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المجلة العراقية لبحوث السوق وحماية المستهلك

EFFECT OF LOCAL HONEY PRODUCTION AREAS ON ITS CONTENT OF SOME HEAVY METALS

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ABSTRACT

This study was conducted to estimate some heavy metals cadmium, lead, nickel and iron in 15 samples of Iraqi honey with 3 replicates for each sample which were collected from apiaries near potential contamination areas in five Iraqi governorates, including Baghdad, Karbala, Babylon, Diyala and Salah al-Din. The atomic absorption technique was used to estimate the concentrations of heavy metals, the results showed that there were significant differences at (P≤0.05) between the concentrations of these elements in the honey samples, the highest concentrations of cadmium 0.123 mg/kg were recorded in Baghdad, near the petrochemical production complex, lead 4.657 mg/kg and nickel 0.023 mg/kg in Babylon near the power plant, iron was 1.863 mg/kg in Karbala near the waste collection and incineration plant, and all the concentrations of cadmium and lead in the studied honey samples were higher than the acceptable limits set by the European Commission Regulation.

Keywords: Honey, heavy metals, pollution.

أثر مناطق إنتاج العسل المحلي في محتواه من بعض المعادن الثقيلة

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الخلاصة

أجريت هذه الدراسة لتقدير بعض المعادن الثقيلة كالكادميوم والرصاص والنيكل والحديد في 15 عينة من العسل العراقي بواقع 3 مكررات لكل عينة والتي جمعت من مناحل بالقرب من مناطق التلوث المحتملة في خمس محافظات عراقية شملت بغداد وكربلاء وبابل وديالى وصلاح الدين، استعملت تقنية الامتصاص الذري لتقدير تراكيز العناصر الثقيلة، أظهرت النتائج وجود فروق معنوية عند (P≤0.05) بين تراكيز هذه العناصر في عينات العسل، وسجلت اعلى تراكيز للكادميوم 0,123 mg/kg في بغداد بالقرب من مجمع انتاج البتروكيمياويات، والرصاص 4,657 mg/kg والنيكل0,023 mg/kg في بابل بالقرب من محطة توليد الكهرباء، والحديد1,863 mg/kg في كربلاء بالقرب من محطة تجميع وحرق النفايات، وكانت جميع تراكيز عنصري الكادميوم والرصاص في عينات العسل المدروسة أعلى من الحدود المقبولة التي وضعتها التشريعات الصادرة عن المفوضية الاوربية.

الكلمات المفتاحية: عسل، معادن ثقيلة، تلوث.

INTRODUCTION

Honey is one of the oldest known natural foods that humans use it as a complete food all over the world, it is used in various drugs and medicines to treat many diseases **(Patial *et al.*, 2018)**, according to the **European Commission (2001)**, honey is the natural sweet-tasting substance produced by honey bees (*Apismelifera*) from the nectar of plants or from some living secretions of plants, as honey bees absorb the nectar and collect it inside a special bag with certain special substances, then it secretes it outside the bag to be deposited, dried and stored inside the honeycomb discs to mature. The main nutritional components in honey make it easy to digest, the most important of which are trans sugars such as glucose and fructose, which provide the body with energy, as well as secondary components that are considered useful nutrients such as proteins, amino acids, vitamins, oils, volatile chemical compounds, flavonoids, phenols, and minerals **(Baglio 2018)**, in addition to its high nutritional value, honey is one of the foods with unique therapeutic properties. It is used in traditional medicine to treat diabetic ulcers, external wounds, some allergic conditions, pharyngitis, coughs, and digestive problems. It has antimicrobial properties **(Alvarez-Suarez *et al.*, 2010)**. The quality of honey and its biochemical properties depend on the source of nectar that the bee absorbs, the geographical area, climatic conditions, maturity period, production methods, processing and storage conditions **(Oses *et al*., 2016)**, and to ensure its safety as a food, honey must be free from any undesirable pollutants such as heavy metals, the presence of which has recently become more evident in many foods, including honey, and because it has a long biological half-life and is unable to degrade in the environment, it is included in the food cycle of plants, animals and humans, the process of consuming food is the main way for these minerals to reach the human body, and long-term consumption of food contaminated with heavy metals such as arsenic, lead, mercury, cadmium and others causes the accumulation of these minerals in the various organs of the body, causing serious damage to public health, it may lead to the development of cancer, cardiovascular and neurological disorders, and significant risks to the growth and development of fetuses **(Abu- Almaaly & Al-Tamimi 2020; Mahmoudi *et al.*, 2015)**, the concentration of heavy metals in honey depends on the geographical origin and the environment in which the flower grows, and its presence indicates that the beehives were near the sources of pollution, the conditions of air movement and the soil in the region play an important role in increasing the pollution of honey with metals. The honey bee flies and covers

