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Organochlorines Pesticides in Sediments of Tigris River in Misan Governorate, Southern Iraq

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Abstract - Pesticides are chemical compounds used worldwide for different purposes. These chemicals are well known for their long life, high toxicity, and slow degradation process. Many countries including Iraq banned the use of pesticides for their adverse effects. However, several pesticides are found incessantly in rivers. To highlight the recent situation of pesticide contamination in Tigris river at Misan governorate, southern Iraq. The study aims to determine the concentrations of selected organochlorine pesticide residues which are (Alpha lindane, Lindane, Delta-lindane, Heptachlor, Aldrin, Epoxy heptachlor, DDE, Dieldrin, DDD, Endrin aldehyde, Endrin ketone, Methoxychlor, Endrin, and Endosulfan) in the surface sediments of the ,Amara, Kumait ,Ali Al-Gharbi and Ali Al-Sharqi, four stations in Tigris Rivers at Misan Governorate, Iraq by using Gas Chromatography mass spectra .In general, higher total concentrations of organochlorine pesticide were found in the Amara station (17.05 µg/kg) and the lower organochlorine pesticides were found in the Ali Al Gharbi station (2.87 µg/kg).it is evident that the banned pesticides are used regularly by peoples and thus contaminating the environment. Therefore, the formulations of appropriate rules and their enforcement to control the manufacture and solicitation of such pesticides are an urgent need to save the environment. If we compare our data with other study its fules with these study in the area.

مستويات المبيدات العضوية الكلورية في رواسب نهر دجلة في محافظة ميسان، العراق

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المستخلص - المبيدات الحشرية هي مركبات كيميائية تستخدم في جميع أنحاء العالم لأغراض مختلفة. هذه المواد الكيميائية معروفة بعمرها الطويل وسميتها العالية وعملية تحللها البطيئة. حظرت العديد من الدول بما في ذلك العراق استخدام المبيدات الحشرية لآثارها الضارة. ومع ذلك، يتم العثور على العديد من المبيدات الحشرية بشكل مستمر في الأنهار. كان من الضروري تسليط الضوء على الوضع الأخير لتلوث المبيدات الحشرية في نهر دجلة في محافظة ميسان، جنوب العراق. تهدف الدراسة إلى تحديد تراكيز متبقيات المبيدات العضوية الكلورية المختارة لأربع محطات في نهري دجلة في محافظة ميسان والمتبقيات هي (ألفا ليندان، ليندان، دلتا ليندان، سباعي كلور، ألدرين، إيبوكسي سباعي كلور، DDE، ديلدرين، DDD، إندرين ألدهيد، إندرين كيتون، ميثوكسي كلور، إندرين، إندوسلفان) في الرواسب السطحية في العمارة ,الكميت وعلي الغربي وعلي الشرقي خلال العام 2024باستخدام جهاز الكروماتوغرافية /طيف الكتلة. وبشكل عام، وجدت تراكيز إجمالية أعلى من المبيدات الكلورية العضوية في محطة العمارة (17.05 ميكروغرام/كغم)

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والمبيدات الكلورية العضوية الأقل وجدت في محطة علي الغربي (2.87 ميكروغرام/كيلوغرام). فمن الواضح أن المبيدات المحظورة تستخدم بانتظام من قبل الناس وبالتالي تلوث البيئة. ولذلك فإن صياغة القواعد المناسبة وخصائصها يعد إنقاذ الرقابة على تصنيع هذه المبيدات الحشرية والترويج لها حاجة ملحة لإنقاذ البيئة. إذا ما قارنا بياناتنا بدراسات أخرى فإنها تتوافق مع هذه الدراسات في المنطقة.
الكلمات مفتاحية: مبيدات كلورينية ، الرواسب السطحية ، نهر دجلة ،GCIMS

Introduction

Pesticides represent a wide range of contaminants that are routinely detected in freshwaters and pose detrimental effects to aquatic organisms and the overall ecosystem (Singh *et al*.2024; Pathak *et al.,* 2022; Mishra *et al.,* 2023; Allmon *et al.,* 2018). Pesticides are used worldwide to enhance agricultural output and to control insect-borne diseases. However, a water body can become a pesticide-contaminated habitat if agricultural runoff pollutes the water. Many pesticides preferentially partition into the sediment rather than remain dissolved in the water. (Kiran *et al.,* 2024 and Teklu *et al.*,2022).

