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Ecological Risk Assessment of Organochlorine Pesticide in the Al-Diwaniyah River

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Abstract.

This study aims to calculate the Risk of organochlorine pesticides on the environment residues in the surface waters of Al- Diwaniyah River. Three organochlorine pesticides were targeted (4,4′-DDT, heptachlor, and endosulfan). Ten samples were taken during the pesticide application period from the beginning, middle, and end of the river in the October, the air temperature was 40 degrees Celsius, and the samples were analyzed using Gas chromatography device and the concentration of 4,4′-DDT was from (0.02-0.06 µg/L), heptachlor was from (0.34-0.59 µg/L) and endosulfan was from (0.002-0.03 µg/L). Using the risk quotient method, the ecological risk of these pesticides was calculated, 4,4′-DDT was classified as low risk $0.01 \leq RQ < 0.1$. the RQ value was (1.707-3.414 %), for endosulfan was (0.001-0.0327%) and this classified as very low risk $RQ < 0.01$, for heptachlor was (45.977-61.56%), and this classified as moderate risk $0.1 \leq RQ < 1$. The study's findings show that agricultural practices contribute to increasing the concentrations of organochlorine pesticides in river water, thus increasing the ecological risks of these substances and their impact on the public health of living organisms.

Key words: Organochlorine Pesticide, Ecological Risk, Al-Diwaniyah River

Introduction

Pesticides have the power to stop and manage dangerous organisms. Certain pesticides are hazardous to both people and animals, and their constant use is seriously contaminating the environment and water supplies[1], because pesticides are involved in many different environmental processes, their extensive usage in agricultural and forest plantations poses a constant risk of contaminating water and soil. Runoff, which happens during the rainy season, is thought to be a significant pathway by which contaminants enter surface waterways. Some factors influencing the quantity of water contaminated by runoff are the Chemical and physical attributes of the pesticides(partition coefficients, vapor pressure, solubility in water) , the amount of rainfall after pesticide application, type and slope of the catchment region[2],[3],[4] [5],[6]. Surface water quality is greatly impacted by land usage; during precipitation, materials found on land enter streams. Numerous studies have demonstrated the connection between surface water pesticide pollution and land usage. [7][8][9][10][10]. Organochlorine pesticides (OCPs) are a broad category of semi-volatile and persistent organic pollutants that are frequently encountered in the environment. OCPs' toxicity, long-range spread, bioaccumulation, and persistence have made them a growing global health problem. [11][12][13]. The nine Organochlorine pesticides that were included as part of the Twelfth Stockholm Convention on Persistent Organic Pollutants' "dirty dozen" in 2004 included Dichlorodiphenyl-Trichloroethane (DDT), Heptachlor, Alex Aldrin, Toxaphene, Hexachlorobenzene, Dieldrin, Endrin, and Chlordane. Six more OCPs were added to the enumeration of enduring organic contaminants during the the Stockholm Conference of the Parties' fourth meeting, Among these were lindane, pentachlorobenzene, Technological endosulfan and its associated isomers, α-and β-hexachlorocyclohexane, chlordecone, and lindane [14] .Through soil percolation, agricultural runoff, and atmospheric precipitation, OCPs can infiltrate aquatic habitats. Various pesticide risk indices have been employed as standard practice to assess the possible impact of pesticides to aquatic environments. Along with a range of impact indicators (EC50, NOEC), the majority of them contain specific exposure indicators such as environmental dispersion, bioaccumulation, rate of application, and soil persistence.. [15][16][17]. employing simple dilution models Generally, the indices are constructed using a projected environmental concentration (PEC) or more complex models based on the fugacity approach, including Fugacity Level I, which is specific to surface water inputs..[18][19]. [17] provide a thorough breakdown of the environmental scenarios used to calculate the PEC. Pesticide danger in aquatic ecosystems is determined by the PEC/PNEC rate. [20] [20] [21] This is recognized as the risk quotient (RQ) and is employed as a danger marker. The concentration to which the ecosystem is exposed is known as the predicted environmental concentration (PEC). The anticipated no effect concentration (PNEC) is the concentration below which an undesired effect is unlikely to occur. When a component's anticipated environmental concentration (PEC) exceeds its expected PEC the concentration one anticipates finding in the environment, then the component is considered ecologically friendly. It is believed that the most delicate species determine how sensitive an ecosystem is, and that the community function is safeguarded by the protective ecosystem structure. The extrapolation of the ecosystem's impact from short-term toxicity data for a single species is questionable. Because there is a dearth of solid scientific data, the EPA and OECD have thus developed the assessment factor (AF) [22]

The goal of the current study was to assess the ecological risk of three organochlorine pesticides in the surface water of the Al-Diwaniyah River using the risk quotient (RQ) approach.

