J. Pest Cont. & Environ. Sci. 15 (1): 21 – 41 (2007).

Monitoring of some agrochemical pollutants in surface water in Kafr El-Sheikh Governorate

Masoud. A.H; I.I. El-Fakharany and M.A.S. Abd El-Razik
Department of Pesticides, Faculty of Agric., Kafr El-Sheikh University, Egypt

Abstract

Agrochemical pollutants such as pesticides and heavy metals cause serious problems in the framework of aquatic environment, which lead to adverse effects on water quality and its biota such as fish. Kafr El-Sheikh Governorate presents one of the most areas for rice cultivation and fish culturing. Therefore, it is necessary to protect the environment of this area from hazardous of chemical pollutants. A spatiotemporal monitoring of pesticide residues and heavy metals were conducted in some irrigation and drainage waters from different zones in Kafr El-Sheikh Governorate (Kafr El-Sheikh, Sedi Salem, El-Reiad, Biyala, Al-Hamul and Baltim). To study the pesticide residues in surface water, samples were collected during a period extended from winter (2004) up to summer (2005) from twelve sites distributed at five sites from irrigation canals (Bahr Tirah canal, An-Nile canal and Meet Yazid canal), seven sites of drains from (Al-Gharbiya ar Raisi, Nasir, Hafir Shihab adin, Ash-Sharikah, No. 7, No. 8 and Al-Wastany). The analysis results using GC (ECD and FPD) and HPLC-UV showed that the presence of twenty seven pesticides which were: aldlrin, dieldrin- γ-BHC, β-BHC, δ-BHC, α-BHC, p,p.DDT, p,p.DDE, p,p.DDD, heptachlor, heptachlor-epoxide and γ-chlordane of organochlorine compounds (OCPs), dichlorophos, ethoprophose, cadusaphos, diazinon, chlorpyrifos-methyl, primiphos-methyl, chlorpyriphos, phenthoate, fenitrothion, prothiophos, profenphos and ethion of organophosphorus compounds(OPs), methomyl and oxamyl (carbamates). p,p.DDT and diazinon concentrations were higher than maximum residue level (MRL) especially at mixing waters between irrigation water and drain in summer that was due to high persistence and the precipitation in agricultural water drains, but the lowest two compounds were α. HCH and phenthoate. Seventeen samples were collected from the previous sites for analysis of heavy metal pollutants (Fe, Cu, Ni, Cd, Co, Cr, Mn, Zn and Pb) in surface water using atomic absorption spectrophotometer (AAS). The results indicated that chromium, cobalt and lead were the most abundant trace elements and their residues exceed the proposed permissible limits according to WHO and the Egyptian Ministry of Health Regulation, followed by zinc, manganese and cadmium while iron, cupper and nickel were less than the permissible limits according to WHO.

Keywords: Water, Pesticide residue, Heavy metal, GC (ECD, FPD), HPLC-UV, AAS, Pollution.

INTRODUCTION

Pesticide residues have been a catch cry of environmental and consumer groups since the mid-1960's when Rachel Carson drew the public's attention to the deleterious ecological effects of organochlorine insecticides which were in widespread use at that time.

Water is a very scarce commodity in Egypt and its deterioration represent a major environmental risk due to contamination from nonpoint sources of pollution (NPSP) caused by agricultural activities and point sources of pollution (PSP) from industrial and domestic discharge (Gaber *et al.,* 2003). During 1999, monitoring of pesticides in water of the River Nile at the estuaries of Rosetta and Damiata branches was conducted (Abbassy *et al.,* 1999). Their results indicated that chlorinated hydrocarbon compounds were present in all samples at concentrations ranging between 0.019 – 0.390 µg/L with a higher trend in Damiata branch than Rosetta branch.

For more than 30 years, awareness has been growing about the dangers posed on human health and the environment by ‘‘persistent toxic substances’’ (PTS). Many of the substances of greatest concern are organic compounds characterized by their high persistence in the environment, hardly degradable, and acute and chronic toxicity. In addition, many subjected compounds to atmospheric, aquatic or biological transport over long distances, and are thus globally distributed, detectable even in areas where they have never been used. The lypophilic character of these substances causes them to be incorporated and accumulated in the tissues of living organisms leading to body burdens that pose potential risks of adverse health effects. Toxic chemicals, which are less persistent but for which there are continuous releases resulting in essentially persistent exposure of biota, raise similar concerns (Barakat, 2004). These chemicals have serious health and environmental effects, which may include carcinogenicity, reproductive impairment, developmental and immune system changes, and endocrine disruption thus posing a threat of lowered reproductive success and in extreme cases possible loss of biological diversity (IOMC, 1995). In recent years, using of these insecticides has been restricted in many countries because of suspicion that these compounds are the major source for the environmental hazards (carcinogenic agents). Detectable amounts of these compounds and their transformation products are sometimes found in animal and human tissues, animal and human milk, drinking water and soil (Abbott *et. al*., 1981, Kanja *et. al*., 1986, Kanja *et. al*., 1992, Lommel *et. al*., 1992, Rossel *et. al*., 1993, Asplund *et. al*., 1994 and Hendriks *et. al*., 1995).

On the other hand, it was known that heavy metals could accumulate in tissues during aquatic organism growth (bioaccumulation) and often biomagnified up the food chain interfering with the health and reproduction of both wildlife and humans. (Mansour and Messeha. 2001) studied the distribution of heavy metals in water of Lake Qarun as Zn, Fe, Mn, Cu, Cd, Cr, Ni, Pb, Co and Sn they found in all samples at concentrations ranging between 0.026 - 0.451 (ppb).

Therefore, the objectives of this study was undertaken to survey the residues of pesticides and heavy metals in both irrigation and drainage water samples in Kafr El-Sheikh Governorate.

MATERIALS AND METHODS

Chemicals: Selected pesticides, organochlorine mix 12 (aldlrin, dieldrin- γ-BHC, β-BHC, δ-BHC, α-BHC, p,p.DDT, p,p.DDE, p,p.DDD, heptachlor, heptachlor-epoxide and γ-chlordane) was provided by *Dr., Ehrenstofer* Augsburg, Germany (10 ng/μl) in cyclohexane. Carbamate compounds (methomyl and oxamyl) and organophosphorus compounds (dichlorophos, ethoprophose, cadusaphos, diazinon, chlorpyrifos-methyl, primiphos-methyl, chlorpyriphos, phenthoate, fenitrothion, prothiophos, profenphos and ethion) were obtained from the Environmental Protection Agency (EPA), USA.Hexane, acetone, dichlormethane and methanol were obtained from Merck Co., Germany. The chemicals used were analytical grade for pesticide residues analysis.

