

Bioaccumulation of total petroleum hydrocarbons and measuring the concentrations of some heavy metals in the water and two species of Gastropoda *Melanopsis costata* and *Melanopsis nodosa* in Al-Diwaniyah River, central Iraq

Dr. Qasim M. Al-taher

Departmentt.Science (Biology),

College of Basic Education, University of Sumer

Thi-Qar, Iraq. e-mail qasim20020@gmail.com

Abstract

The current study aimed to detect the level of pollution of the Diwaniyah River water and two species of gastropods (*Melanopsis costata* and *Melanopsis nodosa*) with total petroleum hydrocarbons (TPHs) and some heavy elements. Three stations were chosen to collect water samples and snails. The first station is located at the entrance to the city, the second in the city center far 12 km² and the third at the exit far 10km². chemical tests were conducted on the samples and snails to detect the level of pollution. The total levels of hydrocarbons in the water of the Diwaniyah River, were 2.4, 3.3 and 4.0 µg/g in the month of September for the three stations under study (S1,S2 and S3) respectively, while it was 2.5,3.1 and 4.3 µg/g for the month of October, respectively, for the three stations under study. The THPs in snails in the first station were the lowest 0.23 µg/g for *M. costata* and 0.31 µg/g for *M. nodosa*, followed by the second station, which was the most polluted, then the third station was the most polluted, with a rate for the snails 0.84 µg/g and 0.81 µg/g for above snails respectively. Regarding heavy metals in water, high levels of (Fe) were recorded in station three, reaching 4.1 and 4.66 ppm for the months of September and October, respectively, while (Cu) concentrations were recorded at 0.05 and 0.04 ppm for the above two months, respectively.

Heavy metals in snails were as follow: Station No. 3 was the highest contamination compared to other stations, where the concentration of heavy elements was high for (Cr), it was the highest concentration, where *M. costata* was 0.05 and 0.04 mg/g for September and November, respectively, and for *M. nodosa* 0.75 and 0.79 mg/g respectively, while (Fe) concentrations were 0.71, 0.69, 0.66 and 0.70 mg/g for the same station, species and months, respectively.

Key words: Al-Diwaniyah River, Heavy metals, *Melanopsis costata*, *Melanopsis nodosa*, petroleum hydrocarbons.

Introduction

There is widespread use of petroleum hydrocarbons, as they are used in transportation such as cars, motorcycles, trains, and airplanes, as well as in the operation of small and large factories, in addition to multiple households uses such as cooking, cleaning, and others [1]. Petroleum hydrocarbons leak into the soil, water, and air in several ways, the most important of which may be the unhealthy disposal of waste from factories, homes, and hospitals, which causes them to reach rivers or the soil. The air may be polluted in the event of disposal in the form of smoke or vapours [2 , 3] . What is meant by bioaccumulation of pollutants is the accumulation of these pollutants in the tissues of a living organism. They collect in leaves, plant roots, and even fruits. In animals, they accumulate in muscles, fats, and bodily fluids, which they enter in the form of small doses. However, when a long period passes, these pollutants reach a particularly high and frightening level. When it becomes food that people consume [4]. One of the things used to measure pollutants is bioaccumulation in the bodies of living organisms, as it gives a good indication of the extent of the danger of these pollutants and the extent to which they have reached, which raises the alarm for the concerned authorities to take their role in preventing pollution and imposing the necessary health and environmental control [5]. Al- Diwaniyah River is one of the important geographical features of the city of Al-Diwaniyah. It is the source of drinking and irrigation water in the city. It has been greatly affected recently due to the drought conditions that the region is suffering from. It is an extension and an important branch of the Euphrates River. The water level has become low and its flow is slow, which exacerbates the danger of pollutants and makes the river water not fit for human consumption [6]. Among the molluscs found in freshwater are snails, which are widespread. There are many species in Iraq, the most important of which are *M. costata* and *M. nodosa*, as they may be exposed to levels of pollution, as pollutants can be detected in their bodies. Toxins reach them indirectly when they into by contact with pollutants, and they may reach indirectly when they eat contaminated food [7] .