Iraq is located in a region with limited fresh water resources. The Tigris River and the Euphrates River are the major sources of freshwater in Iraq. Both of these rivers originate from Turkey and continue south through Syria, and then to Iraq. The Tigris River flows through the center of Iraq, while the Euphrates River flows through the southern part of Iraq (Dahshan *et al.,* 2016). These two rivers join in the southern part of Iraq to form the Shatt al-Arab River, which then empties into the Arabian Gulf. Over the past decades, both rivers have been polluted by various contaminants. Since about the 1960s, pesticides have been extensively used in Iraq to enhance agricultural output and to control the spread of diseases. Pesticide use in Iraq peaked in the 1970s but declined significantly during the 1980s due to the Iran–Iraq war. Pesticide use resumed after 2003 but the types of pesticides changed dramatically. The presence and effects of contaminants in the Tigris River have been studied intensively in the past, including heavy metals, polycyclic aromatic hydrocarbons, microbiological contaminants, and toxic metals. However, sediment-bound pesticides have yet to be examined in the Tigris River. In the current study, the distribution and possible sources of pesticides in the sediment samples collected from the Tigris River in Misan Governorate, Southern Iraq were examined.

The Tigris River plays a vital role in the ecology and economy of Iraq and surrounding countries. For instance, most of the communities in Iraq are deriving their livelihoods and sustenance from the river water and cultivating the lands along the riverside (Al-Kafagi *et al.,* 2014). In addition, the Tigris River is used for drinking water (Beyazit, 2020), irrigation, and fishing. Nevertheless, the Iraqi environment has been degraded due to several contributing factors such as deforestation, urbanization, heavy industrialization, and uncontrolled agricultural activities. Poor agricultural practices are one of the critical activities that directly contribute to the degradation of the environment (Ricart and Rico, 2019).

Consequently, the extensive and indiscriminate use of pesticides in the cultivation of crops, in an attempt to increase yield, has resulted in adverse effects on the ecosystem. Therefore, it is generally known that the higher the use of pesticides in an area the more likely it is to pollute water bodies and sediment (Al-Saad and Al-Imarah, 2021) . This agrochemical runoff can have adverse effects on river water and sediment quality, and in many cases, this polluted water and toxic sediment are used for agriculture and may affect human health and aquatic life, giving rise

to the call for policies controlling the use and reducing the risk of pesticides(Cui,2020). Pesticides have been linked to a wide range of human health hazards (Gabar,2023)

As a result of exposure which ranges from short-term impacts such as headaches and nausea to chronic impacts on the nervous system and long-term consequences such as cancer and damage to the reproductive system. Nevertheless, pesticides can also cause physical deformities and genetic mutations, often leading to detrimental impacts on the survival of an organism or species. In developing countries, pesticides like organochlorine are still being used. Organochlorine pesticides are synthetic chemicals that are toxic to a wide range of insects, pests, and molds (Mishra *et al.,* 2023) due to their environmental persistence and bioaccumulation. These pesticides have brought a broad range of adverse effects on living organisms and have been detected in many ecological compartments in virtually every region. Studies have shown that these pesticides are still used in Middle Eastern countries, and unfortunately, no data is currently available on the specific use and amount of these pesticides in Iraq.

The present study aimed to identify the level and extent of contamination of major waterways, in the Tigris River, with Organochlorines at the Misan Governorate as a preliminary site. In addition, the execution of this work will indicate whether an extensive study should be conducted in the future, where the selection of Misan was appropriate, as many OCPs were used for farming and disease control in this area.