Collection of surface water samples: Four liter of water samples in cleaned, sterilized and solvent washed glass bottels were collected from Bahr tir'ah canal (Biyala, Al-Hamul and Baltim region), consisting 5 collection sites (samples No:1-5), An-Nil canal (Baltim, Biyala, Al-Hamul and Bilqas region), consisting 1 collection site (sample No: 6), Meet yazid canal (Kafr El-Sheikh, Seedy Salem and El-Ryad region), consisting 2 collection sites (samples No:7,8). Also, 9 sites represents waters from drains were included samples No: 9-17 (9, 10 and 11 of Al-Gharbiyyah ar-Ra′isi, 12 of Nasir, 13 of Hafir Shihab ad-Din, 14 of ash-Sharikah, 15 of Al-Wastany, 16 of No.8 and 17 of No.7), Fig. (1).

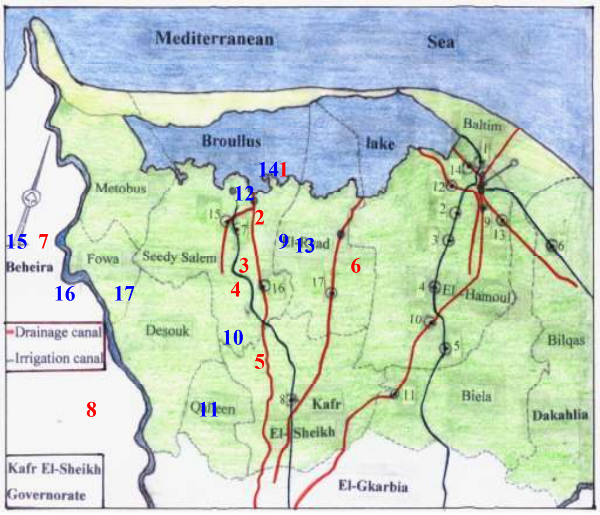


Fig (1): Map showing the studied area and the sites of sample collection.

Water samples were collected during December 2004, (winter), June 2005, (summer). The collected water samples were transferred immediately to the laboratory in ice container. The samples had been filtered through fiberglass filter to remove turbidity and debris and stored at 4°C prior to extraction (during 24 hr.) and analyzed for pesticides and heavy metals.

Solid- Phase Extraction Technique: In the laboratory, the collected water samples were extracted using disposable solid phase extraction (SPE) with octadecyl-bonded silica cartridges (C_{18} BSCs) (500 mg; Phenomenex Scientific), performed by passing 1liter of water sample through C_{18} extraction cartridges. Cartridges were conditioned prior to use (washed) with eluting 5 ml of 1:1:1 hexane: acetone: dichloromethane (v/v), followed by 5 ml methanol, and finally 5 ml deionized (DI) water. Next, samples were passed through the SPE cartridges under vacuum at a rate of ca. 18-20 ml per minute. After the entire sample was extracted, the vacuum was left on and air allowed passing through the SPE for 10 min as drying step. Analytes were eluted from the SPE by 6 ml rinses of 1:1:1 hexane: acetone: dichloromethane (v/v). The final extract had transferred quantitatively by rinsing with 1 ml aliquots of the organic solvent into a concentrator tube and then evaporated to dryness. The residue was dissolved in *n*-hexane and One microliter was injected into the GC in the split-less mode. This method was according to Belden *et al.,* (2000), with minor modification.

Determination of OCPs and OPs pesticide residues: Residues of monitored pesticides were analyzed by using gas chromatograph (Hewlett Packard model 6890 equipped with electron capture detector (Ni^{63}-ECD) for detection of chlorinated pesticides. A Flam Photometric Detector (FPD) with phosphorus filter was employed to determine the OPs. DB-17 (J&W scientific) capillary column (30m X 0.32mm, i.d, 0.25µm film thickness) was used. For Ni^{63}-ECD carrier gas: N_2 at a flow rate of 4 ml/min; injector and detector temperatures were 300˚C and 320˚C, respectively. The initial column temperature was initial oven temperature, 160˚C (2min), (3˚C /min) 230˚C (10˚C /min), 260˚C hold to 13min. For FPD, the carrier gas was nitrogen at 3 ml/min, and hydrogen and air were used for the combustion at 75 and 100 ml/min, initial oven temperature, 170 ˚C for (2 min), (10 ˚C / min) 240 ˚C held to 20 minutes, respectively.

Table (1): Organochlorine (OC), organophosphorus (OP) and carbamate pesticides-recovery rates (%) from irrigation and drainage waters

Pesticide	Fortified level (ppb)	Recovery (%)	Pesticide	Fortified level (ppb)	Recovery (%)
OC compounds			OP compounds		
α.HCH	0.09	85.80	Dichlorofos	17	88.2
γ.HCH	0.12	97.88	Ethoprophos	4	78
β.HCH	0.47	145.34	Cadusafos	11.5	67.03
δ.HCH	0.36	108.45	Diazonon	20	93.10
heptachlor	0.18	50.95	Chlorpyriphos-methyl	4	82.2
aldrin	0.20	37.17	Pirimiphos-methyl	22	71.11
hepta. Epoxide	0.31	55.91	Dimethoate	4	95.70
γ.Chlordane	1.11	98	Chlorpyriphos	4	86.30
dieldrin	0.72	77.98	Fenitrothion	12	84.23
p,p.DDE	0.45	28.65	Phenthoate	6	88.21
p,p.DDD	0.80	61.91	Prothiophos	7.5	96
p,p.DDT	1.58	81.96	Profenophos	17	92.50
			Ethion	14	76.50
Carbamate compounds					
oxamyl	0.03	63			
methomyl	0.03	84			

Determination of carbamate residues: Analysis of final extracts was conducted using HPLC (Knauer) equipped with an ultra violet detector (UV) at wavelength of 230 nm, sample injector equipped with a 20 µl sample loop, a reversed-phase (RP) C_{18} analytical column Novapak (25 cm X 4.6 mm I.d., 5 µm) was used. The mobile phase of the HPLC system consisted of acetonitrile (solvent A) and water (solvent B) gradient as follows: time 0 min, 50:50, time 5 min, 53:47, time 15 min,55:45. Detection at 230 nm, the mobile phase flow-rate was 0.8 ml/min and the injected volume was 20 µl. Samples were analyzed in the Central Agricultural Pesticides Laboratory, Dokki, Egypt. Pesticides recovery rates (%) from irrigation and drainage water were presented in Table (1).