1.2 Aim of study:- Measuring the total petroleum hydrocarbons (TPHs) in water and evaluate them in snails belonging to *Melanopsis costata* and *Melanopsis nodosa* this is done by identifying three sample collection stations measuring the level of pollutants in the biomass of the snails above.

1.3 Description study area :

Al-Diwaniyah River is a river branching off from the banks of the Shatt al-Hilla branching off from the Euphrates in the Al-Qadisiyah Governorate, Iraq. Its length is 135 kilometers, including 121 kilometers in the Al-Qadisiyah Governorate, its width is between 20 and 25 meters, and its depth is between two and four meters. It ends at the junction of the Al-Kata'a and Abu Sukhair branches.

The city of Diwaniyah is one of Middle Euphrates region. It is the administrative, economic and political center of Diwaniyah Governorate, where all administrative and governmental institutions are located. A branch of the Euphrates River passes through it, known as Al-Diwaniyah River. It included three stations along the river course, first one at the entrance Al-Suniya district is located about 15 km north of the city, the second in the city center and the third at Al-Sudair district is located 18 km south of the city of Diwaniyah identity agricultural character.

2. Material and methods :

2.1 Collection of samples

Standard methods have been adopted for sample collection, purification and preservation for physical and chemical analysis according to the American Public Health Association (APHA, 2005). Water samples for the measurement of hydrocarbons were collected in opaque glass bottles with a capacity of 5 L and fixed in the field using carbon tetrachloride. Water samples were taken under 30 cm depth of Diwaniyah river in three locations. The first location was at the river entrance to the city of Diwaniyah at the Al-Furat neighborhood bridge, the second was in the center of the city at the Education Bridge, and the third was at the end of the city in the Rifaat neighborhood [8]. The current study included identifying three areas for collecting the snails under study, namely the two species, *M. costata* and *M. nodosa*. The snails were collected in the morning. At ten o'clock in the morning, the collection of water and snails continued weekly for two months, from September to November, when the snails were washed many times to clean them then placed in a collection of ice boxes and transported to the laboratory [9].

3. Petroleum Hydrocarbon extraction

Hydrocarbons were extracted according to the method adopted by the United Nations Environmental Protection Program (UNEP) [10]. The suspended petroleum hydrocarbons in the water were extracted as long as the suspended petroleum hydrocarbons in water were used using the blindness of the method mentioned by [11]. The quantitative concentration of aromatic hydrocarbons is measured using a fluorescence spectrophotometer, which is characterized by high sensitivity to low concentrations of aromatic compounds [12]. Hydroaromatic compounds have a high degree of stability (resonance) as well as have a sufficient ability to fluoridate, especially compounds that have multiple aromatic nuclei as it is one of the most severe compounds for fluorescence. The heavy metals in water samples were measured by using an Absorption Atomic Spectrophotometer and according to [10].

3.1. TPHS and heavy metals in snails

At each interval, 40 g of the snail flesh (after removing the shell and the operculum) was washed in saline and stored at -20°C till processing for HPLC analysis. 30 g of biomass was put in flasks and extracted by adding 60 ml of acetone and dichloromethane (1:1 v/v). TPHS were extracted by shaking method according to [14].

4. Results and discussion :

4.1. TPHs in water of Diwaniyah river :

The current study showed variable results regarding the total levels of hydrocarbons in the water of the Diwaniyah River, as it was 2.4, 3.3 and 4.0 $\mu\text{g/g}$ in September for the three stations under study (S1,S2 and S3) respectively, while it was 2.5, 3.3 and 4.3 $\mu\text{g/g}$ for October, respectively, for the three stations under study (figure 1).

This relatively high concentration is due to several reasons, including waste thrown directly and indirectly into the river by residential neighbourhoods, factories, hospitals, and some daily activities carried out on both banks of the river, such as unlicensed washing stations for washing and changing automobile oils, as well as sewage water that is dumped directly in the river bed. Power stations may play an important role, as well as brick factories that spread on the outskirts of the city [15,16] . The first station was the least concentrated in hydrocarbons, followed by the second station, then the third station, which was the most polluted. This may be because the river at the beginning of the city had not yet been exposed to waste being poured into it, unlike the second and last station, which suffered from polluting the river with hydrocarbon waste [17,18,19] .

