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Study of Pollution by Some Heavy Metals in the Water of the Tigris River in Some Areas of Salah Al-Din Governorate

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ABSTRACT

One - year study was designed in Salah al-Din Governorate from June 2022 to the end of May 2023 to evaluate the concentration of some heavy elements (lead, zinc, copper and cadmium) in the water of the Tigris River. Six sites were selectedin the governorate under study, taking into account the locations close to the sources of pollution with heavy metals and the direct effects of population centers, which are: Al-Boujwari village, Al-Hajjaj village, Wadi Sheshin area, Al-Balaj, Al-Alam district and Al-Mahzam area. Water samples were taken three times for each site during the four seasons of the year. The results of the study showed that the concentrations of heavy metals varied temporally and spatially, as the values of lead, zinc, copper and cadmium ranged between 0.62- 0.04, 0.52- 0.02, 0.88- 0.26, and 0.03- 0.005mg/ L, respectively, in the water of the study sites. Compared to the other elements, an increase in the overall rate of lead concentrations was observed. Notably, an increase was detected in most concentrations of heavy metals during summer.

INTRODUCTION

Water pollution is defined as the case of a change in the components or quality of water beyond normal ranges due to external impacts, most of it is due to human activity and all kinds of waste, including factory waste and sewage waste health, acid rain, excessive use of pesticides and chemical fertilizers, as well as the waste of animals, oil waste and its derivatives **(Vareda *et al.*, 2019)**. The sources of water pollution are diverse and numerous. It is likely that new sources will appear in the future as a result of continued progress in the field of science, technology and industry. Natural water sources, whether surface or groundwater, are polluted with heavy metals through human and animal waste that are not treated adequately, resulting in an accumulation of toxic elements such as lead, zinc, copper and cadmium. To avoid these risks, water must be subjected to treatment before distributing it into the public network. These elements are present in water in trace amounts and measured in parts per million (ppm) **(Satarug *et al.*, 2023)**. Heavy elements are defined as the elements whose specific density exceeds 5gm/ cm^3. Lead and zinc are considered among the elements necessary for life in low concentrations, they contribute to building living systems and when these elements appear in aquatic environments in high concentrations, they are usually life-limiting, meaning they are toxic **(Briffa *et al.*, 2020)**. These elements are dangerous due to its rapid accumulation in the tissues and organs of these animals. Their slow dissolution during the metabolic process or excretion exacerbates their harmful effects **(Wu *et al*., 2022)**. This disruption causes significant economic losses. Additionally, these elements are transported through human food chains, causing a lot of health damage since all heavy elements are considered toxic if they are present in high concentrations, as they have the ability to interact with cell components, disrupting their functions whether in plants, animals, or humans **(Qin *et al.*, 2021)**.

Al-Sarraj *et al*. (2019) studied the estimation of the concentrations of some heavy elements in the water and sediments of the Tigris River. Similarly, **Hashem and Dhiab (2017)** reported the concentrations of some heavy elements in different sources in the water of the Tigris River in the city of Samarra. Additionally, **Al-Obaidi *et al*. (2014)** mentioned the distribution of some heavy elements in the Tigris River. Given the danger of these elements, the current study aimed to determine the extent of water pollution with heavy elements (lead, copper, zinc, and cadmium) in the water of the Tigris River in Salah al-Din Governorate, as well as determining its suitability for drinking.