Analysis of heavy metal pollutants in surface water: Water samples were directly analyzed using atomic-absorption spectrophotometer (AAS) (Perken Elmer, model 2180) after filtrated them as described by Shaheen (2005).

RESULTS AND DISCUSSION

Measurements of pesticide levels in surface waters: Residue analysis of chemical pollutants, especially pesticides and heavy metals in surface water represents one of the most important factors to solve the problems of the environmental pollution. Pesticide chemicals pollutants in this study such as OCPs aldrin, dieldrin, γ.BHC, β.BHC, δ.BHC, α.BHC p,p-DDT, p,p-DDE, p,p-DDD, heptachlor, heptachlor–epoxide and γ.chlordane are one of the most persistent organic micropollutants present in water (Gangesh *et. al.,* 2006). OPPs (dichlorvos, ethoprophos, cadusafos, diazonon, chlorpyriphos-methyl, pirimiphos-methyl, dimethoate, chlorpyriphos, phenthoate, fenitrothion, prothiophos, profenofos and ethion) and carbamate compounds (methomyl and oxamyl) (Ministry of Agriculture Report, 1980-1995) are common use in plant protection and caused pollution in agricultural lands and surface water according to, (WHO, 1993 and EMOH, 1995). In Egypt, organochlorine insecticides have been use in agricultural practice since 1950, El-Nawawy (1981).

The results of monitoring pesticides indicated that 12 OCPs (γ.BHC, β.BHC, δ.BHC, α.BHC p,p-DDT, p,p-DDE, p,p-DDD, γ.chlordane, aldrin, dieldrin, heptachlor and heptachlor–epoxide). 13 OPPs (dichlorvos, ethoprophos, cadusafos, diazonon, chlorpyriphos-methyl, pirimiphos-methyl, dimethoate, chlorpyriphos, phenthoate, fenitrothion, prothiophos, profenofos and ethion), and 2 carbamates pesticides (methomyl and oxamyl) were detected in winter and summer either in irrigation or drainage waters at all sampling sites (Tables 2-5). With the concerning to sampling time the concentration levels of detected pesticides such as cadusafos, diazonon, phenthoate, prothiophos, profenofos and methomyl were higher in summer than in winter either in irrigation or drainage waters at most sampling sites. These resultes are in agreement with those of Ashry *et.al.*, (2006). They reported that the concentration of identified OCPs and OPs residues were higher in spring and summer seasons.

Among sampling sites 1, 7, 10, 14, 16 and 17 were highly contaminated sites with organochlorine pesticides comparing to other sampling sites in the both types of water. While the concentration levels in sampling sites 5, 6 and 15 were lowest contaminated sites with organochlorine pesticides. The organophosphorus and carbamate pesticides in sites 1, 7, 8, 10, 14 and17 were the highest contaminated in both types of water. While 5, 6, 12, 13, 15 and 16 sites were the lowest contaminated sites except diazinon which was contaminated all sites in both types of water especially in summer season.

DDT was the highest concentration levels 58.168 µg/L, Table (3) in both types of water either in summer or winter seasons at all sampling sites, and the lowest one was α.HCH 0.003 µg/L, Table, (2). On the other hand, the highest concentration levels detected for organophosphorus and carbamate pesticides was diazinon 117.288 µg/L, Table, (5), and the lowest one was phenthoate 0.019 µg/L, Table, (4).

Drainage waters were generally highly contaminated with organochlorine pesticides than irrigation waters in both summer and winter at all sampling sites. However, for organophosphorus and carbamates the same phenomena was found except for dichlorvos, cadusafos, phenthoate, fenitrothion, prothiophos, profenofos and oxamyl which highly contaminated irrigation waters than drainage waters in both summer and winter at all sampling sites (Tables 2-5).

The concentration levels of organochlorine pesticides in summer were ranged from 0.227 µg/L, heptachlor-epoxide to 58.168 µg/L, p,p.DDT, Table (3). Nevertheless, in winter the levels were 0.003 µg/L, α.BHC to 4.669 µg/L, dieldrin, Table (2). Our results concerning the level of OCPs residues in purified water are in agreement with those reported by Abd Allah and Hesham (2003) and El-Sebae and Abu Elamayem (1978). While organophosphorus and carbamate pesticides in summer were ranged from 0.016 µg/L, fenitrothion to 117.288 µg/L, diazinon, Table (3). But in winter were ranged from 0.019 µg/L, phenthoate to 37.179 µg/L, primiphos-methyl, Table (4).

The concentration levels of HCH isomers were ranged from (0.031 to 20.544) µg/L, (0.237 to 8.266) µg/L, (0.016 to 0.689) µg/L and from (0.017 to 0.176) µg/L, γ.HCH, β.HCH, δ.HCH and α.HCH, respectively. The results showed that δ.HCH less frequently within all pesticides and it was found in only 6 in all sampling sites for HCH isomers (Tables 2 and 3). The results agreed with the observation of Prakash *et.al.,* (2004), who found that, the concentration of β.HCH ranged from 0.3 to 15 µg/L, γ.HCH (0.1 to 8.0 µg/L) and δ.HCH was found in only four samples. However, residues of α.HCH (0.01 to 0.19µg/L) and δ.HCH (0.01 to0.05 µg/L) were very low concentration in water samples and detected less frequently. The same trend was β.HCH in the ranged from 0.145 to 1.272 µg/L, predominant being γ.HCH (Sankararamakrishnan *et. al.,* 2005). It was also noticed that γ.HCH was more predominant than the other isomers which indicated recent usage of the gamma isomer through agricultural activities with very low level of trends formation into α.isomer. It was worth mentioned that most of these organochlorine pesticides have been virtually phased out many years ago and their presence in the watersheds reflects residues from pest application and indicates the very persistent nature of these compounds (Ahmed *et. al.,* 2003). While the concentration levels of our results of HCH isomers was higher than the maximum permissible limit for drinking water (0.2 µg/L) according to (WHO, 1993). Some of the isomers detected might be the result of their prolonged persistence in the environment (Prakash *et. al.*, 2004).