Materials and Methods

For sediment sampling and analysis, the methods used in this study involve careful selection of sites along the Tigris River and attention to the integrity of the samples throughout processing. A waterway was along the river, slowly steering a boat or canoe. At each site, the location was recorded using a Global Positioning System (GPS), and triplicate sediment samples were collected from each station bank. This systematic approach ensured that sediment samples were representative of the diverse environments along the river. Sediment sampling sites were selected to cover the Tigris River in Mesan governorate focusing on locations that represented four different environmental conditions. Site 1, Amara, Site 2, Kumait, Sites 3and 4 Ali Al-Sharqi, and Ali Al-Gharbi, respectively is rural with low human activity.

Surface sediment (5-10) cm was collected from four stations as shown in (Fig. 1.) using a van Veen Grab Sampler during 2024 and stored in an ice box after being wrapped in aluminum foil until reaching the laboratory.

Fifty of the sieved samples were hot extracted for 24 hrs. using dichloromethane solvent. The samples were evaporated to near dryness. The process of removing fat was carried out by adding 25 ml of acetonitrile and 25 ml of hexane according to the method described in AL-Ali (2012). Pesticides were purified and separated by passing the sample on a separation column consisting of a layer of sodium sulfate, then flurosil, then a layer of sodium sulfate (EPA, 2007; AL-Ali, 2012; Taban *et al.,* 2024). The quality and quantity of residues were determined using a GC-MS device AGILENT-type.

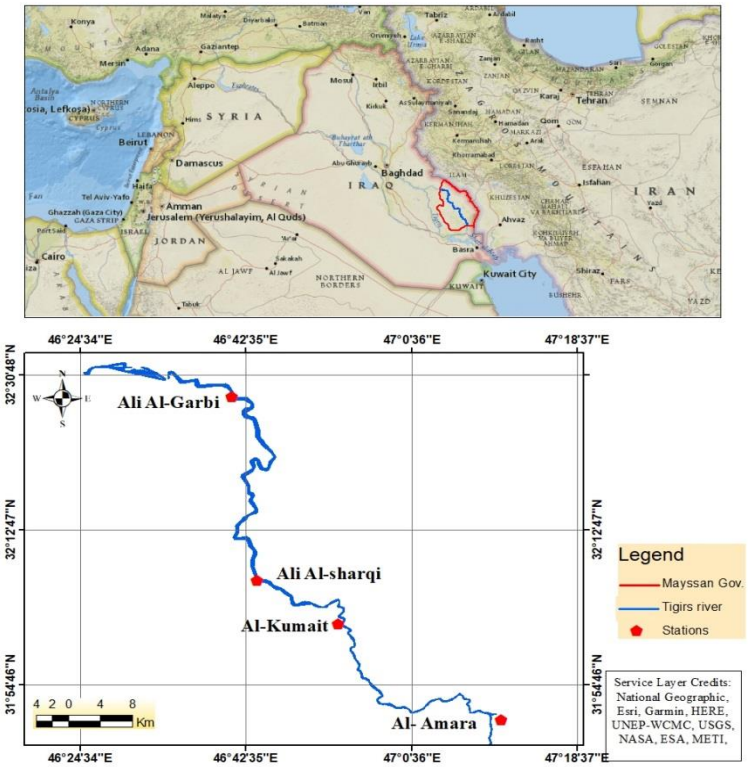

Figure 1. Map of Tigris river in Misan city and sample location

Result and Discussion

Table (1) shows the concentrations of organochlorine pesticides in the surface sediments of the Amara, Ali Al-Gharbi, Ali Al-Sharqi, and Kumait stations. In general, higher total organochlorine pesticide residues were found in the Amara station (17.05 µg/kg) and the lower organochlorine pesticides were found in the Ali Al Gharbi station (2.87 µg/kg).

The highest residues of organochlorine pesticides compounds in the surface sediments of the Ali Al- -Gharbi station was endrin compound (0.73 µg/kg), and the lowest concentration was endrin-aldehyde and alpha lindane (0.01 µg/kg) Table (1).