2. Materials and methods

Study area

The Al-Diwaniyah River serves as the province of Al-Diwaniyah's primary source of water for drinking, agriculture, and other uses. This Shatt Al-Hilla branch has its origins in the province of Babylon, which is situated north of the Al-Diwaniyah province. The Sadr l-Daghara area, which is situated north of the province of Al-Diwaniyah, is the source of this river. The river has a length of around 120 kilometers. It heads southwest and passes through the following provinces: Al-Diwaniyah City, Alhamza, Sidair, and Saniyah. Finally, it enters Al-Muthannah, which is situated south of Al-Diwaniyah. The Al-Diwaniyah River flows 45 m3/s on average per year, whereas the project's design discharge is 60 m3/s. This river helps irrigate around 410000 acres of agricultural land on both banks of the river and provides the bulk of the water needed by the city off Al- Diwaniyah and surrounding areas for a number of uses, including drinking and irrigation[23] The study was conducted at three Station along the Al- Diwaniyah River's (table 1)

Table 1. study station

Station	Latitude (N)	Longitude (E)
Daghara	44 46' 23"	39 03' 32".
Al-Diwaniyah	44 53' 51"	14 0' 32".
Hamzah Al-Sharqi	44 58' 36"	28 43' 31"

Method of collecting samples

Using previously cleaned plastic bottles, 500 mL of samples were collected from three study stations at a depth of 30 to 50 cm. All of the samples were collected in October, which is a warm month with 40-degree Celsius temperatures. Before sampling, each container was washed three times with water from the same portion of the river to make sure the sample was typical of that specific site. After that, it was covered with aluminum foil and kept in an ice box until the water samples were gathered and the lab was discovered.[24]. They were brought to the lab for examination. Using a GC-ECD equipment, the pesticide content in the river water was ascertained.

The substance was evaluated using a GC-ECD (Shimadzu, Japan) equipped with a DB-5MS capillary column (30 m × 0.25 mm i.d., film thickness 0.25 _m, J&W, USA). The flow rate of the carrier gas, N2, was 5.0 milliliters per minute.A material injection using the split mode was finished with a split ratio of 1. The GC injection and detector temperatures were set at 270 and 350◦C, respectively. The temperature program for the GC column was as follows: a three-minute start temperature of 100 °C, followed by a five-minute temperature rise of 10 °C/min to 280 °C.

Extraction of OC Pesticides

For 20 minutes, Using a 70 ml acetone:n-hexane (5:2, v/v) combination, ultrasonic agitation was used to remove chlorinated pesticides from 100 ml of samples Following the removal of any leftover water using filter paper containing 5 g of sodium sulfate, the extract was poured into a 250 ml round flask. Another extraction was carried out. The extracted solvent was dried and then redissolved in 50 milliliters of acetonitrile, which is not very lipid-soluble. Lipids were frozen by storing acetonitrile extract in the freezer for thirty minutes at -24 ◦C. The majority of the lipids formed a concentrated, light yellow lump on the surface of the glassware. To get rid of frozen lipids, filter paper was used to filter the cold extract at -24 ◦C right away. In order to repeat the filtration process using the same method, 50 milliliters of acetonitrile were used to resolubility the precipitated lipid on the surface of the glassware. A rotary evaporator was used to condense the filtered extract to 1 milliliter[25].

Assessment of ecological risk

The risk quotient (RQ) method was used to evaluate the ecological danger for the OCPs found in the Al-Diwaniyah River's surface water. This was accomplished by calculating the RQ. [26].

$$RQ\% = EEC/PNEC \quad (1)$$

Where:

-RQ: risk quotient

-EEC: the environmental effect concentration for organochlorine pesticides, mg/L

-PNEC: the predicted no-effect concentration for a certain OCP, mg/L; was calculated as follows [27]:

$$PNEC = HC5/AF \quad (2)$$

Where:

-HC5 : the OCP concentration, mg/L; at which 5% of species are exposed to chronic hazards

-AF :Assessment factor that takes into account the variability between laboratory toxicological testing and the real environment,. In this study, AF=100[28].