The values of their residues were more than the maximum residue limit (MRL) for drinking water according to (WHO, 1993 and EEC, 1980), such as organochlorine (γ.HCH, β. HCH, p,p-DDT, γ.chlordane, aldrin, dieldrin, heptachlor and heptachlor–epoxide), and organophosphorus pesticides (dichlorvos, diazonon, pirimiphos-methyl, fenitrothion and prothiophos. The previous presence results in frequency more than the other pesticides in water samples, in either summer or winter seasons, specially, organochlorine pesticides (γ.HCH, β. HCH, p,p-DDT and heptachlor), and organophosphorus pesticides (diazonon, pirimiphos-methyl and fenitrothion), the most commonly occurring reaction in the environment to cyclodiene insecticides are epoxidation reaction to produce dieldrin for aldrin.

The results showed that diazinon was at high concentration levels in summer than winter in all sampling sites, due to diazinon was used to insect control rice in summer according to (Technical recommendation from agricultural pest control, 2001). The low concentration levels of diazinon in winter than in summer due to hydrolysis. Diazinon slowly hydrolyzed in alkaline media and more rapidly in acidic media: DT_{50} (20°C) 11.77hrs (PH 3.1), 185d (PH10.4). Decomposes above 120°C (A World Compendium The Pesticide Manual incorporating The Agrochemicals Handbook, 1994).

Variation in residual levels in these samples could be due to locations and timing of the sampling. The results of this survey showed that the irrigation and drainage waters in this area have particular problems with respect to pesticide residues, so these waters must have been remediation from these contaminations.

Measurements of heavy metal levels in surface waters: Toxic metal pollution of waters and soils was a major environmental problem. The main problem concerned with water pollution was heavy metals when water containing these metals, as a pollutants, used for irrigation, it will be contaminate and enrich soils and crops, (Mireles, 2004).

With concerning to sampling time, the concentration levels of detected heavy metals were higher in summer than in winter except Cu, Mn, Zn and Pb in both types of waters at most of sampling sites. Among sampling sites 2, 5, 6, 9, 14, 15 and 17 were highly contaminated sites with heavy metals comparing to other sampling sites in both types of waters. On the other hand, sampling sites 4, 11 and 16 were the lowest contaminated sites with heavy metals.

With reference to detected heavy metals the highest concentration levels was Cr, (6.34 mg/L), Tables (6-7). and the lowest one was Cd, (0.001 mg/L), Drainage waters was generally highly contaminated by heavy metals than irrigation waters in both summer and winter at all sampling sites except for Cd, Co and Zn were highly contaminated in irrigation waters than drainage waters (Tables 6 and 7).

Table (2): Organochlorine compounds levels in irrigation and drainage waters in December 2004, obtained from the area of study.

Site	µg/l (ppb)											
NO:	γ.HCH	β.HCH	δ.HCH	α.HCH	p,p.DDT	p,p.DDE	p,p.DDD	γ.chlordane	aldrin	dieldrin	heptachlor	heptaehlor epoxide
1*	0.127	0.822	ND	0.091	0.014	ND	0.330	0.078	1.50	0.03	ND	0.437
5*	0.123	ND	ND	0.017	0.040	ND	0.028	ND	0.11	0.01	0.150	0.069
6*	0.080	0.237	0.02	0.041	0.061	0.129	0.019	0.075	0.14	0.14	0.201	ND
7*	0.048	ND	ND	0.061	0.021	0.061	0.007	ND	0.56	1.10	ND	0.107
8*	0.451	3.479	ND	ND	0.009	0.141	0.019	ND	0.25	2.53	ND	0.158
10**	0.031	ND	ND	0.176	0.009	0.171	0.007	0.027	0.14	0.14	0.158	0.441
12**	0.160	ND	0.212	0.161	0.011	0.0329	0.014	ND	0.28	0.21	0.667	0.132
13**	0.188	ND	0.430	0.072	0.015	0.016	0.062	ND	0.61	0.05	1.063	0.395
14**	ND	ND	0.016	0.038	0.043	0.121	0.079	0.100	0.07	0.11	0.140	ND
15**	0.137	0.458	ND	0.003	0.159	0.038	0.015	0.031	0.33	0.06	ND	ND
16**	0.037	ND	ND	ND	0.018	ND	0.011	ND	0.68	1.18	ND	0.136
17**	0.044	ND	ND	ND	0.016	ND	0.026	ND	0.54	4.67	ND	0.173

* Samples collected from irrigation waters.

** Samples collected from drainage waters.

Table (3): Organochlorine compounds levels in irrigation and drainage waters in June 2005, obtained from the area of study.

Site NO:	µg/l (ppb)											
	γ.HCH	β.HCH	δ.HCH	α.HCH	p,p.DDT	p,p.DDE	p,p.DDD	γ.chlordane	aldrin	dieldrin	heptachlor	heptaehlor epoxide
1*	0.931	2.381	ND	ND	4.036	ND	ND	ND	ND	ND	ND	ND
5*	0.459	ND	ND	ND	5.535	ND	ND	ND	ND	ND	ND	ND
6*	1.223	2.467	ND	ND	20.075	ND	ND	0.331	0.42	ND	ND	0.335
7*	17.154	ND	ND	ND	19.189	ND	ND	1.428	1.36	1.05	1.287	0.757
8*	1.628	ND	ND	ND	2.784	ND	ND	0.521	0.25	ND	ND	ND
10**	1.288	ND	ND	ND	8.900	0.875	0.875	ND	ND	ND	ND	ND
12**	1.380	5.914	ND	ND	8.954	ND	ND	0.215	0.30	ND	ND	0.227
13**	4.449	ND	ND	ND	33.061	ND	ND	0.898	1.05	0.67	0.866	0.536
14**	10.040	ND	0.602	ND	58.168	0.568	0.568	1.226	1.25	0.83	0.710	0.548
15**	0.617	ND	ND	ND	2.322	ND	ND	0.448	0.26	ND	0.441	ND
16**	20.544	ND	0.689	ND	23.902	ND	ND	1.153	1.01	0.75	3.357	ND
17**	4.016	8.266	ND	ND	6.162	ND	ND	ND	ND	ND	ND	0.418

* Samples collected from irrigation waters.
** Samples collected from drainage waters.

