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Impact of Chlorpyrifos on Mosquito Larvae as Bioindicator in El-Beheira Governorate, Egypt.

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Abstract

Pesticides are the major source of concern as water pollutants. Persistent organochlorines can accumulate in food chains. Chlorpyrifos (O,O -diethyl O -(3,5,6-trichloro-2-pyridinyl) phosphorothioate; CAS No. 2921-88-2; CPY). CPY is a widely used organophosphorus insecticide that is available in a granular formulation for treatment in soil. Pesticides are used to control a wide range of pests including Mosquitoes. Mosquito borne diseases infect millions of people every year globally. The aim of current study was to screen the fresh water pollutants, water quality parameter in irrigation water from El Mahmodia stream, El-Beheira Governorate, Egypt and to determine the adverse effects of Chlorpyrifos on the larvae of Culex mosquito larvae as bio-indicator. The LC_{95} of Chloropyrifos insecticide was 6331.30 at 24h and increased to 230506.4 after 48h of exposure to the Chloropyrifos insecticide. It is noted that the effect of the exposure time of Chloropyrifos insecticide on the LC_{50}, LC_{25} and LC_{95} values had a synergistic interaction with time, as it increased after 48h of exposure when compared to 24 h of exposure. The 0.09 ppm concentration of Chloropyrifos had no effect on the second instar Culex larvae, as there is no mortality over time; the same result is also with the control 0 ppm. There is no effect after 72, 96h of exposure of the population to the detected insecticide. This study concerns with studying the pollutants along El Mahmodia stream in El Beheira governorate in Abo Homs city with its abundance during the four seasons (2016-2017), as well as studding the physicochemical parameters in it. Another concern of this study is estimating the effect of one of this pesticides (Chloropyrifos) insecticide on the second instar Culex mosquito larvae, determining the lethal concentration of this insecticide on the Culex larvae. Along the study area, pesticides are used within a high ratio on the agriculture scale with its four main categories organophosphates, organochlorine, pyrthoid and carbamates. Organophosphates and organochlorine are used at a wide range. Pollutants measuring achieved by using GC-MS as water samples collected seasonally and analyzed, there is a big number of Pollutants which was found as well as other compounds which are banned, such as DDT. The physicochemical parameters Turbidity, COD, BOD in El Mahmodia stream exceeded the desirable limits of (Egyptian Law 48/1982), (WHO, 1993) and (FAO, 1985) although the other parameters as EC, PH, DO,TDS TSS are to be within the permeable limits. HCO_3, NH_4. Cu also was found to exceed the desirable limits while, Pb, Mn, Fe and Cd within the permeable limits. Chloropyrfos as an organophosphate pesticide used in the present study which was found with 0.09 mg/l in the

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Introduction

Persistent organochlorines can accumulate in food chains. This bioaccumulation has been well documented with the pesticide dichlorodiphenyltrichloroethane (DDT) [1, 2, 3]. Organochlorine pesticides are washed into the aquatic ecosystem by water runoff and soil erosion. Pesticides can also drift during application and contaminate aquatic systems samples [4, 5]. Wild birds and mammals are damaged by pesticides and these animals are bio indicator species [6, 7, 8]. Organophosphate pesticides have been the insecticides most commonly used by professional pest control bodies [9]. Chlorpyrifos (O,O - diethyl O -(3,5,6-trichloro-2-pyridinyl) phosphorothioate; CAS No. 2921-88-2; CPY). CPY is a widely used organophosphorus insecticide that is available in a granular formulation for treatment in soil [10]. Pesticides are used to control wide range of pests including Mosquitoes. Mosquito borne diseases infect over 7000000 people every year globally, being prevalent in more than 100 countries across the world [11, 12-14]. WHO has declared mosquitoes as "public enemy number one". Worldwide, malaria causes one to two million deaths annually. Lymphatic filariasis has been reported to affect at million people in 73 countries including Africa and Pacific Islands [15]. Mosquitoes serve as vectors of life threatening diseases such as malaria [16, 12, 5]. The current study aimed to monitor water pollutants (persistent organic, minerals and pesticides) and to assess the potential adverse effect of polluted water on the bio indicator insects; mosquitoes. The aim of the current study was to Screen the pollutants, water quality parameters and mineral content in irrigation water from El Mahmodia stream, El-Beheira Governorate. Determine the adverse effects of some the detected-pesticides (Chlorpyrifos) on the larvae of second instar Culex mosquito larvae as a bio-indicator. Water requirements of different sectors increase rapidly with time due to rapid population increase, ambitious agricultural expansion [17]. Quality of Nile water worsened dramatically in the past few years [18, 2, 3]. It is anticipated that the dilution capacity of the River Nile system will diminish as the program to expand irrigated agriculture moves forward and the growth in industrial capacity increases the volume of pollutants discharged into the Nile [19, 12, 5]. The major pollution sources of Nile and main canals are effluents from agricultural drains and treated or partially treated industrial and municipal wastewaters [20, 13, 14].

There are 76 drains discharging drainage water into Nile system with annual volume of about the half of the total drainage water [21]. Impact of this drainage water on Nile quality has been reported by several authors [18]. Statistics indicate that over one billion of the world population lack access to safe water, and nearly two billion lack safe sanitation worldwide [22, 7, 8]. A growing number of water related diseases such as diarrhea and lymphatic filariasis are responsible for the major health problems in the majority of rural and urban residents [23, 13, 14]. The quantities and quality of wastewater from agricultural lands are highly variable. The most important pollutants found in runoff from agricultural areas are sediments, animal wastes, plant nutrients in addition to domestic wastes [2, 3]. Water pollution sources, has become of public interest. Natural events and anthropogenic influences can affect the aquatic environment in many ways [12, 5]. Discharge of partially treated, industrial and domestic wastewater, leaching of pesticides and residues of fertilizers are the factors that affect the quality of water [19].Water pollution occurs when a body of water is adversely affected due to it is unfitting for its intended use [24, 3,7, 8].The aquatic environment is subjected to various types of pollutants which enter water bodies [25, 2]. Among the various pollutants, heavy metals are the most toxic, persistent and abundant pollutants that can accumulate in aquatic habitats [26, 13, 14].

Trace metals such as Zn, Cu and Fe play biochemical role in the life processes of all aquatic plants and animals. In the Egyptian irrigation system, the main source of Cu and Pb are industrial wastes, while that of Cd is the phosphatic fertilizers [27, 2, 3]. The most anthropogenic sources of metals are industrial sources as paints and petroleum contamination [28, 12, 5]. The agricultural drainage water contains pesticides [2, 3, 13, 14]. The physicochemical characteristics of the Nile water include temperature, turbidity, water electrical conductivity (EC), total suspended solids (TSS) and total dissolved solids (TDS), pH value, dissolved oxygen (DO), nutrients, biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), major anions and cations and heavy metals [2, 7, 8]. There are more than half a million tons of unused in several developing and transitional countries [29]. Obsolete pesticides have accumulated in almost every developing country or economy in transition over the past several decades [30]. The FAO is recording the inventories of Latin America [31, 2, 3]. It is difficult to estimate the exact quantities of obsolete pesticides because many of the products are very old and documentation is often lacking [32, 7, 8].

Chlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) were routinely used in large quantities for agricultural and industrial purposes [33, 2, 3]. Insecticides overuse led to several ecological drawbacks over the past years [34]. Mosquitoes of family Culicidae, are vectors for a number of mosquito borne infectious diseases [35] that are maintained in nature through the biological transmission by blood feeding mosquitoes to susceptible vertebrate hosts causing malaria and filariasis [36]. Mosquitoes are a major public health threat as they play a vital role in transmitting serious human diseases to million people annually [37]. *Culex pipiens* is a worldwide mosquito transmitting many dangerous diseases as filarial worms and avian malaria [38]. With the emergence of *C pipiens* resistance to many insecticides, control is becoming more difficult [39]. The control of mosquito is becoming challenging because climate change and global trade favor the spread of invasive mosquito species [40], and strongly increase the associated risk of vector borne diseases [41]. Most strategies for mosquito control are based on the use of insecticides [42] and developing resistance [43]. Treated populations can recover after application of the insecticide. Vector control is by far the most successful method for reducing incidences of mosquito borne diseases [6]. The discovery of the subsequent development of organochlorines, organophosphates and pyrethroids suppressed natural product research, as the problem for insect control were thought be solved [44, 2, 3,7 8].

Material and Methods

Water samples were taken from El Mahmodia stream 31° 06' 16" N 30° 18' 52" E. Water samples (2.5 L) were collected in clean glass bottles at water surface and 50 cm below water surface. Water samples were collected during the period of September 2016 to August 2017 (samples were taken seasonally); [45]. The four sites were chosen to represent different regions along El Mahmodia stream. Water samples were taken (about 20 cm) below the water surface to avoid floating matter. Determination of Zn, Cu, Fe, Mn, PO_4, NO_3, NH_4, HCO_3, K, Na, Ca, Cl, Pb and Cd in the streams water were carried out according to (APHA, 1995). Field instruments (pH and conductivity) were measured in situ [46]. Water temperatures were measured in situ using a calibrated thermometer [46]. Turbidity test determined by Turbidity meter type WTW TurpSS0 calibrated using 0, 10 and 1000 Unit (NTU) [46]. Electric conductivity (EC); samples were measured at 25°C as a standard temperature using ATC bench electric conductivity meters, Jenway, model 4310 [46]. Total dissolved solids (TDS); samples were measured at 25°C as a standard temperature using ATC bench electric conductivity meters, Jenway, model 4310 [46]. Turbidity was measured using the Turbid meter WTW Turb model 550 [46]. The Dissolved oxygen (DO) was measured using WTW Model 315i electronics was used to determine the dissolved oxygen value [46]. Biological oxygen demand (BOD) was determined using WTW-TS-type 606/4-i BOD [46]. After digestion, COD is determined by using spectrophotometer PF-11 Viso Colour Model Nanocolour Macherey-Nagel (MN) [46].

Ammonia (NH_3) measured using Kjeldahl closed system model Gerhardt Vabodest 10S according to [47]. Nitrate (NO_3) was determined in water samples by using Kjeldhal closed system model Gerhardt Vabodest 10S according to [47]. Chloride was determined by methods of [47]. Carbonates and bicarbonates were determined by using the methods of [47]. Calcium and magnesium were determined according to [46]. Phosphate was determined according to [47] by using spectrophotometer Model 6405. Sodium was determined using Sherwood Flame Photometer Model 410 [46]. Potassium was determined using Sherwood Flame Photometer Model 410 [46].

Heavy metal ions were measured by using the Atomic Absorption spectrophotometer Model THERMO SCIENTIFIC ICE 3000 series AAS with hollow cathode lamp for each element being measured (Cu, Pb, Zn, Cd and Fe) according to [48]. Microbiological examination (MPN) was carried out according to [47], using Mac Conky broth w/Natural Red (HIMEDIA M007) medium.

GC-MS analysis of water: Extraction of water samples using Empore disc technology according to EPA 3535 [49] with little modification was used to extract pesticide residues from water [49]. Instrumentation analysis of pollutant residues in water Extracts of water (2 µl) were analyzed utilizing a GC-MS. The GC-MS was controlled by a computer system which has EI-MS libraries (Willey spectral library of more than 140000 compounds). The carrier gas was at a constant flow rate of 1.1 ml/min. The target compounds were identified by their full scan mass spectra and retention time using the total ion current as a monitor to give a Total Ion Chromatogram (TIC).

Insecticide

The percentage of 48% EC chlorpyrifos (devagro kimya tarim san vetic Torkey) was used to determine the lethal concentration LC_{25}, LC_{50} and LC_{95} against Culex larvae.

Mosquitoes culture and rearing: Mosquitoes culture brought from Alexandria University faculty of Agriculture and accommodate for (2) weeks in laboratory.

Bioassay of Detected Pollutant in Water

The mosquito larvae were exposed to a wide range of tested concentrations to find out the activity range of the materials under test. After determining the mortality of larvae in this wide range of concentrations, a range of 5 concentrations, yielding between 10% and 95% mortality in 24 h or 48 h is used to determine LC_{50} and LC_{95} values. Batches of 20 insects at the second instar larvae were transferred by means of droppers to Petri dish each containing 20 ml of water. Small, unhealthy or damaged larvae were removed. The appropriate volume of dilution is added (20 ml) water to Petri dish to obtain the desired target dosage, starting with the 100, 10, 1, 0.1, 0.09 ppm concentration. Five replicates were set up for each concentration and an equal number of controls (5 replicates) are set up simultaneously with tap water. After 24 h exposure, larval mortality was recorded. For slow acting insecticides, 48 h reading was required. Moribund larvae are counted and added to dead larvae for percentage mortality. Dead larvae are those that cannot be induced to move when they probed with a needle in the siphon or the cervical region. Moribund larvae are those incapable of rising to the surface or not showing the characteristic diving reaction when the water is disturbed. The results are recorded to detect the LC_{25}, LC_{50} and LC_{95} values. The form will accommodate sex separate tests of four concentrations, each of five replicate.

Statistical Analysis

Analyzing the data occurred by using SAS and LDP Line The first analysis examined the abundance of the physicochemical parameters and heavy metals in the water samples which collected from EL Mahmodia stream, measuring its mean ,SD and 95% SD of it. The second analysis examined the lethal concentration LC_{25}, LC_{50}, LC_{95} and X^2 of Chlorpyrifos insecticide on Culex larvae.