MATERIALS AND METHODS

1. Study locations

The study period lasted for one year covering four seasons from June 2022 until the end of May 2023, during which water samples were collected from six locations that were chosen according to a field survey conducted during that period, taking into account the locations close to the sources of heavy metal pollution and the direct effects of population centers in these locations in Salah al-Din Governorate, as shown in Fig. (1). The first location (L1): Baiji District, Albujwari Village. The district is considered the industrial front of the governorate due to the presence of oil refineries and thermal and chemical factories. It is also a hub for pipelines. Albujwari Village represents one of the agricultural villages affiliated with the district, which witnessed extensive military operations on its land during the past few years. This was reflected on the health of its residents and the nature of its ecosystem. The second location (L2): Al-Hajjaj village, which is one of the districts affiliated with Baiji District. This area is located south-east of the district. The Tigris River is located to the east of this area, 30km from Tikrit District, and is characterized by a rural agricultural character. The third site (L3): Tikrit District, Wadi Sheshin area. In this site, there are joint drainage networks for rainwater and house sewers, where rainwater and sewage are drained to this site by Tikrit sewers, in addition to sewage drainage from houses to the same site. The fourth site (L4): Al-Balaj. It is located in the center of the city of Tikrit and is characterized by its residential and recreational nature. It also contains fish ponds. The fifth site (L5): Al-Alam District. This area was chosen due to its complete distance from pollution. Furthermore, this area has the same geological environment and almost the same climate as the other sites, and it is of a rural agricultural nature. Lastly, site six (L6): Al-Mahzam which characterized by its agricultural nature and also contains a gravel quarry.

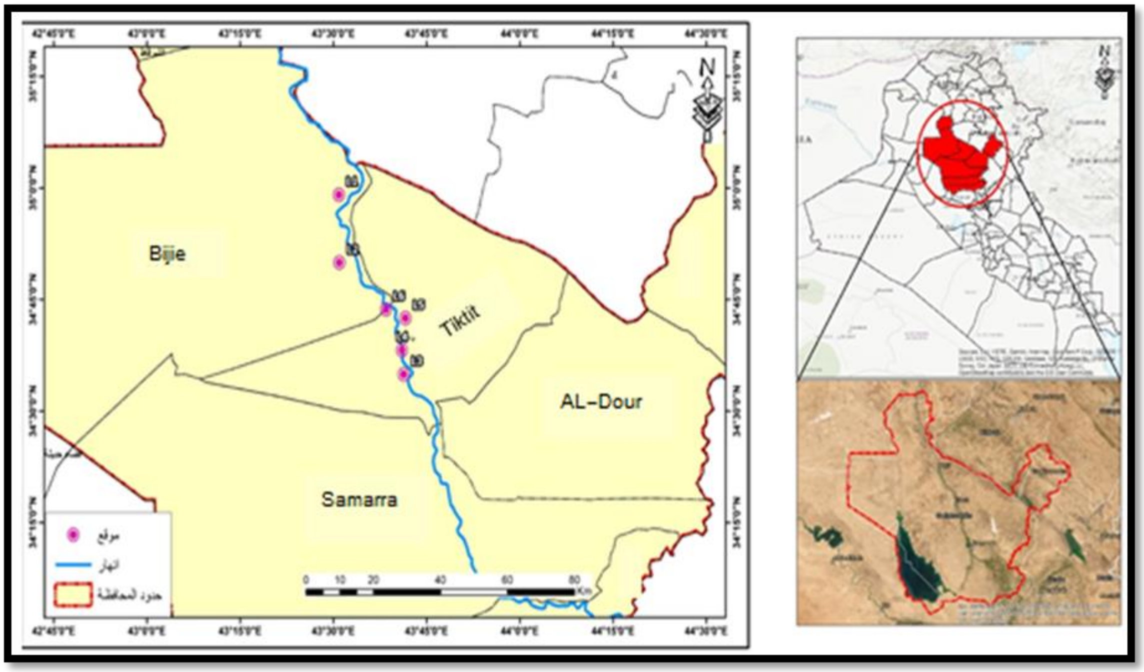

Fig. 1. A map for study locations, L1: Bijie District, Albujwari Village, L2: Al-Hajjaj village, L3: Tikrit District, Wadi Sheshin area, L4: Al-Balaj, L5: Al-Alam District, and L6: Al-Mahzam

2. Water samples collection

Dark, sterile laboratory glass bottles were used to collect water samples from several areas in three replicates for one site, some laboratory tests were conducted and real-time measurements were taken for each site.