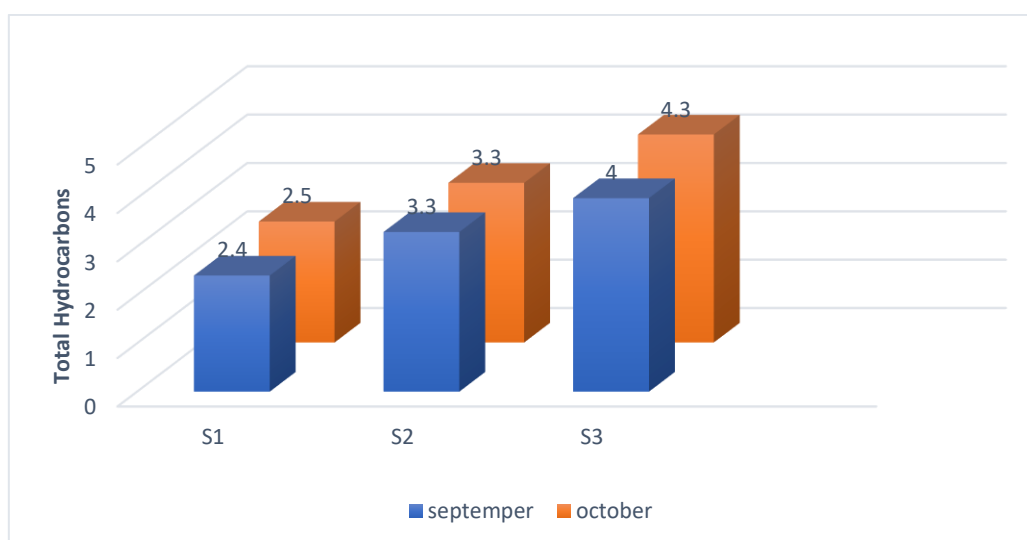


Figure (1): levels of TPHs in Al-Diwaniyah river water ($\mu\text{g/g}$)

4.2. THPs in snails:- The current study showed the presence of varying concentrations of total petroleum hydrocarbons in the tissues of snails. The first station was the lowest, as it was 0.23 $\mu\text{g/g}$ for *M. costata* and 0.31 $\mu\text{g/g}$ for *M.nodosa*, followed by the second station, which was the most polluted, then the third station was the most polluted, with a rate for the snails 0.84 $\mu\text{g/g}$ and 0.81 $\mu\text{g/g}$ for above snails respectively.

Our current study is consistent with the study of [20,21,22] , which found that aquatic organisms, especially snails, are prone to hydrocarbon pollution, which accumulates in their tissues over time, and this may cause different disease conditions for these organisms as it may be transmitted through the food chain to humans.

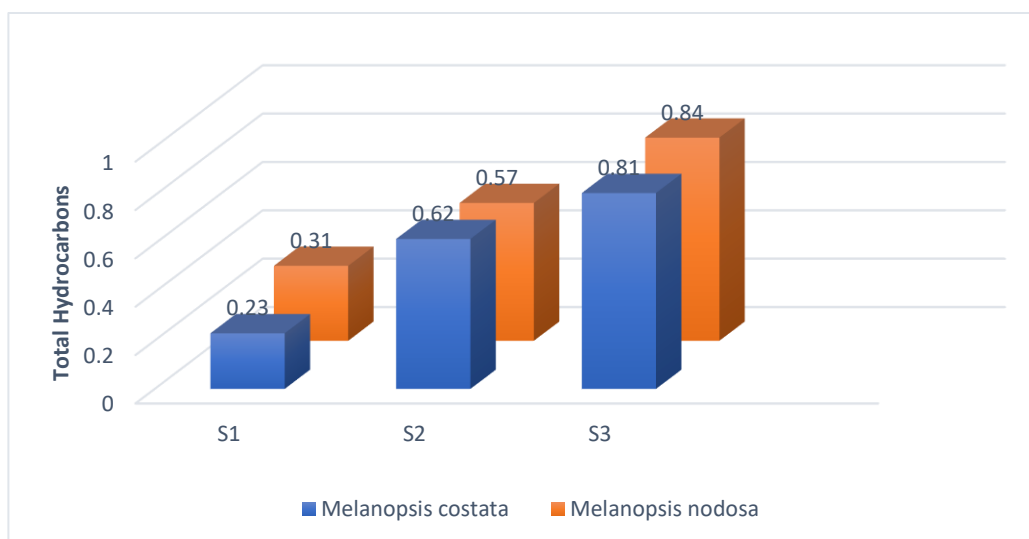


figure (2): levels of TPHs in Snails tissues (µg/g)