The lowest concentration was endrin-aldehyde and alpha lindane (0.01 µg/kg), While in Ali Al-Sharqi station the highest concentration of pesticide was DDD (1.23 µg/kg), and the lowest concentration of pesticide was delta lindane (0.04 µg/kg). In Kumait station the highest concentration of pesticide was aldrine (2.03 µg/kg), and the lowest concentration of pesticide was delta-lindane (0.46 µg/kg). In Amara station, the highest concentration of pesticide was aldrin (2.10 µg/kg), and the lowest concentration of pesticide was endrin ketone (0.64 µg/kg) as shown in Table.1

Table 1. Concentrations of organochlorine pesticides (µg/kg) in the surface sediments of the Tigris River at Misan Governorate, Iraq.

Compound Name	Ali Al-Gharbi	Ali Al-Sharqi	Kumait	Amara
alpha-lindane	0.01	0.97	1.23	1.03
Lindane	0.03	0.85	1.03	1.05
delta-lindane	0.12	0.04	0.46	1.93
Heptachlor	0.23	0.36	0.85	2.03
Aldrin	0.25	0.38	2.03	2.10
epoxy heptachlor	0.17	0.54	0.79	0.98
D.D.E	0.31	0.63	1.64	1.25
Dieldrin	0.27	1.03	1.32	1.35
D.D. D	0.42	1.23	1.73	1.03
endrin aldehyde	0.01	0.65	0.93	1.89
endrin ketone	0.03	0.86	0.74	0.64
methoxy choler	0.20	0.93	0.54	0.85
Endrin	0.73	0.75	1.20	1.98
Endosulfan	0.52	0.63	0.64	0.93
Total	2.87	9.58	15.9	17.05

In Ali Al-Gharbi station high concentrations of Endosulfan, Endrin, And D.D.D were observed (Fig 2.), while in Ali Al-Sharqi station high concentrations of alpha-lindane, dieldrin, and D.D.D were observed (Fig. 3.). In station of Amara high concentration of delta-lindane, heptachlor, aldrine, endrin aldehyde and Endrine were observed (Fig. 4.).

The current study showed that there is a local variation in the total concentrations of pesticides. The highest total of pesticides was recorded in the Amara station because the station has many farms that leach pesticides from agricultural lands. There are a lot of fishing boats painted with pesticide materials, and it may be the result of sedimentation of suspended substances that carry pesticides, as organochlorine pesticides are poorly soluble in water and have a high tendency to bind to sediments, especially clay, and silt (DouAbul *et al.*,1987).

The second station that has the highest total pesticides was Kumait (15.9 µg/kg) because this station has many animal sheds and the use of pesticides is frequent. The area is also surrounded by agricultural lands, and pesticides are usually used on farms as mention by (Al-Ali, 2012; Tram *et al*., 2020).