Table (4): Organophosphorus and carbamate compounds levels in irrigation and drainage waters in December 2004, obtained from the area of study.

Site NO:	µg/l (ppb)														
	Organophosphorus													Carbamates	
	cadusafos	diazinon	fenitrothion	pirimiphos-methyl	phenthoate	prothiophos	profenophos	chlorpyriphos	chlorpyriphos-methyl	dichlorvos	dimethoate	ethion	ethoprophos	methomyl	oxamyl
1*	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.386	ND	ND	ND	ND	0.384
5*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6*	0.085	0.114	0.103	ND	ND	ND	ND	ND	ND	0.970	0.125	ND	ND	ND	ND
7*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
8*	ND	ND	2.016	ND	ND	ND	ND	ND	ND	ND	ND	0.387	ND	ND	ND
10**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
12**	ND	ND	ND	ND	ND	ND	0.588	ND	ND	ND	ND	ND	ND	ND	ND
13**	ND	ND	ND	ND	0.019	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
14**	ND	ND	0.344	ND	ND	ND	ND	ND	ND	0.528	ND	ND	ND	ND	ND
15**	ND	0.085	ND	ND	ND	ND	0.048	0.049	0.036	ND	ND	ND	ND	ND	ND
16**	0.181	ND	ND	ND	0.075	ND	ND	ND	ND	ND	ND	ND	ND	0.089	ND
17**	ND	ND	0.340	37.179	ND	0.918	0.200	0.404	0.039	1.045	0.871	0.713	1.162	ND	ND

[+] Samples collected from irrigation waters.

[++] Samples collected from drainage waters.

Table (5): Organophosphorus and carbamate compounds levels in irrigation and drainage waters in June 2005, obtained from the area of study.

Site NO:	µg/l (ppb)														
	Organophosphorus													Carbamates	
	cadusafos	diazinon	fenitrothion	pirimiphos-methyl	phenthoate	prothiophos	profenophos	chlorpyriphos	chlorpyriphos-methyl	dichlorvos	dimethoate	ethion	ethoprophos	methomyl	oxamyl
1*	ND	62.947	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.327	ND
5*	0.206	81.351	0.186	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6*	ND	72.909	0.078	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
7*	1.062	23.540	0.884	14.692	0.090	0.090	0.631	ND	ND	ND	ND	ND	ND	ND	ND
8*	ND	59.388	0.061	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.244	ND
10**	ND	117.288	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.567	ND
12**	ND	93.267	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.876	ND
13**	ND	76.338	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
14**	ND	66.395	0.062	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.224	ND
15**	0.497	103.384	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
16**	ND	ND	ND	ND	0.075	ND	ND	ND	ND	ND	ND	ND	ND	0.089	ND
17**	ND	ND	0.340	ND	ND	0.918	ND	0.404	0.039	ND	0.871	0.713	ND	ND	ND

*Samples collected from irrigation waters.

**Samples collected from drainage waters.

The concentration levels of heavy metals in summer were ranged from 0.02 to 6.34 mg/L, 0.029 to 0.384, 0.01 to 1.67, 0.001 to 0.306, 0.16 to 4.25, 0.01 to 6.34, 0.012 to 0.384, 0.033 to 0.468 and 0.04 to 0.28, mg/L. On the other hand in winter, it were ranged from 0.01 to 0.30, 0.039 to 0.504, 0.01 to 1.24, 0.002 to 0.060, 0.22 to 3.88, 0.43 to 4.80, 0.050 to 0.750, 0.121 to 2.140 and 0.01 to 0.55, mg/L, for Fe, Cu, Ni, Cd, Co, Cr, Mn, Zn and Pb, respectively (Tables 6 and 7).

For Cu level it was noticed that the concentration ranged from 0.029 to 0.504, mg/L, (Tables 6 and 7), and it was lowest than the (MRL) by WHO, 1993, 2 mg/L. On the other hand, the highest concentration levels were for Ni, Cd, Co, Cr and Zn comparing to (MRL) by WHO, (1993) 0.02, 0.003, 0.1, 0.05 and 0.01 mg/L, respectively (Tables 6 and 7). Heavy metals reach soil either from dust fall, fertilizers and/or irrigation waters, especially those of low quality. The increased amount of municipal and industrial wastewater and its disposal was considered one of the most important problems around the world. The attempts to reuse those wastes as a source of irrigation, particularly in the semiarid and arid regions, have been reported by Hobbelen *et al*., (2004).

The high levels of Ni, Cd, Co, Cr and Zn might be due to the pollution with the industry wastes or by the factories which produced oil, soap or textile and dyes in El-Gharbia and Kafr El-Sheikh Governorates. The increase of Co and Cd concentrations in El-Gharbia main drain water more than the (MRL) were stated before by El-Azab (1997) and Heba (2003). Also, it could be stated that, re-use of drainage water without treatment for irrigation may increase the hazard effects for increasing the content of heavy metals in fluvial soils with time causing insidious effects to animal and man Shaheen (2005). The high levels of heavy metals in irrigation and drainage waters in summer might be due to the water current speedily in summer faster than in winter and the rate of evaporation was relatively high. Results obtained agreed the findings of Beg *et.al.* (1992), Nag and Das (1993), Hamed (1997), Pathak *et.al.* (1992) and Shaheen (2005).

ACKNOWLEDGMENTS

Sincere thanks are due to Prof. Dr. Islam Noaman, Professor of Pesticides Residue Analysis, Central Pesticides Laboratory, Dokki, Cairo, for his kind helps in the analysis part.