5. Concentration of heavy metals in water :-

The result of current study appeared that the concentration of heavy metals in water of Diwaniyah river It was the highest in the last station in the months of September and October, respectively, while it was the lowest in the first station. This may be due to the fact that the river, during its passage through the city, is exposed to the throwing of waste due to the fact that the city is densely populated, and this is accompanied by a steady increase in pollution, including These are different types of pollutants that may be organic or inorganic and may be heavy elements, especially those that are used in the manufacture of electrical appliances or that are used in wrapping things such as gifts, which may be thrown directly into the river or transformed into other forms and then make their way into the river later [17] .

High levels of iron were recorded in station three, reaching 4.1 and 4. 66 ppm for the months of September and October, respectively, while copper concentrations were recorded at 0.05 and 0.04 ppm for the above two months, respectively. Heavy metals are among the most dangerous pollutants that must be taken care of and treated immediately because they may cause cases of diseases and physiological disorders such as cancers, fetal deformities and infertility. They also affect crops and threaten food security. The process of getting rid of them is adifficult because they quickly accumulate in the environment and it is difficult to excrete them or convert them into Eco-friendly form [23] .

Table (1): concentrations of heavy metals in Al- Diwaniyah river water (ppm)

Heavy metals	S1		S2		S3	
	September	November	September	November	September	November
Cadmium						
Lead	0.000	0.002	0.001	0.000	0.003	0.002
cooper	0.01	0.01	0.03	0.02	0.05	0.04

Iron	1.22	2.00	3.55	3.61	4.10	4.66
Cadmium	0.00001	0.00000	0.00003	0.00002	0.00004	0.00004
Chromium	0.013	0.016	0.022	0.021	0.033	0.035
Mercury	0.0000	0.0000	0.0001	0.0001	0.0002	0.0003

5.1. Heavy metals in snails

Station No. 3 had the highest contamination compared to the rest of the stations, where the concentration of heavy elements was high for chromium, it was the highest concentration, where *M. costata* was 0.05 and 0.04 mg/g for September and November, respectively, and for *M. nodosa* 0.75 and 0.79 mg/g respectively, while iron concentrations were 0.71, 0.69, 0.66 and 0.70 mg/g for the same station, species and months, respectively.

Heavy elements accumulate in the bodies of living organisms when exposed to non-lethal concentrations of them, as they accumulate inside the fat and are temporarily neutralized in preparation for their excretion, but in the case of continued exposure, the proportion of heavy elements inside the body will increase, as they become fatal in the near future, and living organisms that live in water are important indicators as they give a useful picture of what pollution rates and the validity of water and rivers for human and non-human use have reached [24].

Table (2) : Concentrations of heavy metals in snails (mg/g)

Heavy metals	S1				S2				S3			
	<i>M.costata</i>		<i>M.nodosa</i>		<i>M.costata</i>		<i>M.nodosa</i>		<i>M.costata</i>		<i>M.nodosa</i>	
	Sep.	Nov.	Sep.	Nov.	Sep.	Nov.	Sep.	Nov.	Sep.	Nov.	Sep.	Nov.
Cadmium	0.11	0.14	0.20	0.13	0.22	0.24	0.26	0.25	0.33	0.29	0.30	0.34
Lead	0.33	0.31	0.29	0.34	0.46	0.40	4.28	4.80	0.61	0.55	0.58	0.60
Cooper	0.14	0.16	0.20	0.18	0.25	0.27	0.25	0.20	0.44	0.37	0.38	0.40
Iron	0.33	0.32	0.35	0.33	0.61	0.59	0.60	0.57	0.71	0.69	0.66	0.70
Cadmium	0.00	0.00	0.02	0.02	0.01	0.00	0.03	0.002	0.05	0.04	0.03	0.03
Chromium	0.31	0.33	0.32	0.33	0.61	0.59	0.66	0.60	0.81	0.77	0.75	0.79
Mercury	0.11	0.15	0.14	0.16	0.22	0.25	0.26	0.21	0.47	0.50	0.38	0.41