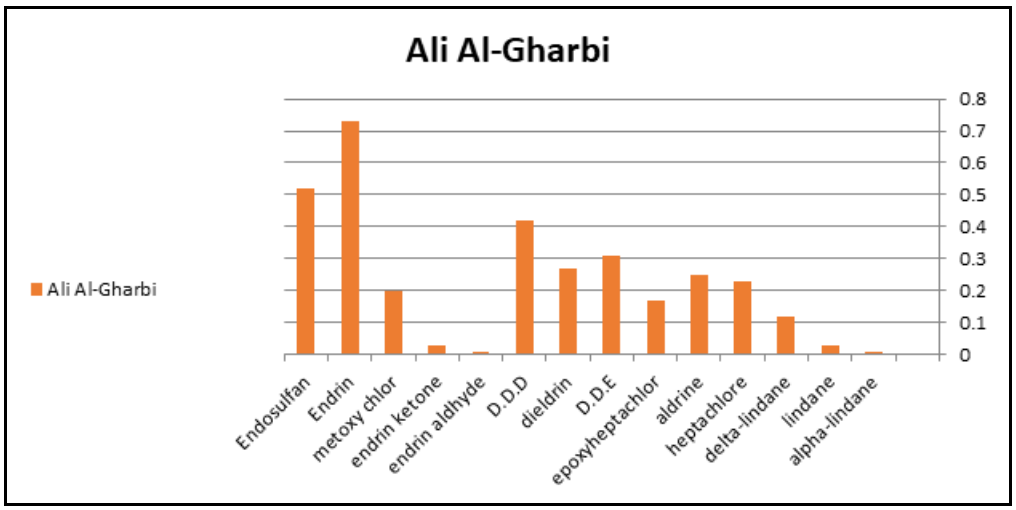

Figure 2. Concentration of organochlorine pesticides (µg/kg) OCP compounds in Ali Al-Garbi station

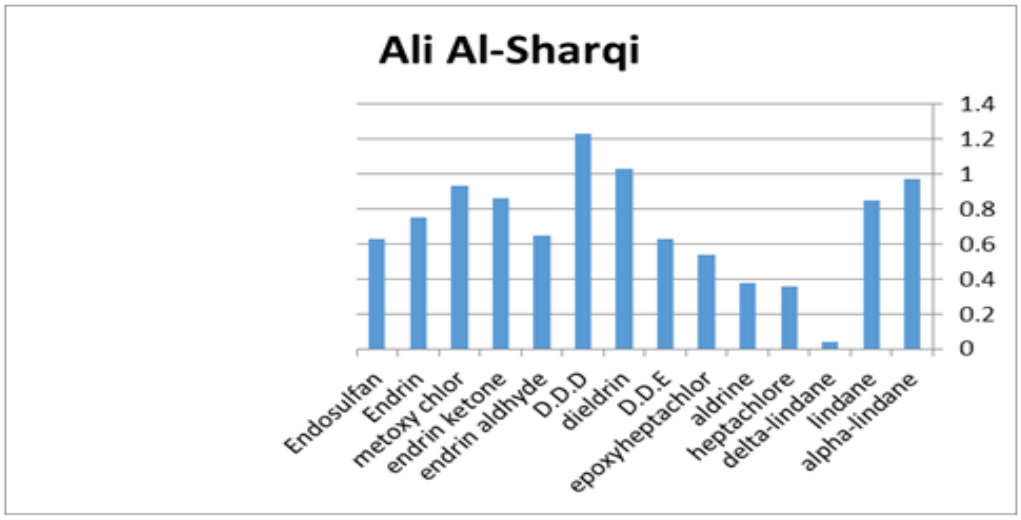

Figure 3. Concentration of organochlorine pesticides (µg/kg) OCP compounds in Ali Al-Sharqi station.

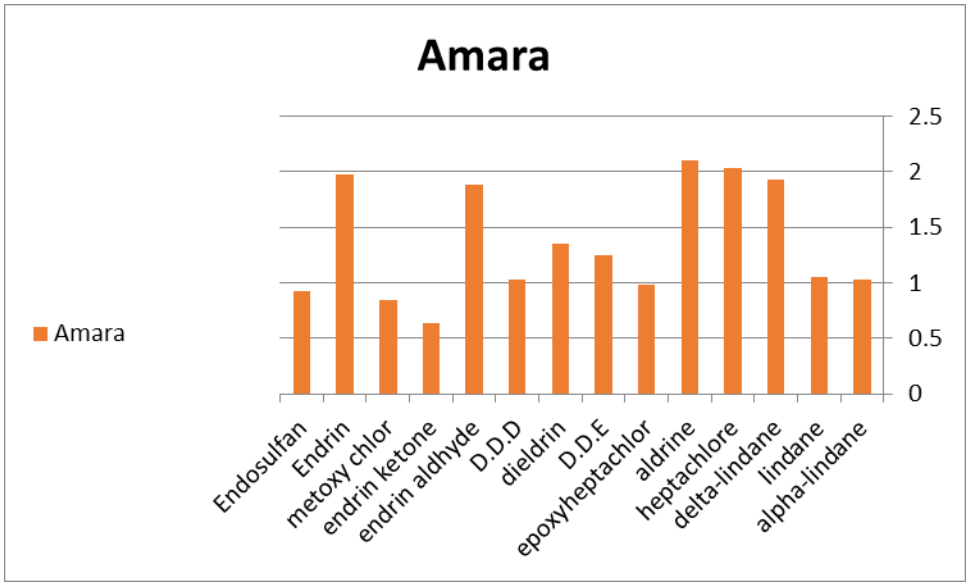

Figure 4. Concentration of OCP compounds in Amara station.