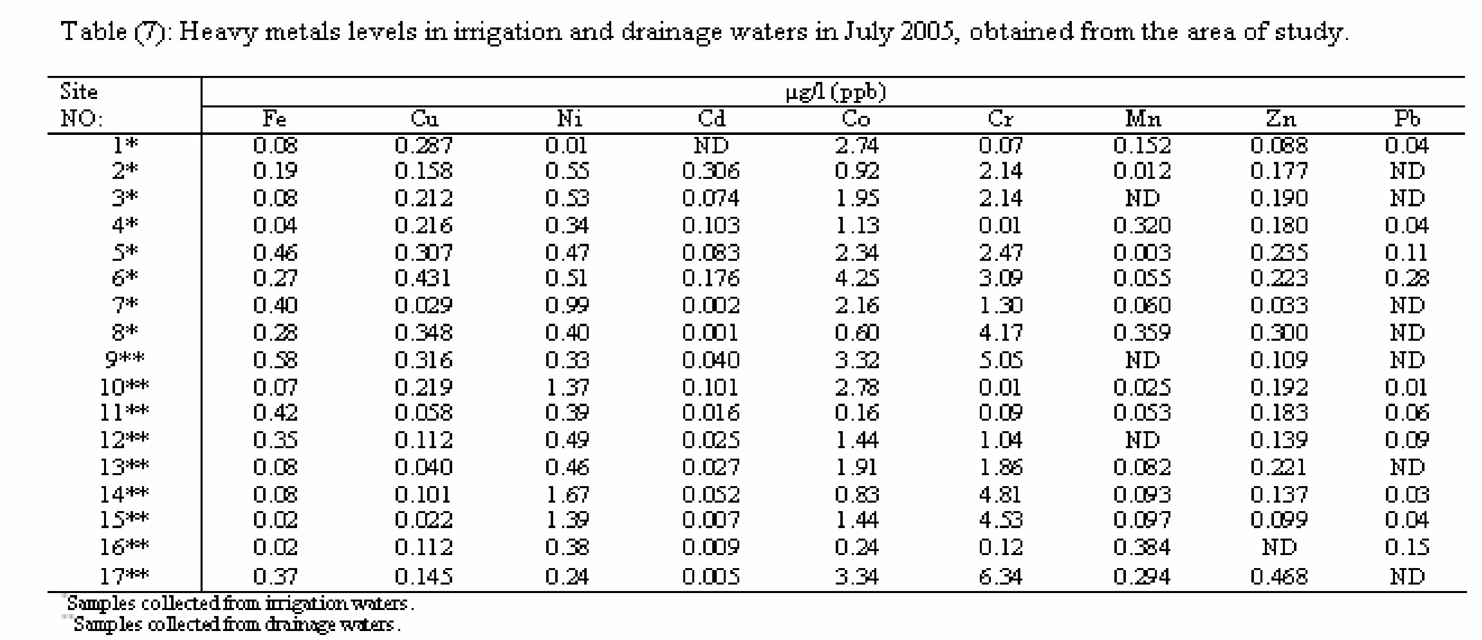
Table (6): Heavy metals levels in irrigation and drainage waters in December 2004, obtained from the area of study.

Site NO:	µg/l (ppb)								
	Fe	Cu	Ni	Cd	Co	Cr	Mn	Zn	Pb
1*	0.29	0.293	0.13	0.019	1.40	1.49	0.233	0.214	0.07
2*	0.07	0.146	0.25	0.017	1.89	0.44	0.291	0.313	0.03
3*	0.05	0.227	0.22	0.011	0.22	1.94	0.260	0.205	0.01
4*	0.21	0.104	0.24	0.026	1.15	ND	ND	0.933	0.10
5*	0.25	0.263	0.44	0.005	2.33	0.54	0.149	2.140	0.07
6*	0.23	0.159	0.37	0.044	1.11	2.05	0.100	0.670	0.29
7*	0.09	0.263	1.24	0.010	0.53	0.29	0.216	0.179	0.09
8*	0.26	0.137	0.01	0.002	0.61	0.59	0.672	0.197	0.15
9**	0.25	0.039	0.67	0.015	2.46	0.43	0.220	0.220	0.55
10**	0.02	0.219	0.20	0.017	0.32	ND	0.260	0.220	0.52
11**	ND	0.217	0.30	0.005	0.31	1.57	0.050	0.237	0.09
12**	0.01	0.206	0.12	0.006	1.42	1.51	0.210	0.324	ND
13**	0.30	0.357	0.30	0.022	1.42	3.30	0.750	0.143	0.03
14**	0.21	0.136	0.30	0.015	1.27	4.80	0.120	0.242	0.01
15**	0.23	0.504	0.92	0.060	2.70	1.64	0.050	0.121	0.34
16**	0.05	0.050	0.07	0.030	1.82	ND	0.193	0.239	0.01
17**	0.04	0.111	0.97	0.010	3.88	1.84	ND	0.128	0.34

[*] Samples collected from irrigation waters.

[**] Samples collected from drainage waters.

Table (7): Heavy metals levels in irrigation and drainage waters in July 2005, obtained from the area of study.



Site NO:	µg/l (ppb)								
	Fe	Cu	Ni	Cd	Co	Cr	Mn	Zn	Pb
1*	0.08	0.287	0.01	ND	2.74	0.07	0.152	0.088	0.04
2*	0.19	0.158	0.55	0.306	0.92	2.14	0.012	0.177	ND
3*	0.08	0.212	0.53	0.074	1.95	2.14	ND	0.190	ND
4*	0.04	0.216	0.34	0.103	1.13	0.01	0.320	0.180	0.04
5*	0.46	0.307	0.47	0.083	2.34	2.47	0.003	0.235	0.11
6*	0.27	0.431	0.51	0.176	4.25	3.09	0.055	0.223	0.28
7*	0.40	0.029	0.99	0.002	2.16	1.30	0.060	0.033	ND
8*	0.28	0.348	0.40	0.001	0.60	4.17	0.359	0.300	ND
9**	0.58	0.316	0.33	0.040	3.32	5.05	ND	0.109	ND
10**	0.07	0.219	1.37	0.101	2.78	0.01	0.025	0.192	0.01
11**	0.42	0.058	0.39	0.016	0.16	0.09	0.053	0.183	0.06
12**	0.35	0.112	0.49	0.025	1.44	1.04	ND	0.139	0.09
13**	0.08	0.040	0.46	0.027	1.91	1.86	0.082	0.221	ND
14**	0.08	0.101	1.67	0.052	0.83	4.81	0.093	0.137	0.03
15**	0.02	0.022	1.39	0.007	1.44	4.53	0.097	0.099	0.04
16**	0.02	0.112	0.38	0.009	0.24	0.12	0.384	ND	0.15
17**	0.37	0.145	0.24	0.005	3.34	6.34	0.294	0.468	ND

*Samples collected from irrigation waters.