Conclusion : We conclude from the current study that there are pollutants from petroleum hydrocarbons and heavy metals in the water of the Diwanayah River, as well as in the snails under study, and that these pollutants increase as the river passes through the city of Diwanayah. This is due to population density and the accompanying pollution that may find its way into the river directly or indirectly.

Recommendation : Government agencies must monitor proper sanitary landfilling in designated places and ensure that pollutants do not reach the environment, especially rivers, which are the source of life. They must also find environmentally friendly ways to get rid of pollutants and not burn them or bury them underground because this does not solve the problem, and extensive studies must be conducted on the issue of pollution. Water as well as the snails under study can be considered as bioindicators of pollution.

References

- [1] S. Eriksson, L. Hallbeck, T. Ankner, K. Abrahamsson, and Å. Sjöling, "Indicators of petroleum hydrocarbon biodegradation in anaerobic granitic groundwater," *Geomicrobiology Journal*, vol. 23, no. 1, pp. 45-58, 2006.
- [2] E. V. dos Santos, C. Sáez, P. Cañizares, D. R. da Silva, C. A. Martínez-Huitle, and M. A. Rodrigo, "Treatment of ex-situ soil-washing fluids polluted with petroleum by anodic oxidation, photolysis, sonolysis and combined approaches," *Chemical Engineering Journal*, vol. 310, pp. 581-588, 2017.
- [3] H. C. Helgeson, A. M. Knox, C. E. Owens, and E. L. Shock, "Petroleum, oil field waters, and authigenic mineral assemblages Are they in metastable equilibrium in hydrocarbon reservoirs," *Geochimica et Cosmochimica Acta*, vol. 57, no. 14, pp. 3295-3339, 1993.
- [4] D. A. Vroblesky and F. H. Chapelle, "Temporal and spatial changes of terminal electron-accepting processes in a petroleum hydrocarbon-contaminated aquifer and the significance for contaminant biodegradation," *Water resources research*, vol. 30, no. 5, pp. 1561-1570, 1994.
- [5] M. N. Rahi, A. J. Jaeel, and A. J. Abbas, "Treatment of petroleum refinery effluents and wastewater in Iraq: A mini review," in *IOP Conference Series: Materials Science and Engineering*, 2021, vol. 1058, no. 1: IOP Publishing, p. 012072.
- [6] H. A. Walli, S. A. Abed, L. I. Hossain, and Z. M. Kadam, "Water quality assessment of some rivers in Al-Qadisiyah province, middle euphrates/Iraq," *Journal of Global Pharma Technology*, vol. 10, no. 11, pp. 883-891, 2018.
- [7] A. S. Al-Jasimee and H. M. Hussein, "Biodiversity of Mollusca in Dalmaj Marsh, Southern Marshland, Al-Diwaniya City, Iraq," in *IOP Conference Series: Earth and Environmental Science*, 2023, vol. 1215, no. 1: IOP Publishing, p. 012021.
- [8] M. M. Al-Hejuje, N. Hussain, and H. Al-Saad, "Total Petroleum Hydrocarbons (TPHs), nalkanes and Polynuclear Aromatic Hydrocarbons (PAHs) in water of Shatt Al-Arab River-part 1," *Global Journal of Biology Agriculture and Health Sciences N*, vol. 4, pp. 88-94, 2015.
- [9] H. FOLYÓIRAT, "Földtani Közlöny," *Földtani közlöny: a Magyarhoni Földtani Társulat folyóirata*, vol. 23, p. 161, 1893.
- [10] C. A. Petsonk, "Role of the United Nations environment programme (UNEP) in the development of international environmental law," *Am. UJ Int'l L. & Pol'y*, vol. 5, p. 351, 1989.
- [11] M. Goutx and A. Saliot, "Relationship between dissolved and particulate fatty acids and hydrocarbons, chlorophyll a and zooplankton biomass in Villefranche Bay, Mediterranean Sea," *Marine Chemistry*, vol. 8, no. 4, pp. 299-318, 1980.
- [12] M. I. Badawy and F. Al-Harthy, "Hydrocarbons in seawater, sediment, and oyster from the Omani coastal waters," *Bulletin of Environmental Contamination and Toxicology;(United States)*, vol. 47, no. 3, 1991.
- [13] G. O. Adewuyi, T. O. Etchie, and O. T. Ademoyegan, "Determination of petroleum hydrocarbons and heavy metals in surface water and sediment of Ubeji river, Warri, Nigeria," *Bioremediation, Biodiversity and Bioavailability*, vol. 5, pp. 46-51, 2011.
- [14] J. C. Akan, S. Mohmoud, B. S. Yikala, and V. O. Ogugbuaja, "Bioaccumulation of some heavy metals in fish samples from River Benue in Vinikilang, Adamawa State, Nigeria," 2012.
- [15] K. M. Hussein, S. Al-Bayati, and S. Al-Bakri, "Assessing water quality for Al-Diwaniyah River, Iraq using GIS technique," *Engineering and Technology Journal*, vol. 37, no. 7, pp. 256-264, 2019.
- [16] S. T. Jawed, Q .M. Al-Taher, A. F. Shihab. *Melanoides tuberculata* as Bioindicator of the Heavy Metal Contamination in Water and Sediment Pollution of Euphrates River at Thi-Qar province, Iraq. *Health Education and Health Promotion*. 2022 ;10(2):247-253