3. Estimation of heavy metals in water

The concentrations of the heavy metals under study (lead, zinc, copper and cadmium) were estimated according to the guidelines of **APHA (2017)**. 50ml of water samples were taken from the study sites, and 5ml of concentrated nitric acid (HNO_3) was added to digest the samples. They were heated on a hot plate till reaching the pre-drying stage, then 5ml of concentrated nitric acid was added again to the samples, and heating was continued until precipitation occured. The solution was left to cool down, then distilled water was added to fill the volume to 25ml. The solution was filtered, and the samples were ready to estimate the concentrations of heavy metals in them. The absorbance of these digested samples was measured using an atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

1. Lead (Pb)

Table (1) and Fig. (1) illustrate the highest value of lead in the water of the study sites, being 0.62mg/ L in summer at the first site (Al-Bogwari village), while the lowest value was 0.04mg/ L in the winter season at the fifth site (Al-Alam District). The high concentrations may be due to the use of agricultural fertilizers containing high levels of lead, as the Albujwari village area is characterized by its agricultural character. The reason may be traced back to the fuel resulting from the use of agricultural machinery since the combustion of fuel with added tetraethyl lead ($Pb(C_4H_3)_4$) and tetramethyl lead ($Pb(CH_3)_4$) to reduce crackling inside engines can result in lead pollution, as well as the fallout of lead-contaminated particles directly into the water **(Dokmeci, 2020; Najeeb & Saeed, 2023)**. The low concentrations of lead in the Al-Alam region are ascribed to its high and rapid absorption capacity, as well as its formation of organic complexes. The results indicate that the values of lead concentrations in the study stations exceeded Iraqi specifications for the System for the Protection of Rivers from Pollution No. (25) of 1967, as well as the Iraqi specifications for drinking **(US-EPA, 2002; CEOH, 2003)**. According to the Central Agency for Standardization and Quality Control (1996), permissible lead levels should range from 0.05- 0.01mg/ L **(Radhi *et al.*, 2000)**. It was noticed that, lead concentration reached 0.049mg/ L in this study, surpassing the acceptable thresholds. These findings align with those recorded in previous studies **(Khwaidem, 2012; Mahmood & Saeed, 2023)**, where lead concentration values reached 0.04mg/ L.

Table 1. Concentration of lead in water during the study period (mg/ l)

Location / Season	L1	L2	L3	L4	L5	L6	Mean of location
Summer	**0.62**	**0.20**	**0.42**	**0.40**	٠.٣١	٠.٤٢	0.39 A
Autumn	**0.023**	**0.09**	**0.09**	**0.05**	٠.٠٥	**0.54**	0.15 C
Winter	**0.12**	**0.09**	**0.25**	**0.04**	٠.٠٤	٠.٠٥	0.10 C
Spring	**0.33**	**0.22**	**0.41**	**0.10**	٠.٠٨	٠.٠٨	٠.٢٠ B
Mean of season	0.27 a	0.15 a	0.28 a	0.15 a	0.12 a	0.28 a	

[1] The letter a represents the highest value that appears in the results. [2] Values bearing the same letter are not significantly different from each other.