Results

Physicochemical determination of water samples were collected in August 2017 from four locations repeats along El Mahmodia stream, Water samples were taken (about 20 cm) below the water surface to avoid floating matter. The Electrical Conductivity (Ec) was determined with a mean of 0.50 mg/l and ± 0.01 for SD (Table 1). From Fig 1, it is detected that the Electrical Conductivity has a significance differences (p

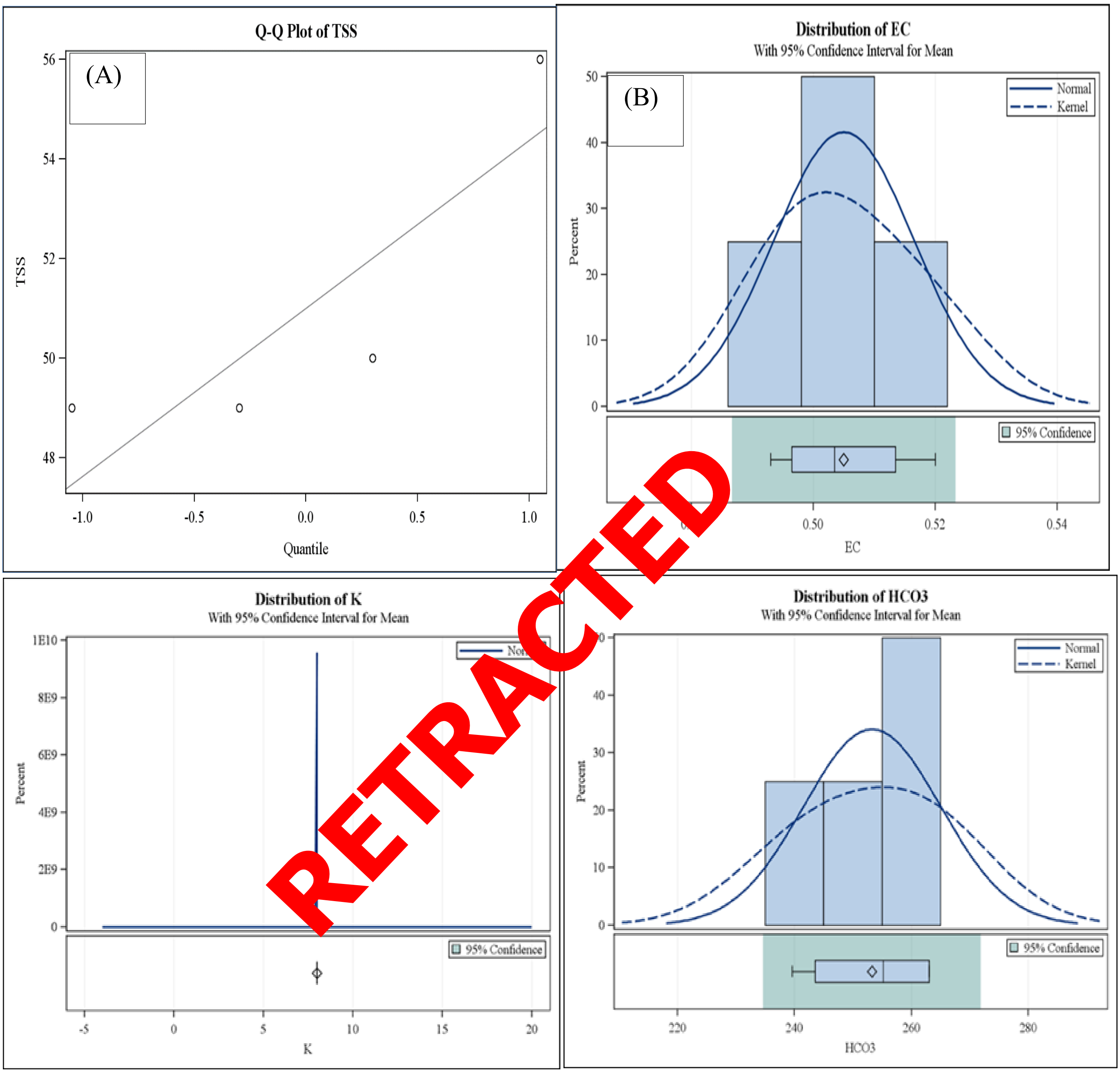

Figure 1. (A) Distribution of EC with 95%confidence Interval for Mean, (B) Q-Q Plot of TSS, (C) Distribution of HCO_3 with 95% confidence Interval for Mean, (D) Distribution of K with 95% confidence Interval for Mean.

<0.05). It was also noted that the mean of the pH was 7.68 mg/l, ±0.05 for SD (Table 3). The Total Dissolved Solids (TDS) recorded with a mean of 249 mg/l, SD was ±14.16. Turbidity Also recorded with the mean of 9.17 mg/l, SD of ±2.66 (Table 1(.The Total Suspended Solids (TSS) recorded with a mean of 50 mg/l, SD was ±3.36, it is detected that the Total suspended solids has a significance differences (p <0.05).

The total solids (TS) were determined with the mean of 293.3mg/l, ±27.83 for SD. The Dissolved Oxygen (DO) detected with 4.35 mg/l for its mean, SD value was ±0.1 (Table 1(.The mean the Biological Oxygen Demand (BOD) was 23.75 mg/l, ±2.5 for SD, the BOD has a significance differences (p <0.05(.It is detected also the Chemical Oxygen Demand (COD) with a mean of 24.75 mg/l SD value was ±3.86. The Microbiological examination (MPN) determined with 12075 mg/l for its mean ±3379.7 for SD (Table 1) ,it is detected with 49.91 mg/l for its mean, SD value was 0 (Table 2) (Fig 2)

The potassium (K) determined with 7.99 mg/l for mean value. The calcium (Ca) means detected with 31.8 mg/l, SD value was±4.54. 16.38 mg/l is the value of magnesium (Mg) mean which recorded, SD value was ±5.30 (Table 2(.The chloride (Cl) mean was 56.40 mg/l, with SD ±3.28. The detectable mean of bicarbonate alkalinity (HCO_3) was 253.3 mg/l, with SD ±11.71 HCO_3, as shown that the HCO_3 has a significance differences (p <0.05(.Ammonia (NH_4) detected with a mean of 1.42 mg/l, SD value was ±0.93. NO_3 (Nitrate) mean value was 5.89 mg/l, with SD ±0.93. Phosphorus (PO_4) detected with 0.01 mg/l for its mean, SD value was ±0.004. Iron (Fe) detected with a mean value 0.65 mg/l, with SD ±0.24 (Table 2(. Copper (Cu) detected with a mean of 10.91 mg/l, SD value was ±2.59. Manganese (Mn) detected with a mean value 0.09 mg/l, SD value was ±0.01. 0.002 mg/l was the mean value of cadmium (Cd), with SD ±0.001(Table 2).

GC-Ms Analysis

Extraction Efficiency (Recovery tests): For assessment the efficiency of SPE approach as extraction tools for extraction the pesticide residues in water samples, the average percentage of recoveries (%Rec.) from fortified blank samples of water were determined and the percent relative standard deviation (%RSD) for recoveries were calculated. For that purpose a laboratory water blank were fortified with the mixture of OPCs to reach the final concentration of 0.1 ug and 1ug/l. Fortified water samples were extracted and analyzed as previously mentioned. Average percentage of recoveries (%Rec.) were determined and the percent relative standard deviation (%RSD) for recoveries were calculated. All data of residue analysis were corrected according to these obtained recovery percentage values. (Table 3, 4)