The species sensitivity distribution (SSD) approach was used to determine HC5 [29]. The acute toxicity data for three OCPs (4,4′-DDT, Endosulfan, and Heptachlor) were retrieved from ECOSAR version 2.0 (USEPA, USA). These data included Lethal concentration (LC50) and effective concentration (EC50) median or fish (seawater), and shrimp (seawater) ,fish (freshwater), earthworm (freshwater), daphnia (freshwater), green alga (freshwater), as shown in (Table 2).

Table 2. acute toxicity data of OCPs to 6 organisms (LC50/EC50, mg/L)

Details	Heptachlor	Endosulfan	4,4′-DDT
CAS Number	76-44-8	959-98-8	50-29-3
log K_{ow}	5.8644	3.4967	6.7945
Fish (freshwater)	0.022	3.442	0.014
Daphnia (freshwater)	0.023	3.082	0.013
Green alga (freshwater)	0.102	6.842	0.059
Earthworm (freshwater)	255.307	407.375	196.163
Fish (seawater)	0.007	1.806	0.019
Shrimp (seawater)	0.005	0.981	0.001

No observed effect concentration (NOEC) or the lowest observed effect concentration (LOEC) of three OCPs (endosulfan, heptachlor, and 4,4′-DDT) in freshwater fish, daphnia, and green algae was calculated using version 2.0 of ECOSAR **(USEPA, USA)** due to the paucity of data on chronic toxicity. (Table 3)

Table 3. Chronic toxicity data of OCPs to 3 organisms (NOEC/LOEC, mg/L)

Details	Heptachlor	Endosulfan	4,4′-DDT
CAS Number	76-44-8	959-98-8	50-29-3
log Kow	5.8644	3.4967	6.7945
Fish (freshwater)	0.001	0.535	0.002
Daphnia (freshwater)	0.02	0.127	0.004
Green alga (freshwater)	0.128	2.943	0.041

The value of HC5 was obtain from version 2.0 of ECOSAR **(USEPA, USA)** [30] as shown in (table 4)

Table4 The best SSD models and their parameters for HC5 of OCPs

Details	Heptachlor	Endosulfan	4,4′-DDT
Best SSD model	Boltzmann	Exponential	Exponential
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0
Parameters	A1=-0.57, A2=0.86, x0=-2.35, dx=0.64	y0=0.90, A1=-0.39, t1=0.73, A2=-0.39, t2=0.73	y0=0.99, A1=-0.13, t1=2.70, A2=-0.13, t2=2.70
AHC_5（mg/L)	2.98E-03	0.871	6.337E-03
HC_5（mg/L)	9.57E-04	0.122	1.757E-03

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distinct assessment criteria and management goals led to distinct ecological risk classifications. [28][31][32][33], When the RQ value is more than 1, OCP concentrations in the environment are frequently higher than predicted no-effect values. The RQ values obtained in the literature previously classified ecological risks into five categories: extremely low risk (RQ<0.01), moderate risk (0.01≤RQ <1), high risk (1 ≤RQ <10), and extremely high risk (RQ≥10). [33] [30].

Results and discussion

OCP in Water

The three Diwaniyah River stations had total concentrations of organochlorine pesticides ranging from (0.02-0.06),(0.34-0.59), and (0.002-0.03) ppb, respectively, for 4,4′-DDT ,heptachlor, and endosulfan. For for 4,4′-DDT pesticide, the highest concentration was recorded in the third station with a value of 0.06 ppb and the lowest value was 0.02 ppb in the third station, For the heptachlor pesticide, the highest concentration was 0.62 ppb and the lowest concentration was 0.44 ppb in the third station, As for endosulfan pesticide, the highest concentration was 0.04 ppb and the lowest concentration was 0.008 ppb also in the third station. There was no consistent pattern in the concentration of heptachlor observed throughout the three research stations. There were times when the heptachlor content was higher than the WHO recommended level of (0.1 ug/L). the concentration of 4,4′-DDT was quite high at many places; however, it was within safe limits of WHO guideline value (1ug/ L) [26] .Iraqi Standard Specification No. 35 of 1967 for the system of protecting rivers from pollution requires the percentage of DDT to be zero.