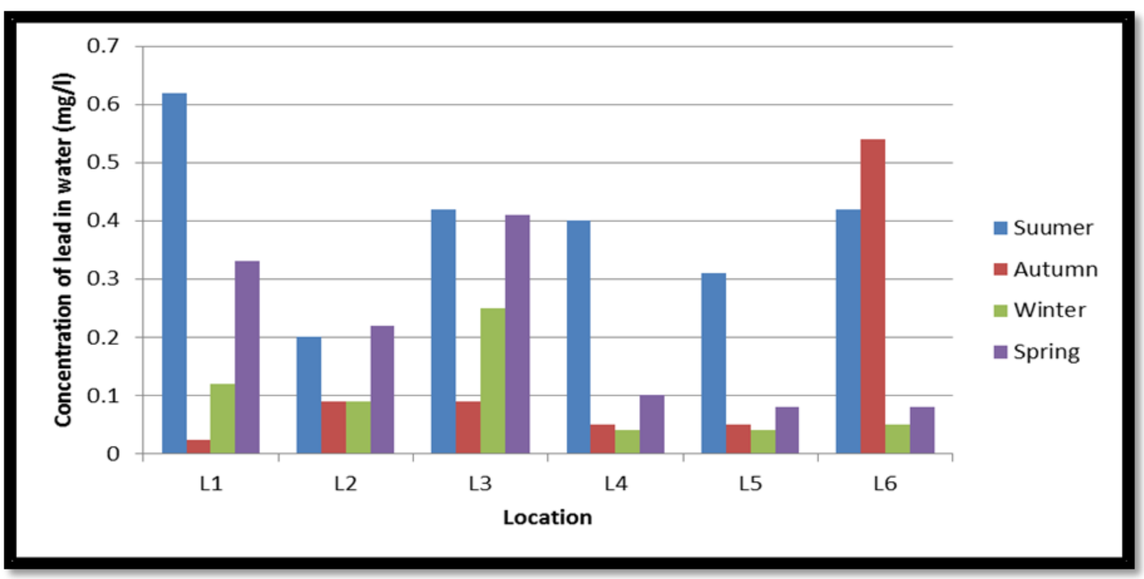

Fig. 2. Lead concentrations in water (mg/ l)

2. Zinc (Zn)

The highest value of zinc in Table (2) and Fig. (2) is 0.52mg/ L in summer at the third site (Wadi Sheshin area), and the lowest value was recorded as 0.02mg/ L in winter at the fifth site (al-Alam District). The high values in the Wadi Sheshin area were due to waste drainage. Agricultural wastes from lands are adjacent to the river that contain rodenticides such as zinc phosphorus. When ingested by animals, zinc phosphorus reacts with hydrochloric acid in the stomach, forming zinc chloride. For the remainder, which did not react with the acid, it turns into zinc hydroxide, which produces the element zinc after interacting with acids **(Satariya *et al*., 2017)**. Among them, the increase recorded in zinc concentration during summer and its decrease in winter result from the rise in water levels. Higher water levels during the summer may lead to dilution of zinc concentrations, resulting in a decrease, which aligns with our results. however, it contradicts the findings of **Al-Hamdani (2018)** and **Alwan *et al.* (2024)**, who noticed an increase in the accumulation of elements in the dry season more than in the season when rainfall increases. **Hussein (2012)** elucidated that the highest concentration of zinc is in the summer and the lowest concentration in the spring, and this confirms its absorption by plants. The sites are considered to have little pollution since they do not exceed the Iraqi limits for water adult rivers of 0.5mg/ L.

Table 2. Concentration of zinc in water samples during the study period (mg/ L)

Location / Season	L1	L2	L3	L4	L5	L6	Mean of location
Summer	٠.٣٢	٠.٤١	٠.٥٢	٠.٤١	٠.٢٢	٠.٣١	0.36 A
Autumn	٠.٢١	٠.١٨٧	٠.١٦	٠.١٤	٠.١٢	٠.١١	0.15 C
Winter	٠.٠٤	٠.٠٦	٠.٠٨	٠.٠٥	٠.٠٢	٠.٠٤	0.05 D
Spring	٠.٢٣	٠.٢٢	٠.٣0	٠.١٩	٠.١٤	٠.١٦	٠.٢٠ B
Mean of season	0.20 a	0.21 a	0.26 a	0.19 a	0.12 a	0.15 a	

[1] The letter a represents the highest value that appears in the results. [2] Values bearing the same letter are not significantly different from each other.