As shown in Table (3), Decamethylcyclopentasiloxane, 1-(2-Acetoxyethyl)-3,6-diazahomoadamantan-9-one oxime, 2',6'-Dihydroxyacetophenone, 4H-1-Benzopyran-4-one, 2-(3,4-dimethoxyphenyl)-3,7-dimethoxy - are a detected compounds repeated in autumn and winter seasons together. Although Phthalic acid, butyl tetradecyl ester, Dasycarpidan-1-methanol, acetate (ester), n-Hexadecanoic acid, Are a detected compounds found in autumn, winter and spring seasons together. 1,2-Benzenedicarboxylic acid, diethyl ester is a detected compound found in autumn, winter and summer season together. Nonadecane, Phenol, p-tert-butyl-, cis-13-Eicosenoic acid, were detected compounds repeated in spring and summer together. The detected compounds in autumn stream water samples were: 2-Propanol, 1-(2-methoxy-1-methylethoxy)- 1,3-Hexanediol, 2-ethyl-1-Propene, 1-(methylthio)-, (E)-1-Propene, 1-(methylthio)-, (Z)- Hydrazine, 1,1-diethyl-3-Hexene, 1-[1-ethoxyethoxy]-, (E)-2,7-Anhydro-l-galacto-heptulofuranose, trans-2-undecenoic acid, Silane, ethenyltrimethyl-1,3-Dimethyl-4,8-dioxatricyclo[5.1.0.0(3,5)]octane-2,6-diol, Sulfurous acid, isohexyl 2-propyl ester, Sulfurous acid, butyl isohexyl ester, Sulfurous acid, butyl hexyl ester, 3-Heptanol, 2,4-dimethyl-, 3-Heptanol, 2,6-dimethyl.

The detected compounds in winter stream water samples are: Decamethylcyclopentasiloxane, 1-(2-Acetoxyethyl)-3,6-diazahomoadamantan-9-one oxime, (2-[(Aminoacetyl)amino]-4-methylpentanoyl)amino) acetic acid, 2',6'-Dihydroxyacetophenone, bis (trimethylsilyl) ether, 4H-1-Benzopyran-4-one, 2-(3,4-dimethoxyphenyl)-3,7-dimethoxy-, 11,16-Bis (acetyloxy)-3,20-dioxopregn-4-en-21-yl acetate, 9,12-Octadecadienoic acid (Z,Z)-, 2,3-bis[(trimethylsilyl)

Table 1. Detected level of water samples physicochemical compared to the reference values

Parameter	Mean	SD	95% Confidence Limits		Reference values	Ref Association
EC	0.50	± 0.01	0.006	0.043	0.31–1.87mS cm^{-1}	A
pH	7.68	±0.05	0.03	0.1985	7.94–8.50 6-8.5 6.5 - 8.4	B C A
TDS	249	±14.16	8.02	52.81	500 mg/l	B
Turbidity	9.17	±2.66	1.51	9.94	5 NTU	D
TSS	51	±3.36	1.90	12.552	<100	B
TS	293.3	±27.83	15.76	103.8	-	-
DO	4.35	±0.1	0.05	0.3729	[illegible]	B
BOD	23.75	±2.5	1.41	9.3214	<6-10 mg/l.	B
COD	24.75	±3.86	2.18	14.4004	<10-15 mg/l	B
MPN	12075	±3379.7	1914.6	1260[illegible]4	5000/100cm^3	B

EC: Electrical Conductivity , TDS: Total Dissolved Solids , TSS: Total Suspended Solids , TS :total solids , DO: Dissolved Oxygen , BOD: Biological Oxygen Demand, COD: Chemical Oxygen Demand, MPN : Microbiological examination. FID: Fold of increase or decrease = (detected value – reference value)/ reference value * 100. * A,

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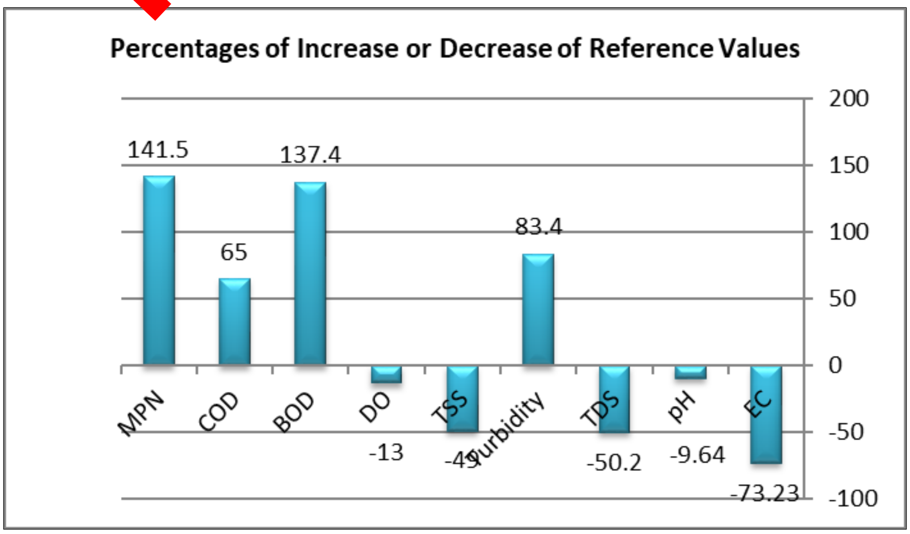

Figure 2. Percentages of Increase or Decrease of Reference Values

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Table 2. Detected level of water samples heavy metal compared to the reference values

Parameter	Mean	SD	95% CL SD		Reference	Ref Association
Na	49.91	0	.	.	200mg/l	C
K	7.99	0	.	.	12 mg/l	E
Ca	31.8	±4.54	2.57	16.93	-	-
Mg	16.38	±5.30	3.004	19.77	100mg/l	E
Cl	56.40	±3.28	1.86	12.24	(less than 200 mg/l)	B, C
HCO_3	253.3	±11.71	6.63	43.66	<200 mg/l	B
NH_4	1.42	±0.14	0.08	0.55	<0.5	B
NO_3	5.89	±0.93	0.53	3.48	(not exceed 45 mg/l).	B
PO_4	0.01	±0.004	0.002	0.01	[illegible] mg/l	B
Fe	0.65	±0.24	0.12	0.12	(<[illegible]g/l)	B, C
Cu	10.91	±2.59	1.46	9.6[illegible]	(<1.0 mg/l)	B,C,F
Mn	0.09	±0.01	0.007	0.[illegible]3	(<0.5 mg/l)	B, C
Cd	0.002	±0.001	0.007	[illegible]04	0.003mg/l	C

(Na): sodium, (K): potassium, (Ca): calcium, (Mg): magnesium, (HCO_3):bicarbonate alkalinity, (NH_4):Ammonia, (PO_4): Phosphorus, (NO_3):Nitrate, (Fe): Iron, (Cu): Copper, Manganese, (Cd): cadmium. A, FAO 1985 .,* B, law 48/1982,* C, WHO (1993) ,* D, the guide-

Table 3. Average recovery percentages (Rec. %) and relative standard deviation (RSD) for pesticides extracted from spiked water samples.