Ecological risk assessment:

1-Heptachlor

Table 5 PNEC and ecological risk assessment for heptachlor

Sample	EEC (ug/ L)	EEC (ng/L)	PNEC (ng/L)	RQ%= EEC/PNEC	Risk%	Reason
1	0.59	590	9.57	61.56	moderate risk	0.1≤RQ<1
2	UDL	0	0	0	0	0
3	UDL	0	0	0	0	0
4	0.55	550	9.57	57.47	moderate risk	0.1≤RQ<1
5	UDL	0	0	0	0	0
6	UDL	0	0	0	0	0
7	0.51	510	9.57	53.291	moderate risk	0.1≤RQ<1
8	0.44	440	9.57	45.977	moderate risk	0.1≤RQ<1
9	0.5	500	9.57	52.24	moderate risk	0.1≤RQ<1
10	0.58	580	9.57	60.6	moderate risk	0.1≤RQ<1

The results of the ecological risk assessment and predicted no-effect concentration (PNEC) values for heptachlor in the river waters of Al-Diwaniyah are shown in (Table 5) ,9.57 ng/L was the heptachlor PNEC result. This proved that aquatic life is the most negatively impacted. In the first station for sample 1, the ecological risk was 66.56% and is classified as moderate risk ,for samples 2 and 3, no risks were recorded because there is no concentration of organochlorine pesticides in these samples, because this type of pesticide is not used in this area, or the pesticide application areas are relatively far from the surface waters of the river, and therefore it is difficult for them to reach the water, in sample 4, it was 57.47% .In the second station for sample 5 and sample 6, there is no risk because these areas are residential and no concentration of organochlorine pesticides was recorded there. Sample 7 at the third station had an ecological risk of 53.291%, which is categorized as moderate risk. It was 45.977% in sample 8, which is categorized as moderate risk. Sample 9 had an ecological risk of 52.24%, which is categorized as moderate risk. Similarly, sample 10 had an ecological risk of 60.6%, which is also classed as moderate risk. Graphical representation of the risk quotient for Heptachlor shown in (Figure 1)

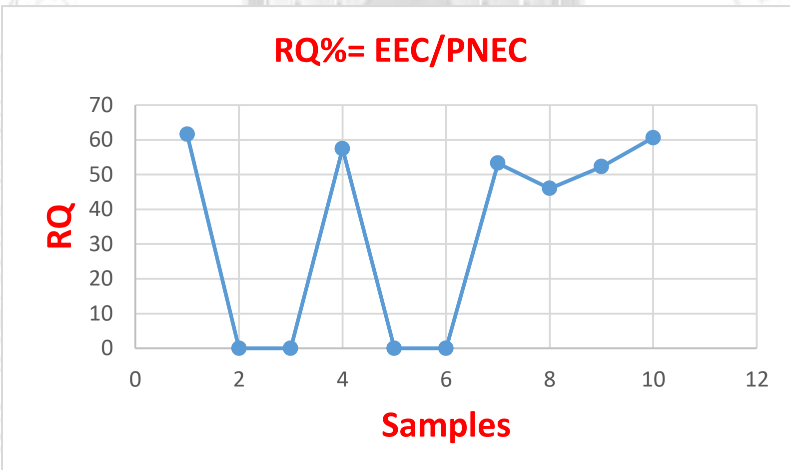

Figure 1 Risk quotient for Heptachlor

2-Endosulfan

Table 6 PNEC and ecological risk assessment for Endosulfan

Sample	EEC (ug/ L)	EEC (ng/L)	PNEC (ng/L)	RQ=EEC/PNEC	Risk%	Reason
1	0.018	18	1222.6	0.0147	very low risk	RQ<0.01
2	UDL	0	1222.6	0	0	0
3	UDL	0	1222.6	0	0	0
4	0.03	30	1222.6	0.0245	very low risk	RQ<0.01
5	UDL	0	0	0	0	0
6	UDL	0	0	0	0	0
7	0.011	11	1222.6	0.00899	very low risk	RQ<0.01

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8	0.008	8	1222.6	0.00654	very low risk	RQ<0.01
9	0.002	2	1222.6	0.001	very low risk	RQ<0.01
10	0.04	40	1222.6	0.0327	very low risk	RQ<0.01