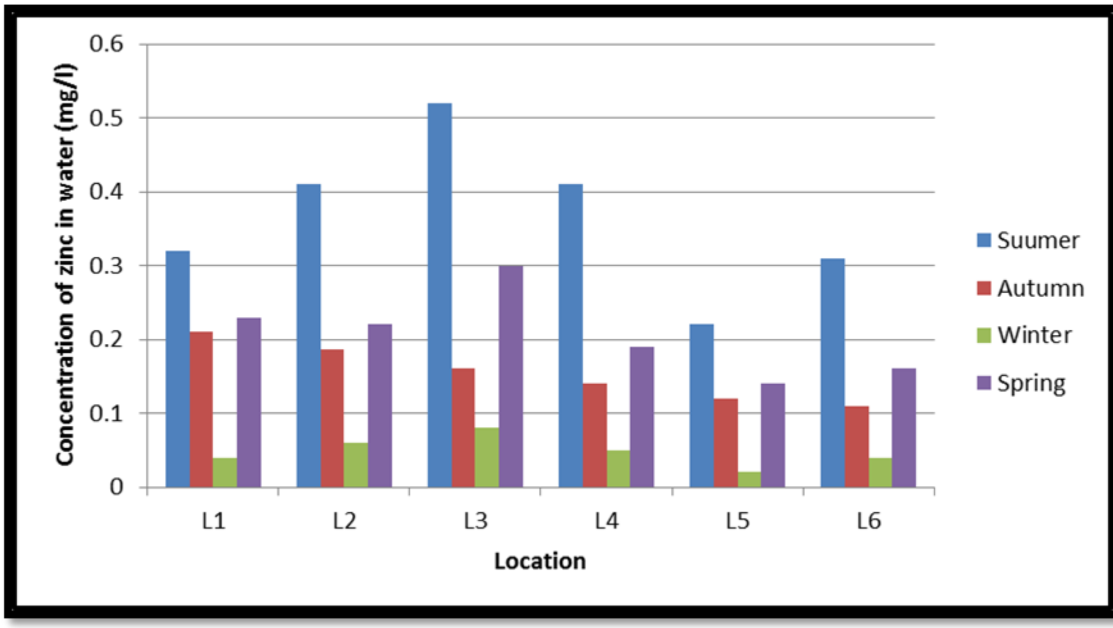

Fig. 3. Zinc concentrations in water (mg/ l)

3. Copper (Cu):

Table (3) and Fig. (3) indicate that the highest value of copper in the water of the study sites was 0.88mg/ L in the summer at the second site (Al-Hajjaj Village), and the lowest value was 0.26mg/ L in the winter at the first site (Al-Bogwari Village). The decrease in values in the first location may be because aquatic plants and animals absorbed it or because it was deposited to the bottom **(Al-Mashhadani, 2019)**. Additionally, this may be caused by the characteristics of the medium, such as oxygen concentration, quality of salts, and temperature, as indicated by **Al-Hayek (2017)**. The present values are lower than those recorded in the study of heavy metal pollution in the Mahrut River in Diyala by **AL-Obaidy *et al.* (2014)**, where they recorded values that ranged from 47- 62mg/ L, while the values are higher than those recorded by **Shartoon (2017)**, whose range was between 0.01- 0.07mg/ L, and **Al-Sarraj *et al.* (2019)**, whose range was between 0.046- 0.04mg/ L. However, the currrent values are similar to those recorded in the study of **Al-Shindah (2008)**.

Table 3. Concentration of copper in water during the study period (mg/ l)

Location / Season	L1	L2	L3	L4	L5	L6	Mean of location
Summer	٠.٤٣	٠.٨٨	٠.٦٦	٠.٧٥	٠.٣٣	٠.٥١	0.59 A
Autumn	٠.٣٤	٠.٢٦	٠.٣	٠.٢٤	٠.٢٢	٠.١٨	0.25 C
Winter	٠.٢٦	٠.٢٧	٠.٤	٠.١٥	٠.١٢	٠.١٤	0.22 C
Spring	٠.٤٢	٠.٤٨	٠.٦٢	٠.٣٣	٠.٢١	٠.٣١	٠.٣٩ B
Mean of season	0.36 a	0.47 a	0.49 a	0.37 a	0.22 a	0.28 a	

[1] The letter a represents the highest value that appears in the results. [2] Values bearing the same letter are not significantly different from each other.