OCPs	(Rec. %) ± RSD 1ug/l
Chlorpyrifos-methyl	99.3 ± 4.0
Heptachlor	92.8 ± 6.2
Dieldrin	99.1 ± 1.2
p,p-DDD	95.6 ± 1.5
p,p-DDT	102.3 ± 4.0
Methoxychlor	99.3 ± 4.0

Table 4. Detected compounds repeated in the four seasons

N	Rt	COMPOUND NAME	A	W	Sp	Su
1	5.37	Decamethylcyclopentasiloxane	√	√		
2	5.65	1-(2-Acetoxyethyl)-3,6-diazahomoadamantan-9-one oxime	√	√		
3	5.76	Nonadecane			√	√
4	6.1	2',6'-Dihydroxyacetophenone, bis(trimethylsilyl) ether	√	√		
5	6.3	4H-1-Benzopyran-4-one,2-(3,4-dimethoxyphenyl)-3,7-dimethoxy-	√	√		
6	6.41	11,16-Bis(acetyloxy)-3,20-dioxopregn-4-en-21-yl acetate	√	√		
7	6.57	9,12-Octadecadienoic acid (Z,Z)-, 2,3-bis[(trimethylsilyl)oxy]propyl ester	√	√		
8	7.03	m-Dioxane, 5-(hexadecyloxy)-2-pentadecyl-, trans-	√	√		
9	7.13	Dodecamethylcyclohexasiloxane	√	√		
10	7.28	2-(9-Borabicyclo[3.3.1]non-9-yloxy)-3-([2-(9-borabicyclo[3.3.1] phenyl non-9-yloxy)ethyl]sulfanyl)propyl ether	√	√		
11	7.95	Sulfurous acid, butyl hexyl ester	√			√
12	8	1-Tridecene			√	√
13	8.04	5((LPregnane- 3,20 L diol, 14à,18à-[4-methyl-3-oxo-(1-oxa-4-azabutane -1,4-diyl)]-, diacetate	√	√		
14	8.21	2,7-Diphenyl-1,6-dioxopyridazino[4,5:2',3']pyrrolo[4',5'-d]pyridazine	√	√		
15	9.15	Phthalic acid, butyl tetradecyl ester	√	√	√	
16	10.05	Phenol, p-tert-butyl-			√	√
17	10.91	3-Hydroxyspirost-8-en-11-one	√	√		
18	11.1	Hexadecamethyl-cyclooctasioxane	√	√		
19	12.18	Dasycarpidan-1-methanol, acetate (ester)	√	√	√	
20	13.3	Phthalic acid, isobutyl octadecyl ester	√	√	√	
21	13.37	Phthalic acid, butyl 2-ethylbutyl ester	√	√		
22	14.24	n-Hexadecanoic acid	√	√	√	
23	14.32	1,2-Benzenedicarboxylic acid, dibutyl ester	√	√		√
24	15.95	Phenol, 3,5-bis(1,1-dimethylethyl)-	√		√	
25	17.89	1,2-Benzenedicarboxylic acid, butyl phenylmethyl ester	√	√		

26	18.18	2,3-Bis[(trimethylsilyl)oxy]propyl (9E,12E,15E)-9,12,15-octadecatrienoate	√	√		
27	19.83	6,9,12,15-Docosatetraenoic acid, methyl ester	√		√	
28	19.83	Fenretinide	√		√	√
29	20.45	Methyl((24-oxo-3,7,12 tris[(trimethylsilyl)oxy]cholan-24-yl) amino)acetate	√	√		
30	21.22	cis-13-Eicosenoic acid			√	√
31	21.44	Propanoic acid, 2-(3-acetoxy-4,4,14-trimethylandrost-8-en-17-yl)-	√	√		
32	22.08	Cyclopropaneoctanoic acid, 2-octyl-, methyl ester	√		√	
33	24	Estra-1,3,5(10)-trien-17β-ol	√		√	
34	25.59	Dihydroxanthin	√		√	
35	26.23	1-Hexadecanol, 2-methyl-	√		√	
36	26.5	Corynan-17-ol, 18,19-didehydro-10-methoxy-, acetate (ester)	√		√	
37	26.61	16-Octadecenoic acid, methyl ester	√		√	
38	27.06	Pentadecanoic acid, methyl ester	√		√	
39	27.12	1,2,4-Trioxolane-2-octanoic acid, 5-octyl-, methyl ester	√		√	
40	31.46	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16)-diepoxy-	√		√	
41	32.19	9,12,15-Octadecatrienoic acid, 2,3-bis[(trimethylsilyl)oxy] propyl ester, (Z,Z,Z)-	√		√	
42	32.52	1H-Cyclopropa[3,4]benz[1,2-e]azulene-5,7b,9,9a-tetrol, 1a,1b,4,4a,5,7a,8,9-octahydro-3-(hydroxymethyl)-1,1,6,	√		√	
43	33.24	Oleic acid, 3-(octadecyloxy)propyl ester	√		√	
44	33.88	Phthalic acid, di(2-propylpentyl) ester	√		√	
45	33.92	Bis(2-ethylhexyl) phthalate	√		√	√
46	34.41	Benzeneacetonitrile, α-[[4-(dimethylamino)-2,5-dimethoxyphenyl]methylene]-4-nitro-	√		√	
47	34.59	9-Desoxo-9-x-acetoxy-3,8,12-tri-O-acetylingol			√	√
48	35.05	Olean-12-ene-3,15,16,21,22,28-hexol, (3β,15α,16α,21β,22α)-	√		√	
49	35.21	Oleic acid, eicosyl ester	√		√	
50	36.81	Pregnane, 3,11,17,20,21-pentamethoxy-, (3α,5β,11β,17α,20β)-	√		√	

oxy]propyl ester m-Dioxane, 5-(hexadecyloxy)-2-pentadecyl-, trans-, Dodecamethylcyclohexasiloxane, 2-(9-Borabicyclo[3.3.1]non-9-yloxy) ([2-(9-borabicyclo [3.3.1]non-9yloxy)ethyl]sulfanyl)propyl phenyl ether. The detected compounds in Spring stream water samples are: Hexadecane, Octane, 2,4,6-trimethyl-, Dodecane, 2,7,10-trimethyl-, Decane, 2,4,6-trimethyl-, Undecane, Octane, 2,4,6-trimethyl-, Sulfurous acid, hexyl octyl ester Nonadecane, Ethane, hexachloro-, Hexachloroacetone. The detected compounds in Summer stream water samples are: 1-Butanamine, N-methyl-, Tetracosane, pentane, 3-methyle, Hexane, 1-chloro-, 2-methylpropene, pyrimidine, 1,4,5,6-tetrahydor-1,2-, 2-(Dimethylamino)-3-methyle-1-buten, 2, 5-pyrrolidinedione, 1-methyle, 1-octanamine, Cyclobutane,1,2-diethyl-,trans.