**Samples collected from drainage waters.

REFERENCES

Abbott, D.C., G.B. Collins; R. Goulding and R.A. Hoodless (1981). Organochlorine pesticide residues in human fat in the UK. Brit. Med. J. 283, 1425.

Abbassy, M. S.; H. Z. Ibrahim and M. M. Abu El-Amayem. (1999). Occurrence of pesticides and polychlorinated biphenyls in water of the Damiatta branches, North of Delta, Egypt. J. Environ. Sci. Health B34(2): 255-267.

Abd-Allah, S.W. and M.G. Hesham (2003). Monitoring of pesticide residues in different sources of drinking water in some rural areas. Alex. J. Agric. Res., 48 (3) 187-199.

Ahmed, S.M. and H.M. Gaber (2003). Monitoring of Pesticide Residues in Different Sources of Drinking Water in Some Rural Areas. Alex. J. Agric. Res., 48 (3): 187-199.

El-Sebae, A.H. and M.M. Abu Elamayem (1978). A survey of expected pollutants drained to the Mediterranean in the Egyption Region. In:Proceedings of the congress and Plenary Assembly of the Int. Comm. Of Sci. Explor. Of the Mediterranean Sea, Antalya, Turkey, 149-153.

Ashry, M.; O.C. Bayoumi; I.I. El-Fakharany; A.S. Derbalah and A.A. Ismail (2006). Monitoring and removal of pesticide residues in drinking water collected from Kafer El-Sheikh Governorate, Egypt. Egypt. J. Agric. Res. Tanta Univ., 32(3) 691-704.

Asplund, L.; B.G. Svensson; A. Nilsson; U. Eriksson; B. Jansson; S. Jensen; U. Wideqvist and S. Skerfving (1994). Poly-chlorinated biphenyls, p,p.DDT and p,p.DDE in human plasma related to fish consumption. Archives of Environmental Health, 49 (6): 477-486.

AWorld Compendium The Pesticide Manual incorporating The Agrochemicals Handbook (1994). European Directory of Agrochemical Products, Editor: Clive Tomlin,Tenth Edition, Barakat, A.O. (2004). Assessment of persistent toxic substances in the environment of Egypt. Environment International, 30: 309– 322.

Beg, M.A.A.; S.N. Mahmood and A.H.K. Yoysufzai (1992). Heavy metals pollution in the coastal environment of Karachi. Pak. J. Mar. Sci., 1(2), 117-133. (C.F. Chemical Abstract Vol. 119, 146164d).

Belden, J.B.; C.S. Hofelt and M.J. Lydy (2000). Analysis of multiple pesticides in urban storm water using solid-phase extraction. Arch. Environ. Contam. Toxicol., 38, 7-10.

EEC (1980). European Community, Drinking Water Directive (80/779), Brussles, Belgium.

El-Azab, Kadria, M. (1997). Effect of different polluted irrigation waters on soil and plants. M.Sc. Thesis, Fac. Of Agric., Kafr El-Sheikh. Tanta Univ., Egypt.

El-Nawawy, A.S. (1981). Impact of pesticides in Egypt on humans and farm animals. Proc. 4th Pesticides Conf., Tanta Univ., 1-11.

EMOH (1995). Egyptian Ministry of Health Regulation Report No 108, (In Arabic).

Gaber, H. N.; S. M. Abd-Allah and F. M. Kishk. (2003). Sustainable land and water resources management in Egypt: A Coneptualization of a holistic agroecosystem approach. Alex. J. Agric. Res. 48(3): In Press.

Gangesh S.; A. Kumar; M. Bhanti; P.E. SJoseph and A. Taneja (2006). Organochlorine pesticide contaminations of ground water in the city of Hyderabad. Environ. International, 32: 244-247.

Hamed, S.A. (1997). Toxicological studies on some side effects on some environmental pollutants. M. Sc. Thesis, Tanta Univ., Egypt.

Heba, M.I.A. (2003). Remediation of some heavy metal polluted soils in Nile Delta Egypt. M.Sc. Thesis, Fac. Of Agric. Tanta Univ., Egypt.

Hendriks, A.J.; W.C. Ma; J.J. Brouns; E.M. de Ruiter-Dijkman and R. Gast (1995). Modelling and monitoring organochlorine and heavy metals accumulation in soils, earthworms and shrews in Rhine-Delta floodplains. Arch. Environ. Toxicol., 29, 115-127.

Hobbelen, P.H.F.; J.E. Koolhaas and C.A.M. Gestel (2004). Risk assessment of heavy metal pollution for detritivores in flood plain soils in the biesbosch, the Netherlands, taking Bioavilability into account. Environmental Pollution, 129, 409-419.

IOMC. (1995). Persistent organic pollutants assessment report, Inter-Organization. Programme for the sound management of chemicals (IOMC).Geneva, Switzerland: WHO, 1995, 2002.

Kanja, L.W.; J.U. Skaare; I. Nafstaol; C.K. Maitai and P. Lokken (1986). Organochlorine pesticides in human milk from different areas of Kenga, 1983-1985. J. Toxicol. Environ. Health., 19:449-464.

Kanja, L.W.; J.U. Skaare; S.B.O. Ojwang and K. Maitait (1992). Comparison of organochlorine pesticide residues in maternal adipose tissue, maternal blood, cord blood and human milk from mother infant pairs. Arch. Environ. Contam. Toxicol., 22, 21-24.

Lommel, A.; H. Kruse; E. Muller and O. Wassermann (1992). Organochlorine pesticides, octachlorostyrene and mercury in the blood of Elb River rsidents. Germany, Arch. Environ. Contam. Toxicol., 22: 19-20.

Mansour, S.A. and Messeha, S.S. (2001). Ecotoxicological studies. 2. Distribution of toxic heavy metals in water and sediment of Lake Qarun, Egypt. J. Egypt. Acad. Soc. Environ. Dev., 2 (1): 57–82.

Ministry of Agriculture Report (1980-1995). Annual Report of Plant Protection Department, Ministry of Agriculture, Egypt (In Arabic).

Mireles, A.; C. Solis; E. Andrade; M. Lagunas-Solar; C. Pina and R.G. Flocchini (2004). Heavy metal accumulation in plants and soil irrigated with wastewater from Mexico City. Nuclear Instruments and Methods in physics research B, In press. WWW. Elsevier. Com, From ScienceDirect. Com.

