND	13.8	25.0	9.6	48.6	42.4	38.3	ND	ND
Carbaryl	28.3	18.6	ND	ND	32.0	ND	48.3	ND	19.8	20.0
PCP	18.2	ND	29.0	ND	130.8	ND	ND	ND	ND	ND
Endosulfan	3.4	ND	3.8	ND	14.0	ND	290.2	ND	11.5	ND
Heptachlor	2.11	ND	3.6	ND	3.7	ND	12.1	ND	4.9	ND
Heptachlor epoxid	10.7	2.5	15.5	ND	14.6	4.3	27.8	13.0	15.5	ND
Drins	58.6	ND	58.9	ND	185.6	10.3	280.7	16.3	37.4	14.6
Total DDT	2.3	ND	8.7	ND	10.3	ND	61.0	ND	8.4	ND
Total BHC	28.7	14.2	26.8	ND	29.4	ND	86.2	16.2	20.7	13.2

by heptachlor were predominant in fish samples collected from the River Nile and the same organochlorine pesticides were found in water samples collected from Manzala Lake and the River Nile. The pesticide endrin was detected in both the River Nile and Giza tap water at concentration of 0.7 and 1.5 ppp, respectively, while in drainage water the presence of endrin was not confirmed but identified 1, 2, 5 trisubstituted aromatic ring and chlorinated compounds were present [1].

Total BHC residues ranged between 20.7 and 86.2 ppp in all water samples. The residues of endosulfan varied from 3.4 in El-Zomor canal water to 290.2 ppp in El-Moheet drain Fig. 2. The levels of other organochlorine pesticides (as average) in canal water were: heptachlor, 3.6 and heptachlor epoxide, 15.0 ppp (Table 3). All results showed that the organochlorine pesticide residues were higher in El-Moheet drainage water than in canal water. The concentrations of organochlorine pesticides are unlikely to occur in large quantities in water because they are relatively insoluble [11].

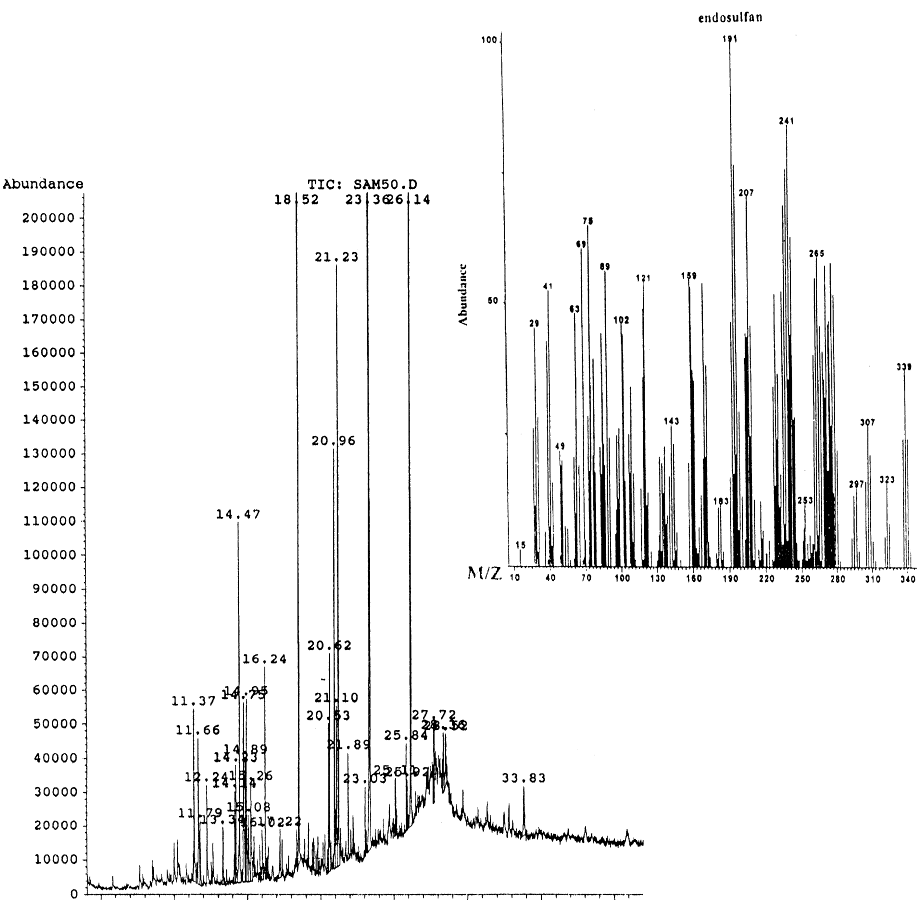

Fig. 3. GC and mass spectrum of El-Moheet drain water sample.

The water-monitoring study confirmed the presence of three organophosphorus compounds in El-Moheet drainage water (chlorpyrifos, parathion and dimethoate) and two carbamate pesticides (carbaryl and aldicarb (Table 3). The results show that chlorpyrifos, carbofuran, aldicarb and carbaryl in addition to seven organochlorine pesticides were detected in canal water (El-Zomor and Abd-el-aal). Oxidizing agents lead to the formation of the epoxide of heptachlor, which is more toxic to all kinds of organisms and less stable than heptachlor.

Six thiophosphorus (OPS) pesticide residues (trichlorfon, phorate, dimethoate, parathion and chlorpyrifos were confirmed in the 48 water samples [12] and 12 different pesticides representing seven chemical classes have been detected in ground water samples [13]. In a study to investigate the leaching of chemical compounds to drainage water from the fields, chemicals in the drainage water were measured after the fields were treated with dichlorprop. A small amount (0.1–1.6 g l^{-1}) of dichlorprop was found in drainage water 4 weeks after application [14].

Finally, no monitoring study can detect all pesticides. It may also be concluded that El-Moheet drainage water was highly polluted and contains much more pesticide residues than different canal waters Figs. 2 and 3. High accumulation of phosphorus pesticides occurs in soil compared to water, due to deposition or preferential adsorption. Pesticides favor certain media so that the concentration will decrease in one and increase in another [12]. It is very important to note that the pesticides were reduced by more than 50% because of their adsorption on the surface of organic materials and chelation with the oligomeric charge hydroxy complex [11].

5. Conclusions

In this work, the dissolved oxygen (DO) in the water samples exhibited fluctuation, so the lowest DO levels were in El-Moheet drain, while DO levels depending on industrial, human and thermal activity at certain points along the sites. It was found also that drainage water samples reached higher total soluble salt content (858 ppm). The persistence of organic chemicals in soil is related to the interacting effects of chemical and soil environmental factor. The soils studied from El-Maryotia (Kerdasa) and Kafer-Hakim sites are sandy with low clay fraction but with high organic carbon contents. Organic carbon is frequently cited as being highly sorptive and could be responsible for the difficulty in extraction of some kinds of pesticides in the soils examined. Before comparing results of different monitoring studies, it is very important to know which kind of pesticide is accepted for use in a special site. The level of pesticide residues in canal and drainage water varied between locations; also the drainage water had been exposed to much industrial and sewage pollution. This may explain why the El-Moheet drainage water was highly polluted and contained much more pesticide residues than the canal waters. The presence of organochlorine compound in the canal water must direct our attention to stop discharging the wastes into the water supplies. Higher accumulation of phosphorus pesticides occurred in soil compared to water because of deposition or preferential adsorption. Finally, it may be also concluded that no monitoring study can detect all pesticides.

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