The side effects on the second instar mosquito larvae:

The present study had been undertaken in order to screen the pollutants, water quality parameter, and mineral content in irrigation water from El Mahmodia stream, El-Beheira Governorate, Determine the adverse effects of detected-pesticides (Chlorpyrifos) on the larvae of Culex mosquito larvae as a bio-indicator, with a serial number of Chloropyrifos concentration (100ppm, 10ppm, 1 ppm, 0.1ppm and 0.09 ppm), cross ponding to determine the lethal dose concentration LC_{25} ,LC_{50} and LC_{95} of cholropyrifos insecticide on Culex larvae. The treatment occurred by a serial concentration of Cholorpyrifos; 0, 0.09, 0.1,1,10,100 ppm applied on the mosquitoes larvae. After 24h, 48h mortality percentage was recorded as; at 24h, Cholorpyrifos killed 50% of the mosquito larvae population at 24.52 ppm. While at a longer time 48h, the 50% of the mosquito larvae population were killed by 755.65 ppm. After 24h, the detected concentration of Cholorpyrifos on 25% population mortality was 2.51 ppm, although it was 72.37 ppm after 48h of Cholorpyrifos exposure to 25% population of mosquitoes. It is detected that after 24h, the Cholorpyrifos killed 95% of the mosquito larvae population at 6331.30 ppm, while after 48h, the 95% of the mosquitoes larva population were killed by 230506.4 ppm. Table 5

Mortality percentage were calculated using LDP line software (Ehab soft, Egypt) according to Finney 1951.

The concentration of 0.09 ppm had no mortality on mosquito larvae in the second 48 h to 1h. The control also not had any mortality population on mosquito larvae. It was noted that after 72 h and 96 h there was no effect on mosquitoes larvae, as the equal number of inserted larvae were constant at the end of the experiment.

Discussion

Various physicochemical parameters like temperature, pH, DO, turbidity, BOD, nitrate, phosphate, TDS, and fecal coliform were determined by following the standard methods [46]. As water temperature increases, the rate of chemical reactions increases. The temperature affects the rate of growth and life cycles of most aquatic organisms. It is known to influence the pH, alkalinity, and DO concentration in the water. Water temperatures along El Mahmodia stream did not show any significant difference (at $p<0.05$). The temperature of El Mahmodia stream is higher than the limited values 31°C as mentioned by Ali *et al.* [55]. The turbidity is derived from silt, clay, and sand particles, while organic turbidity is composed of planktonic organisms and detritus. In the present study,

Table 5. lethal concentrations of Chlorpyrifos

Time	LC_{50}	Confidence Limits of LC_{50}		LC_{25}	LC_{95}	X^2
		Lower	Higher			
24	24.52	14.78	45.65	2.51	6331.30	1.41
48	755.65	258.10	5485.96	72.37	230506.4	1.43

Mortality percentage were calculated using LDP line software (Ehab soft, Egypt) according to Finney 1951.

turbidity value was reported as 9.17 NTU. The increasing of turbidity values is referred to increasing of suspended materials will reduce light penetration and restrict plant growth and hence food resources and habitat for organisms. Results of t-test showed that there was a significant difference ($p<0.05$) between the different sites. The results of turbidity values exceeded the permissible limits of law and the guidelines of WHO [53], (5 NTU) for drinking water. The stream water is valid for drinking after treatment and for irrigation. Electrical Conductivity (EC); the electric conductivity of the El Mahmodia stream water was determined as 0.50 m S/cm. The EC increases in El Mahmodia stream due to increasing of the dissolved ions resulted from the human activities especially agriculture. The measured EC values were within the permissible limits of the water used for irrigation of agricultural crop lands (0.31–1.87 mS cm–1) [50].

The suspended particles are the main source of turbidity in water. In this study, the suspended solid concentration in waters a long El Mahmodia stream was reported as 51 mS/cm. In this study, the suspended solid concentrations in waters along El Mahmodia stream within the permissible limits of law 48/1982 (<100 mg/l). Total Dissolved Solids (TDS) concentration in water samples collected along El Mahmodia stream was 249 mg/l. The TDS show an increase in its values at all recommended sites. In irrigation water, the salinity hazard is related to the high values of TDS. The total dissolved salts along the El Mahmodia stream were less than 450 mg/l and there was no restriction on using it for some susceptible crops [56]. Results of t-test showed that there was a significant difference ($p<0.05$) between different sites along El Mahmodia stream. Generally, all TDS values along the stream water were founded within the permissible limits of law 48/1982 (500 mg/l). The water stream receives fluxes of elements through natural processes by weathering of bed rocks. The basalts contain weak olivine and pyroxene minerals that are enriched in some elements such as Na, Li, Fe, Mn and Mg in addition to Si. These elements transport with water to increase the TDS of the streams, in contrast to the White Nile water that flows from the equatorial highlands enriched mainly in granites. The TDS of Lake Tana, source of the Blue Nile, varies from 50 to 138 mg/l with an average of 103 mg/l [57]. The major ions represented by TDS have been also significantly increased by anthropogenic contaminations. The average salinity of the Nile River at Cairo ranges from 175 to 680 mg/l with an average of 261 mg/l [58]. The pH is an important limiting chemical factor for aquatic life which may affect the aquatic organisms' biochemical reactions. The severe changes of pH of the water may cause a harmful or even lethal effect on aquatic organisms and consequently affect the animal and human health. Water streams have pH ranging, between 6 and 9, and any changes in this range in pH can affect life forms in aquatic systems [59]. In the present study the pH of the stream water was 7.68. The lowering of pH value of El Mahmodia stream that appear from drainage water may be attributed to greater input of organic matter where the high organic matter led to decrease in pH values [52]. The increase of pH values at the streams water is a result of photosynthesis [2, 3, 12, 5]. The unpolluted streams normally show a near neutral or slightly alkaline pH. The stream has pH values within the permissible limits of law 48/1982 (7.94–8.50) and are not harmful for aquatic life and irrigation, where the pH of most natural water ranges between 6 and 8.5 [51]. The range of normal pH for irrigation water is from 6.5 to 8.4 [50]. Dissolved oxygen is essential for aquatic life specially fish and other aquatic species require oxygen. Dissolved oxygen allows aerobic bacteria to degrade a wide variety of organic matter and oxidize inorganic salts. The concentration of DO along the stream was 4.35 (Table 1). The decrease of DO may be attributed to the consumption of DO by respiration of phytoplankton, aquatic plants, and fish, and decay of the aerobic bacteria [60]. Dissolved oxygen value was greatly affected by pollution load where the lowest DO is recorded at all sites, and the excessive effluent discharge of pollution with high load of organic matter into the two stream leads to deoxygenating of water. Waste discharges that are characterized by high inorganic matter and nutrients can lead to decreases in DO concentrations as a result of the increased microbial activity (respiration) occurring during the degradation of the organic matter [61, 2, 3, 62] Radwan, 2014, 2016, 2018).The concentration of dissolved oxygen (DO) in stream water was below the permitted limit in Egypt >5 (Egyptian Law 48/1982).