The results of the ecological risk assessment and predicted no-effect concentration (PNEC) values for endosulfan in the river waters of Al-Diwaniyah are shown in (Table 5). The Endosulfan PNEC result was1222.6, In the first station for sample 1, the ecological risk was 0.0147% and is classified as very low risk . As for samples 2 and 3, no risks were recorded because there is no concentration of organochlorine pesticides in these samples this might be related to avoiding agricultural activities or the fact that these locations do not utilize this type of pesticide, making it more difficult for the pesticide to enter surface waterways. In sample 4, it was 0.0245% and is classified as very low risk, in the second station for sample 5 and sample 6, there is no risk because these areas are residential and no concentration of organochlorine pesticides was recorded there. The ecological risk for sample 7 in the third station was 0.00899%, which is considered very low risk; for sample 8, the risk was 0.00654%, which is considered very low risk; for sample 9, the risk was 0.001%, which is considered very low risk; and for sample 10, the risk was 0.0327%, which is considered very low risk. Graphical representation of the risk quotient for Endosulfan shown in (Figure 2)

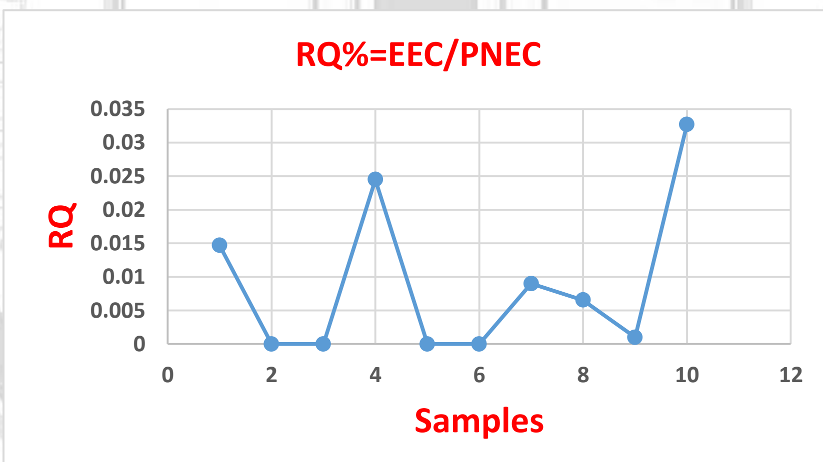

Figure 2 Risk quotient for Endosulfan

3-4,4′-DDT

Table 7PNEC and ecological risk assessment for 4,4′-DDT

Sample	EEC (ug/ L)	EEC (ng/L)	PNEC (ng/L)	RQ=EEC/PNEC	Risk%	Reason
1	0.04	40	17.57	2.276	low risk	0.01≤RQ<0.1
2	UDL	0	0	0	0	0
3	UDL	0	0	0	0	0
4	0.05	50	17.57	2.845	low risk	0.01≤RQ<0.1
5	UDL	0	0	0	0	0
6	UDL	0	0	0	0	0
7	0.03	30	17.57	1.707	low risk	0.01≤RQ<0.1
8	0.02	20	17.57	1.138	low risk	0.01≤RQ<0.1
9	0.03	30	17.57	1.707	low risk	0.01≤RQ<0.1
10	0.06	60	17.57	3.414	low risk	0.01≤RQ<0.1

The results of the ecological risk assessment and predicted no-effect concentration (PNEC) values for 4,4′-DDT in the river waters of Al-Diwaniyah are shown in (Table 6). The 4,4′-DDT, PNEC result wa17.57 ng/L, In the first station for sample 1, the ecological risk was 2.276% and is classified as very low risk , for samples 2 and 3, no risks were recorded because there is no concentration of organochlorine pesticides in these samples this might be related to avoiding agricultural activities or the fact that these locations do not utilize this type of pesticide, making it more difficult for the pesticide to enter surface waterways. In sample 4, it was 2.845% and is classified as low risk. There is no concern in the second station for samples 5 and 6, as these are residential areas with no documented levels of organochlorine pesticides. Sample 7 at the third station had an ecological risk of 1.707% and was categorized as low risk; sample 8 had an ecological risk of 1.183% and was categorized as low risk; sample 9 had an ecological risk of 1.707% and was categorized as low risk; sample 10 had an ecological risk of 3.414% and was categorized as low risk. Graphical representation of the risk quotient for 4,4′-DDT shown in (Figure 3)