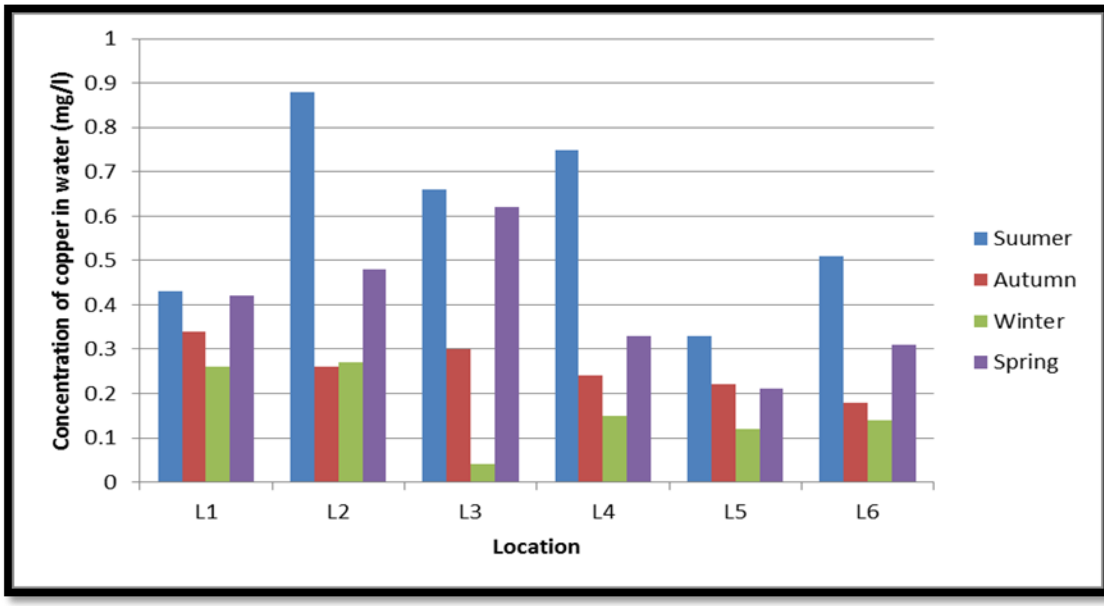

Fig. 4. Copper concentrations in water (mg/ l)

4. Cadmium (Ca)

The results of the current study in Table (4) and Fig. (4) indicate that the highest value of cadmium in the water of the study sites was 0.03mg/ L in the summer at the fifth site (Al-Alam District), and the lowest value was 0.005mg/ L in the fall at the first site, Al-Boujwari village. The increase in the concentration of cadmium in Al-Alam district is due to the direct additions to phosphate fertilizers, as well as the presence of this element in some plant species such as in tobacco, or may be due to population and industrial activity entering into many industries, such as the manufacture of car tires and dry batteries, and in some lubricating fats and engine lubricants, as well as wastewater. Regarding the effect of cadmium on the chemical and physical properties of the soil and the presence of some other elements **(Schaefer *et al.*, 2020)**, its decrease or absence at times may be attributed to factors such as rainfall and floods, which can dilute its concentration, as well as the location's distance from factories releasing cadmium in their waste **(Agyeman *et al.*, 2022; Younis& Saeed, 2023)**. The results of the current study are lower than those recorded by **Hashem and Dhiab (2017)** in their study on the concentrations of heavy metals in the city of Samarra in central Iraq. In addition, the current values are lower than what was recorded by **Muhammad *et al.* (2018)** in their study on the Tigris River, as cadmium values rose to reach 0.14mg/ l. Moreover, the current study findings are consistent with the results of **Al-Mashhadani (2012)** in his study on the quality of the Karkh water project in Tarmiya. Notably, the results of the cadmium values are close to the permissible limit of the Iraqi specifications for the System for the Protection of Rivers from Pollution No. (25) of the year (1967) and the Iraqi specifications for drinking, as well as the the Iraqi specifications for drinking water outlined by the Central Organization for Standardization and Quality Control in (1996), which range from 0.01- 0.003mg/ L.