Oxygen concentration in water is very important for fish. It is worth mentioning that unpolluted waters typically have BOD values of 2 mg/l or less, whereas those receiving wastewater may have values up to 10 mg/l or more, particularly near to the point of wastewater discharge [52]. BOD in this study, recorded with increased Values 23.75 mg/l at El Mahmodia stream. There was an increase in BOD concentration at stream water (Table 1). The values of BOD exceeded the desirable limits of (Egyptian Law 48/1982) [63] which was<6-10 mg/l. The high BOD values indicate excessive export of biodegradable organic matter increasing the de-oxygenation of water to the level where fish and other aquatic life cannot survive [65, 12, 5, 13, 14]. The COD is widely used as a measure of the susceptibility to oxidation of the organic and inorganic materials present in water bodies and in the effluents resulting from sewage and industrial plants [66, 5, 12, 7, 8]. The COD in our study was 24.75 mg/l. The values of COD exceeded the desirable limits of [63] which was<10-15 mg/l. The COD high values indicate excessive export of biodegradable organic matter increasing the de-oxygenation of water to the level where fish and other aquatic life cannot survive [65]. Fecal pollution is a major concern for many rivers where it can originate from human sources and nonhuman sources. Fecal coliform can be used as indicator for water pollution and hence for water quality measure [67]. The fecal coliform was recorded with 12075mg/l. The high value of MPN, where the high levels of organic pollution exist, the values of MPN exceeded the desirable limits of (Egyptian Law 48/1982) which was 5000/100cm^3. The increase of nutrients, ammonia and phosphates, is generally indicative of diffuse pollution (agriculture and septic tanks) and industrial wastewater treatment plants. Nutrients are considered as essential elements needed to the growth and reproduction of plants and animals. Nitrogen compounds occur as nitrate, nitrite, ammonia and organic nitrogen. Ammonia was measured in water samples collected from stream with 5.89 mg/l. Its concentrations were recorded above the detection limit of > 0.01 mg/l. Natural sources of nitrate in surface waters are the interaction with igneous rocks, land drainage, plant and animal debris [56, 2, 3, 62]. Determination of nitrate and nitrite in rivers gives a general indication of the nutrient status and level of organic pollution. The decrease of nitrate along the stream water may be related to the presence of denitrifying bacteria or related to biological uptake. In the study area along the El Mahmodia stream, the nitrate concentrations were found to be within the permissible limits of law 48/1982 (not exceed 45 mg/l). As the World Health Organization [68] recommended maximum limit for drinking water is 10 mg/l NO_3-N, waters with higher nitrate concentrations represent a significant health risk. Comparing the results of nitrate of the stream water with FAO guidelines (5 mg/l N), it was found that there is a restriction on its use for sensitive crops.

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The ammonia NH_3 concentration in stream water was 1.42mg/l, the concentrations exceed the desirable Limits <0.5 (Egyptian Law (48/1982). These high values may be attributed to the increased de nitrification in water, when the oxygen concentration is low. The total alkalinity (HCO_3 concentrations) in water samples was 253.3 mg/l. The concentrations of HCO_3 concentrations was high that can be attributed to the decomposition in the dead phytoplankton leading to the release of CO_2 dissolving to water in the form of HCO_3. The concentration of HCO_3 measured at El Mahmodia stream exceeds the permissible limits of Egyptian Law (48/1982) which was<200 mg/l. Phosphorus is an essential nutrient element for living organisms and exists in water bodies as both dissolved and particulate forms. Natural sources of phosphorus are mainly derived from weathering processes of phosphorus bearing rocks and the decomposition of organic matter [52, 2, 3, 62]. Phosphorus concentration in stream water was 0.01 mg/l. The stream has Total Phosphorus values within the permissible limits of law 48/1982 (1 mg/l). The most common major cations in the study area are Ca^{2+}, Na^+, Mg^{2+}, and K^+. Calcium concentration along the study area of El Mahmodia stream was 31.8 mg/l. It is the major cation of the Nile water, which probably comes mainly from the rocks [69]. The mean average of sodium concentration was 49.91 mg/l. The mean results of sodium concentration level is below the permissible limits of the WHO [51] which was 200 mg/l. magnesium concentration was 16.38 mg /l, it is below the permissible limits of the [53] which was 100 mg/l. The potassium cation occurs in high concentration (higher than 6 mg/l) it recorded at 7.99 mg/l at stream water. The K minerals are below the permissible limits of the BIS [53], which was 12 mg/l. The major anion in the Nile water is the chloride (Cl). The concentration of the anion in stream water was 56.40 mg/l, it is below the permissible limits of law 48 (less than 200 mg/l) and the guidelines of WHO [51].

The term "heavy metal" refers to any metal and metalloid element that has a relatively high density ranging from 3.5 to 7 g/cm3 and is toxic or poisonous at low concentrations [70, 13, 14, 7, 8]. They include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), zinc (Zn), nickel (Ni), copper (Cu), and lead (Pb). It is often used as a group name for metals and metalloids that have been associated with contamination. Heavy metals are natural constituents of the earth's crust [71]. In Egypt and other developing countries, where environmental protection laws have not been enforced, industrial and domestic wastes are dumped randomly into water bodies [72, 12, 5]. Five heavy metal elements were measured in this study. The low concentration values of the heavy metals in the stream water are due to their deposition with sediments on the stream's bottom [73]. The cadmium concentration in the stream water was 0.002 mg/l and this concentration within the allowable limits according to WHO [51], which was (< 0.003mg/l). Lead concentration in the stream water along the study areas was neutral (Table 2). Iron (Fe) is the third most abundant metal in the earth's crust after silicon and aluminum. In the study area, the mean concentration level of Fe was 0.65 mg/l. The concentrations of Fe are within the permissible limits of law 48/1982 (<1 mg/l) and the guideline of WHO [51], which is <1 mg/l. The major sources of manganese (Mn) are ferromanganese production and municipal wastewater. The major sources for manganese in air and water are iron and steel manufacturing and the burning of diesel fuel in the motor cars [2, 3, 13, 14]. The truck mounted fogging machine which are used by farmers in El Mahmodia stream could be a reason for Mn level in El Mahmodia stream water. Along the study area at El Mahmodia stream, the manganese concentration was 0.09 mg/l. The results of manganese were agreed within the permissible limits of law 48/1982 (<0.5 mg/l) and the guideline of WHO [51] is (<0.5 mg/l). The primary sources are domestic wastewater and atmospheric deposition. The high levels of Cu in water can be attributed to industrial and agricultural discharge [56]. Along the study area in El Mahmodia stream, the copper concentration was 10.91 mg/l. This may be attributed to the huge amounts of raw sewage, agricultural and industrial wastewater discharged into the stream [74]. They are above the permissible limits of law 48/1982 (<1.0 mg/l), the values of the measured metal Cu were recorded at El Mahmodia stream. GC–MS analysis of El Mahmodia stream water showed the presence of various organic chemicals, insecticide at different Rts identified using NIST mass spectral library. The peaks were recorded at Rt 5.37, 5.65, 6.1, 6.3, 6.41, 6.57, 7.03, 7.13, 7.28 (Detected compounds repeated in the four seasons) which corresponded to the presence of Decamethyl cyclo pentasiloxane, 1-(2-Acetoxyethyl)-3,6-diazahomoadamantan-9-one oxime, Nonadecane, 2',6'-Dihydroxyacetophenone, bis (trimethylsilyl) ether,4H-1-Benzopyran-4-one,2-(3,4-dimethoxyphenyl)-3,7-dimethoxy-,11,16-Bis(acetyloxy)-3,20-dioxopregn-4-en-21-yl acetate, 9,12-Octadecadienoic acid (Z,Z)-, 2,3-bis[(trimethylsilyl)oxy] propyl ester, m-Dioxane, 5-(hexadecyloxy)-2-pentadecyl -, trans-, Dodecamethylcyclohexasiloxane, 2-(9-Borabicyclo[3.3.1]non-9-yloxy)-3-([2-(9-borabicyclo [3.3.1] phenyl non-9-yloxy)ethyl]sulfanyl)propyl ether, respectively based on the match with NIST library.