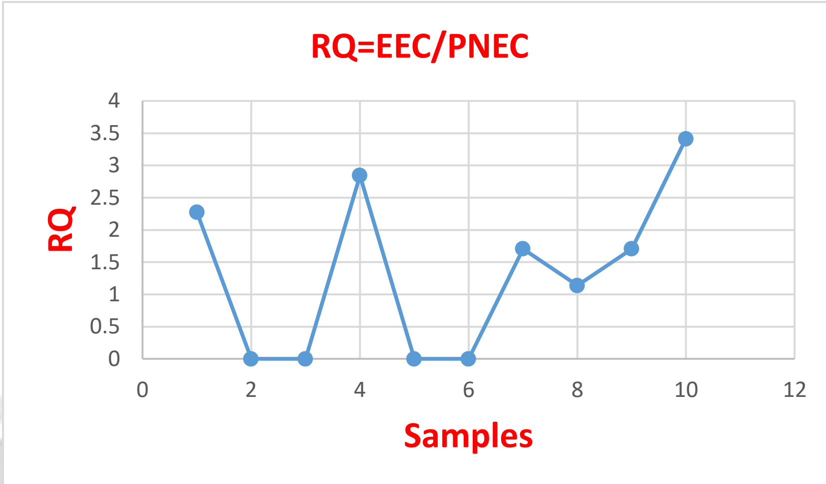

Figure 3 Risk quotient for 4,4′-DDT

Conclusion

The current study was conducted to assess the Ecological risk consequent to the indiscriminate and excessive use of pesticides on the Al- Diwaniyah River during October. The concentrations of three organochlorine pesticides were measured (4,4′-DDT ,heptachlor, and endosulfan) using a gas chromatography , the ecological risk of these pesticides was calculated using the risk quotient (RQ) approach, for 4,4′-DDT was classified as low risk $0.01 \leq RQ < 0.1$, for endosulfan was classified as very low risk $RQ < 0.01$, for heptachlor was classified as moderate risk $0.1 \leq RQ < 1$.The current study recommends further expanded studies and some recommendations should be made by regulatory authorities regarding the use of pesticides

List of Abbreviations

Abbreviation	Indication
OCPs	Organochlorine pesticides
RQ	Risk Quotient
WHO	World Health Organization
EPA	Environmental Protection Agency
UDL	Under Detection Limited
DDT	Dichlorodiphenyltrichloroethan
CAS	Chemical Abstract Service
AF	Assessment Factor
EEC	Environment Effect Concentration
PNEC	Predict No Environment Concentration

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ARTICLE

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تقييم المخاطر البيئية للمبيدات الكلورية العضوية في نهر الديوانية

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الخلاصة :

تهدف هذه الدراسة إلى حساب خطورة المبيدات الكلورية العضوية على البيئة في المياه السطحية لنهر الديوانية. تم استهداف ثلاثة مبيدات آفات عضوية كلورية (4,4′–DDT ، وسباعي الكلور، والإندوسولفين). تم أخذ عشر عينات خلال فترة رش المبيدات من بداية ووسط ونهاية النهر في شهر أكتوبر وكانت درجة حرارة الهواء 40 درجة مئوية، وتم تحليل العينات باستخدام جهاز كروماتوغرافيا الغاز كانت نتائج تركيز 4,4′–DDT بين (0.02–0.06 ميكروغرام/لتر)، وسباعي الكلور (0.34–0.59 ميكروغرام/لتر) والإندوسولفين (0.002–0.03 ميكروغرام/لتر). باستخدام طريقة حاصل المخاطر، تم حساب المخاطر البيئية لهذه المبيدات، حيث تم تصنيف مبيد 4,4′–DDT على انه منخفض المخاطر $0.01 \leq RQ < 0.1$, بينما مبيد سباعي الكلور معتدل المخاطر $0.1 \leq RQ < 1$,اما بالنسبة لمبيد الاندوسولفين كان يصنف خطر منخفض جدا $RQ < 0.01$ وأظهرت نتائج الدراسة أن الممارسات الزراعية تساهم في زيادة تراكيز المبيدات الكلورية العضوية في مياه النهر، وبالتالي زيادة المخاطر البيئية لهذه المواد وتأثيرها على الصحة العامة للكائنات الحية.

الكلمات الدالة: المبيدات العضوية الكلورية، المخاطر البيئية، نهر الديوانية