Nag, J.K. and A.K. Das (1993). Trace metal levels in drinking water scenario of Hooghly district. Indian J. Environ. Prot., 13(1), 20-4. (C.F. Chemical Abstract. Vol 119, 188064 b).

Pathak, S.P.; S. Kumar; P.W. Ramteke; R.C. Murthy; K.P. Singh; J.W. Bhattacherjee and P.K. Ray (1992): Riverine pollution in some northern eastern states of India. Environ. Moint. Assess., 22 (3), 227-263.

Prakash, O.; M. suar; V. Raina; C. Dogra; R. Pal and R. Lal (2004). Residues of hexachlorocyclohexane isomers in soil and water samples from Delhi and adjoining areas. Current Science, 87, No. (1), 10 July 2004.

Rossel, M.G.; J. Obiols; M.J. berenguer; X. Guardino; F. Lopez and J. Brosa (1993). Determination of chlorinated insecticides in blood samples of agricultural workers. J. Chromatography, 655: 151-154.

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. J. Environment International, 31: 113– 120.

Shaheen, S.M.N. (2005). Pedochemical Studies on some Egyptian soils under different depositional environments in relation to their heavy metals content, pollution and remediation. M.Sc. Thesis, Agric. Kafr El-Sheikh, Tanta. Univ., Egypt.

Technical Recommendation from Agricultural Pest Control (2001). Ministry of Agriculture Report, Egypt.

World Health Organization (1992). Alpha- and beta-hexachlorocyclohexanes, Report, Geneva, (Environmental Health Criteria; 123), First draft prepared by Dr. G.J. Van Esch, Bilthoven, The Netherlands

World Health Organization (1993). Guidelines for drinking water quality, 2nd, 1, WHO, Geneva, Swizerland.

J. Pest Cont. & Environ. Sci. 15 (1): 21 – 41 (2007).

الملخص العربي

رصد بعض الملوثات الزراعية في المياه السطحية في محافظة كفر الشيخ (جمهورية مصر العربية)

احمد حافظ مسعود، إسماعيل إبراهيم الفخراني، محمد عبد الرازق صالح عبد الرازق
قسم المبيدات، كلية الزراعة، جامعة كفر الشيخ، مصر.

تسبب بعض الملوثات الزراعية مثل المبيدات والمعادن الثقيلة مشاكل عديدة في البيئة المائية ويرجع ذلك لتأثيرها علي صفة الماء والكائنات الموجودة فيه مثل السمك. وتعتبر محافظة كفر الشيخ من أهم المناطق لزراعة الأرز وإنتاج السمك لذا كان من الضروري حماية البيئة من هذه الملوثات. ومن هنا كانت هذه الدراسة التي تم فيها رصد متبقيات المبيدات والمعادن الثقيلة في مياه الري والصرف في مناطق مختلفة من محافظة كفر الشيخ مثل مراكز كفر الشيخ وسيدي سالم والرياض وبيلا والحامول وبلطيم. ولدراسة متبقيات هذه المبيدات في المياه السطحية تم تجميع عينات في شتاء عام 2004م، وصيف 2005م من اثني عشر عينة كالتالي: خمسة عينات من مياه الري من ثلاثة مواقع (عينتين من ترعة بحر تيرة وعينة من ترعة النيل وعينتين من ترعة ميت يزيد) وسبعة مواقع من مياه الصرف عينة من كل موقع (مصرف الغربية الرئيس- مصرف ناصر- مصرف حفير شهاب الدين- مصرف الشركة- مصرف نمره 7- مصرف نمره 8- مصرف الوسطاني). وتم استخلاص هذه العينات بواسطة عمود C_{18} والذي يستعمل مرة واحدة لكل عينة ثم تحليلها بأجهزة التحليل الكروماتوجرافي (G.C-ECD, G.C-FPD, HPLC-U.V) وأوضحت النتائج وجود سبعة وعشرون مبيد تتبع ثلاث مجاميع من المبيدات وهي كالتالي: (1) المبيدات الكلورونية العضوية ومنها (ألدرين والدايلدرين- جاما لندين- بيتا لندين- دلتا لندين- ألفا لندين- بارا، بارا. د. د. ت- بارا، بارا. د. د. أي- بارا، بارا. د. د. د- هتباكلور- هبتاكلور أيبوكسيد- جاما كلوردان). (2) المبيدات الفوسفورية العضوية ومنها (داى كلورفوس- إيثوبروفوس- كادوسافوس- ديازينون- كلوروبيروفوس ميثايل- بيريميفوس ميثايل- دايميثويت- كلوروبيروفوس- فينثويت- فينيتروثيون- بروثيوفوس- بروفينوفوس- إيثيون). (3) المبيدات الكاربماتية ومنها (ميثوميل- أوكساميل). وقد وجدت بعض هذه المبيدات بتركيزات عالية عن الحدود المسموح بها (MRL) مثل بارا، بارا د. د. ت والديازينون وأيضاً تكرر وجودها في أكثر من منطقة خاصة عند مناطق خلط مياه المصارف بالترع وذلك في فصل الصيف ونظراً لثباتها العالي وترسيبها في قيعان المصارف والترع الزراعية. تم أخذ عينات من سبعة عشر موقعاً ثمانية مواقع من الترع وهى (خمسة مواقع من ترعة بحر تيرة وموقعين من ترعة ميت يزيد وموقع من ترعة النيل) وتسعة مواقع من المصارف موقع من كل مصرف وهى (مصرف الغربية الرئيسي ومصرف ناصر ومصرف حفير شهاب الدين ومصرف الشركة ومصرف نمرة 7 ومصر نمرة 8 ومصر الوسطانى). وتم تحليل تسعة من العناصر الثقيلة ومعرفة مستوى هذه العناصر بواسطة (جهاز الامتصاص الذريAAS) في مياه الترع والمصارف وهى (الحديد-النحاس- الكروم- الكوبالت- الكادميوم- النيكل- الزنك- المنجيز- الرصاص). وقد وجد أن (الكروم- الكوبالت -الرصاص) كانت اعلي من الحدود المسموح بها، ويليها بمستوي اقل الزنك والمنجنيز والكادميوم أما (النحاس والحديد والنيكل) فكانت في مستوي اقل من الحدود المسموح بها طبقا لحدود منظمة الصحة العالمية.