In Ali-Al Sharqi station, the total concentration of pesticides was (9.58 µg / kg). Due to the large number of farms in it, in addition to being fishing areas, and pesticides are used in fishing. Also, the nature of the sediments in Ali-Al Sharqi station is sandy thus the suspended pesticide particles increase (Al-Asadi, 2021). The lowest rate was at Ali Al-Gharbi station reaching (2.87 µg/kg). Due to the low pesticide use in this station, there are a few farms in this area.

Iraq has established regulations concerning sediment levels for 15 specific pesticides, whereas nations like Egypt, China, and Brazil currently lack such sediment regulations. In contrast, countries including the USA, the EU, and India have implemented effective sediment regulations; however, these are not as extensive as Iraq's regulations for the identified pesticides. The EU boasts the most thorough regulations, addressing 28 specific pesticides. Research indicates that various countries have successfully minimized pesticide contamination in sediments. Sediment samples collected in 1996 revealed pesticide concentrations exceeding ecotoxicological thresholds, prompting changes in land use practices and adoption of more sustainable agricultural management techniques. By 2003, a more than 50% reduction in pesticide concentrations in sediments was recorded. In the USA, the establishment of a national regulatory framework has led to a decrease in sediment pesticide contamination by over 80% from the 1990s to the 2000s. Consequently, it is 'advisable for Iraq to implement regulations informed by assessment and management approaches similar to those utilized in the USA. While significant advancements have been made in the formulation of national policies aimed at reducing pesticide contamination in sediments in various countries, Iraq still requires the development of similar policies to address river sediments and safeguard river ecosystems. (Mota de Oliveira *et al.*, 2023; Jabeir *et al.*, 2024; Al-Zabad *et al.*, 2024; Al-Dabbas, 2024 ; Al-Kindi and Al-Sultan, 2024; Alshemmari, 2022; Mahmood, 2021; Grmasha *et al.*, 2023). As compared to the results of OCP with other studies, we found out that our results were with the range of previous studies (Table 2).

Table2. Comparison of the concentration of organochlorine pesticides for the current study with previous studies.

Source	Heptachlore	Lindane	∑DDT	Dieldrin	Aldrin	Endrin	Study Area
Latif *et al*., (2013)	0.096	7.9	16.7	-	-	-	Al-Hammar Marshes
DouAbul and Al-Timari(2014)	ND-42	-	0.04-220	ND-22	-	ND-47	Shatt-Al Arab
(Asadi,2021)	ND-3.5	ND	ND-3.8	0-2.1	0-0.14	ND	Shatt-Al Arab
(Gabar,2023)	0.1-1.54	0.03-0.6	0-1.26	0-0..52	0.12-3.32	0-1.35	Al-Hammar Marshes
FAO/WHO (1999)	-	1.38	8.51	6.67	-	62.4	
Current study	0.23-2.03	0.03-1.05	0.31-1.73	0.27-1.35	0.25-2.10	0.73-1.98	Tigris River

Conclusion

In the current study, it was observed that high concentrations of some chlorine pesticides in Tigris River sediments resulted from various human activities, including agriculture, pest control, and other various human activities. It was noted in the current study that the highest value of pesticides was 2.10 mg\kg for Aldrin pesticide recorded in Al-Amara station, because of the densely populated areas and the greater use of insect and rodenticides in homes, in addition to the presence of a proposal Wood and carpentry workshops. The lower organochlorine pesticides were found in the Ali Al Gharbi station (2.87 µg/kg).

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