- [17] S. A. Al-Asadi and H. M. Al-Kafari, "Levels and sources of heavy metals pollution in the water and sediments of Al-Diwaniyah River, Iraq," *Sustainable Water Resources Management*, vol. 8, no. 4, p. 101, 2022.
- [18] S.T. Jawad, F. A. Shihab, , & Q. M. Al-Taher, (2022). Heavy metal concentrations in water, sediments, Cladophora and two fish species from Al-Masab Alamm River, Al-Nassiriya, Iraq. *Caspian Journal of Environmental Sciences*, 20(4), 805-812.
- [19] Q. M. Al-Taher, M. M. Akbar & I. H. Al-Qarooni, (2020). Estimation of heavy metals in water, sediments and bioaccumulation in pseudodontopsis Euphraticus and bellamya bengalensis in Euphrates river in al-nassiriyah city/south of Iraq. *Plant Archives*, 20(2), 1454-1460.
- [20] L. Lee, J. Stassen, A. Mcdonald, C. Culshaw, A. Venosa, and K. Lee, "Snails as biomonitors of oil-spill and bioremediation strategies," *Bioremediation journal*, vol. 6, no. 4, pp. 373-386, 2002.
- [21] Q. M. Al-taher, M. M. Akbar, & I. H. Al-qarooni, (2020). Bioaccumulation Of Total Petroleum Hydrocarbons In Pseudodontopsis euphraticus And Bellamya bengalensis, In Euphrates River, Al-Nassiriyah City/Iraq. *Journal of Basrah Researches ((Sciences))*, 46(2).
- [22] Q. M. Al-Taher, S. T. Jawad, A. F. Shihab & A. A. Maktoof ,(2022). Mollusca as Sensitive Indicator of Heavy Metal Pollution in Euphrates River/South of Iraq. *NEUROQUANTOLOGY*, 20(10), 5603-5612. [23] A. Al, A. A. F. Beg, K. Al, A. Bozdag, and H. B. Ghalib, "Spatiotemporal Analysis of Water Quality Using Water Quality Index and Heavy Metal Pollution Index: A Case Study of Al-Diwaniyah River, Iraq," *Mining Informational and Analytical Bulletin*, 2023.
- [24] A. Eman and A. T. H. T. AL-Saad, "Regional and Seasonal Variation of Polycyclic Aromatic Hydrocarbons in Water and Mollusca at Quarna North of Shatt AL-Arab River," 2019.