Table 4. Concentration of cadmium in water during the study period (mg/ l)

Location / Season	L1	L2	L3	L4	L5	L6	Mean of location
Summer	**0.02**	**0.01**	**0.01**	**0.01**	٠.٠٣	٠.٠١	0.0161 A
Autumn	**0.005**	**0.006**	**0.006**	**0.007**	٠.٠٥	٠.٠٠٧	0.0066 C
Winter	**0.013**	**0.009**	**0.016**	**0.016**	٠.٠١	٠.٠٠٩	0.0124 B
Spring	٠.٠١	٠.٠١٣	٠.٠١	٠.٠١	٠.٠١	٠.٠١	٠.٠١٣٨ AB
Mean of season	0.013 a	0.009 a	0.012 a	0.012 a	0.015 a	0.009 a	

[1] The letter a represents the highest value that appears in the results. [2] Values bearing the same letter are not significantly different from each other.

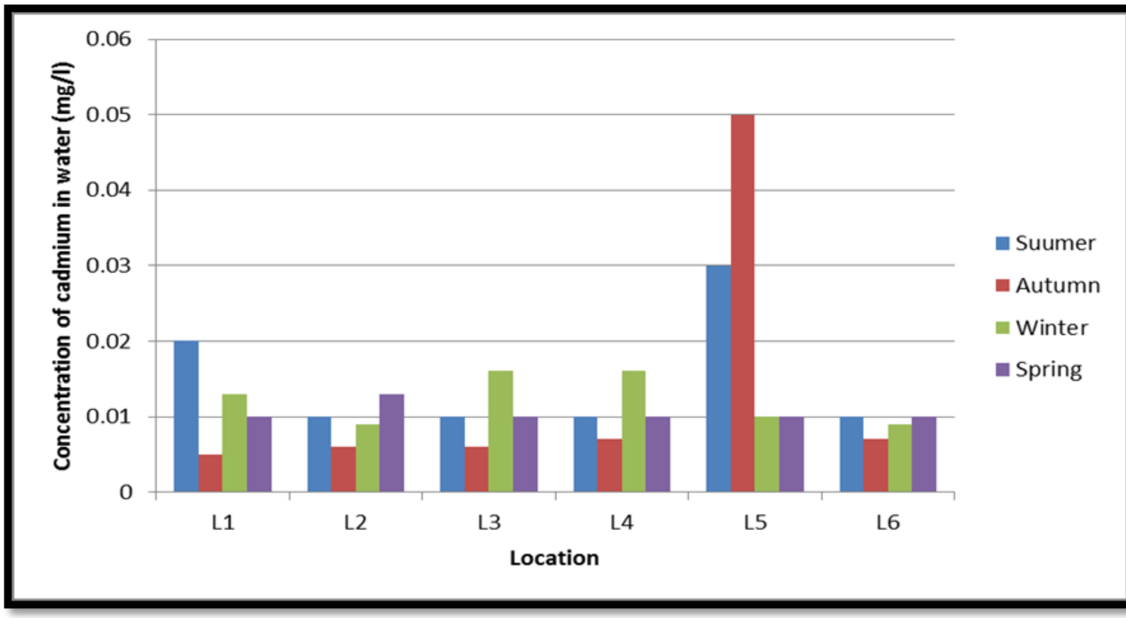

Fig. 5. Cadmium concentrations in water (mg/ l)

CONCLUSION

The study revealed that there was a clear difference in the concentrations of heavy metals during the different seasons of the study, as the concentrations were at their highest in summer and lowest in winter in general, with lead recording the highest pollution rates compared to the other elements. Population and industrial activities have had a clear impact on increasing heavy metal concentrations, particularly in locations closer to the city, where pollution is more prevalent.

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