Most of the organic pollutants detected at the peaks in GC–MS data analysis were identified as endocrine disrupting phthalate esters, fatty acids, phenolic acids, carcinogens, and aquatic toxicants, plasticisers, which are classified as "priority pollutants" due to their severe toxicity in living being [75, 2, 3, 62]. Phthalates such as Phthalic acid, butyl tetradecyl ester, Phthalic acid, octadecyl ester Phthalic acid, butyl 2-ethylbutyl ester, Phthalic acid, di (2-propylpentyl) discharged along with industrial wastewaters cause water pollution and disturb the ecology of the receiving water bodies by creating serious toxicity to aquatic organisms, such as fishes, as result of bioaccumulation and thus cause toxic effects [76]. Phthalates also are reported to cause endocrine disruption in humans and animals upon long term exposure [75]. Phthalic acid is used in industry has been reported to cause mutagenicity, developmental toxicity, and reproductive toxicity in animals [77].

Dihydroxybenzoic acid might be raised in El Mahmodia stream water as a key metabolite of biodegradation of polyaromatic hydrocarbons (PAHs) during wastewater treatment [78]. 2,6-Dihydroxybenzoic has been reported as using in blending and formulating a variety of personal care products including shampoos, and deodorants and as a solvent in commercial dry cleaning products and industrial cleaning fluids [79]. Aquatic toxicants reduce the algal growth in the aquatic ecosystem and thereby reduce photosynthesis and ultimately disturb the ecological functioning of receiving water bodies [80, 13, 14]. Fatty acids (n-Hexadecanoic acid, Hexnedioic acid, trans-9- octadecanoic acid) might have originated in during the industry Benzeneacetonitrile, α-[4-(dimethylamino)-2,5dimethoxyphenyl]methylene]-4-nitro-, 1,2-Benzenedicarboxylic acid, butyl phenylmethyl ester, Benzeneacetonitrile, α-[4-(dimethylamino)-2, 5-dimethoxyphenyl]methylene]-4-nitro-, from other Benzyl compounds are considered to be moderately aquatic toxicant and poses moderate to low toxicity to aquatic animals, such as fishes, and also is listed as a Group 2A carcinogen [81, 18]. The major pollution sources of Nile and main canals are effluents from agricultural drains and treated or partially treated industrial and municipal waste waters [82, 7, 8]. The drainage water contains dissolved salts which washed from agricultural lands as well as residues of pesticides and fertilizers, at the end these pesticides collected in El Mahmodia stream water, causing severe damage to it. Impact of the drainage water on Nile quality has been reported by Abdel-Dayem *et al*. [18]; Radwan *et al.* [7, 8]. In El Mahmodia stream drainage water mixed with drinking water due to human activities along the stream, there is a large amount of organochlorine pesticides detected in the stream water samples such as Dieldrin [83, 84]. There is no access waste water treatment in Abo Homes rural areas, 20% of Egyptian villages have inadequate potable water [85]. In Egypt, water supply and sewage services are not implemented simultaneously. In the rural areas, where half of the population lives, 90% of the people have no access to waste water treatment facilities [86, 87, 13, 14]. The aquatic environment is subjected to various types of pollutants which enter water bodies [88, 12, 5].

It is estimated that the total amount of reused treated wastewater in Egypt was about 1.4 billion m^3 in 2000 [89]. Industrial waste water is considered the second of the main sources of Nile water pollution. There are about 129 factories discharging their waste water into the River Nile system. Effluent wastewater is often partially treated [90]. Major pollutants in agricultural drains are salts, nutrients, pesticide residues, toxic organic and inorganic pollutants [91]. The persistence of the organochlorine compounds and their metabolites, which are often more toxic than the original compound, is dependent on environmental conditions [92, 93]. Toxic substances such as heavy metals and organic micro pollutants occur due to the mixing of domestic with industrial and commercial activities [91]. Organochlorines (OCs) are a generic term for pesticides containing chlorine; however, the term is commonly used to refer to the older persistent materials, including aldrin, BHC, chlordane, DDT, dieldrin, heptachlor, lindane, or toxaphene. Most have now been deregistered or their use has been severely restricted. The present results of winter season showed that the significant effect of season on water samples in El Mahmodia stream comparing with summer season data of Azab et al. who reported that in summer season, organochlorines were significantly higher in water samples.

In the present study, bioassays were carried out to evaluate the insecticidal concentration of chlorpyrifos on the second instar Culex larvae. Surveys in Egypt date back to 1903. According to these surveys eighteen culicine and eleven anopheline species have been encountered in the different parts of Egypt. *Culex pipiens*, the main filariasis vector in Egypt Published field and laboratory studies with mosquito control pesticides have concentrated on differential effects with mosquito larvae. The exposure time has an important effect on the values of LC_{50} in this study. In most cases, the LC_{50} values had synergistic interactions with time; thus, it increased after 48h of exposure when compared to 24 h of exposure (Table 3). Very high concentrations of the Chloropyrifos led to high mortality rates. The LC_{50} of Chloropyrifos insecticide in the case of *Culex pipnes* was 24.52 ppm after 24h, and increased to 755.65 ppm after 48h. The lower value was 14.78 ppm after 24h which also increased to 258.10 ppm after 48 h., the higher value of LC_{50} was 45.6576 ppm after 24h and the same value became 5485.96 ppm after 48h. The LC_{25} of Chloropyrifos insecticide was detected as 2.51 ppm after the first 24h and measured at 72.37 ppm after the second 48h.

The mean level of physicochemical parameters and heavy metals as Turbidity, BOD, COD, NH_4, HCO_3, MPN, Cu and physicochemical parameters which determined showed an increase in its values compared to the standard safety criteria of the Egyptian Law (48/1982), the guideline of WHO [51] and FAO [50]. In El Beheira Governorate, pesticides are used along a large scale. Organochlorine and organophosphate are persistent pesticides which leave residues in drinking water that remain for days to many years.

Organochlorine pesticides, prohibited since the early 1980s, are still detectable in the environment. Organophosphates are found in high rate in the stream, Chloropyrifos is an Organophosphate pesticides found at concentration of 0.09 m/l in the stream water. Effect of the exposure time of Chloropyrifos insecticide on the LC_{50}, LC_{25} and LC_{95} values had a synergistic interactions with time as it increased after 48h of exposure when compared to 24 h of exposure. The 0.09 ppm concentration of Chloropyrifos had no effect on the second instar Culex larvae, as there is no mortality. Also there is no effect on mosquito mortality after 72h and 96h of exposure to the detected concentration of Chloropyrifos insecticide.

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Recommendations

There is an important need for Egyptian agriculture ministry to reduce the numbers and quantities of pesticides used in the agriculture sector. It is clear that the main challenge for the sustainability of water resources is the control of water pollution. The Ministry of the Environment in Egypt is observing the enforcement of the legislation regarding the treatment of industrial and domestic wastewater. It is also advocating organic farming and limiting the use of chemical fertilizers and pesticides to reduce water pollution. Improving the quality of drainage water especially in the main drains.

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