large areas and contacts many surfaces during its activity to search for nectar, so it is the main carrier of heavy metals to beehives and honey (**Roman & Popiela 2011**), the impact of heavy metal pollution as a result of industrial, agricultural and commercial activity on the health of bees and the quality and safety of honey has been documented due to its exposure to potential pollutants from industrial areas, the use of fertilizers and pesticides during agriculture, waste collection and treatment areas, and proximity to electrical stations and highways, which affects air and soil pollution, consequently, it pollutes the flowering plants that grow near those areas (**Lambert et al., 2012; Alisawi 2013**), this makes the study of honey contamination extremely important in the field of food safety, especially if we take into account that the majority of honey consumers are among sensitive groups such as children, adolescents, pregnant and lactating women and the elderly,in addition to its widespread use in most therapeutic foods and medical preparations for all age groups (**Silici et al., 2013**), in view of the wide geographical area in which honey is produced in Iraq from north to south and the different environmental and geographical conditions and economic and consumer activity among them, the study aimed to show the impact of honey production areas in some Iraqi cities in its content of some heavy metals.

MATERIALS AND METHODS
Sample collection

Fifteen samples of local honey were collected with 3 replicates for each sample from 5 Iraqi governorates (Baghdad, Karbala, Babilon, Diyala, Salah al-Din), in the period March to May, 2020, from honey production apiaries closest to the potential contamination sites, as shown in (Table 1), samples (100 g for each) were collected from each governorate, taken from 3 sites close to the pollution areas, and these replicates were mixed together to form one representative sample for each of those governorates, the samples were placed in clean glass containers, and observations were recorded on them, then transferred to the laboratory to be kept in the refrigerator at 4°C until the required analyzes are performed on them.

Table (1): Details of honey samples.

Governorates	No. of samples	Sample code	Possible contamination sites
Baghdad	3	S_1	Petrochemical production complex
Karbala	3	S_2	Industrial waste incineration
Babilon	3	S3	Electrical power plant
Diyala	3	S_4	Oil extraction and refining complex
Salah al-Din	3	S_5	Fertilizers and pesticides production

Preparation of samples and standard solutions and determination of heavy metals

The method adopted by **Chandrama et al. (2014)**, where 5 g of each sample was placed in a silica dish and the dishes were slowly heated on a hot plate until it was completely burned, the dishes were transferred to the incineration oven, which was set at 450°C, for two hr, until the samples turned to ash, the ashes of each sample were placed in a ceramic jar, and a small amount of concentrated HCl was added to it for the purpose of extracting minerals. It was placed on a hot plate to evaporate and dry, and the ashes would turn white, then the extraction process was repeated a second time by adding 10 mL of acid HCl (25%) and filtering the resulting solution and then completing the amount to 50 mL by adding more acid HCl, this solution was used for the determination of the heavy metals lead (Pb), cadmium (Cd), iron (Fe) and nickel (Ni), standard solutions of the elements were prepared according to the instructions of the supplied company, and the concentrations of heavy elements were analyzed

and measured twice for all samples under study by using Shimadzu AA-6200 supplied with ASC 6100 auto sampler atomic absorption spectrometer equipped with acetylene gas.

Statistical analysis

The Statistical Analysis System (**SAS 2012**) program was used to detect the effect of difference factors in study parameters. Least significant difference-LSD test (Analysis of Variation-ANOVA) was used to significant compare between means in this study.

RESULTS AND DISCUSSION

The rates of heavy metals concentrations in honey samples according to potential contamination areas show in (Table 2). Each result represents an average of three samples collected randomly from a specific area, and heavy metal concentrations were compared with the acceptable limits set by the **European Commission Regulation (2006)**, depending on the results of this study, the rates of cadmium concentrations in honey samples ranged between 0.073 to 0.132 mg/kg, all of which are higher than the acceptable limits approved by **European Commission Regulation (2006)** of 0.05 mg/kg, and significant differences appeared at the level ($P<0.05$) between the concentrations of this element according to the honey samples in the potential contamination areas, it is clear from (Figure 1), that the highest pollution levels were in sample S_1 (0.132 mg/kg) in Baghdad near the petrochemical complex and sample S_5 (0.126 mg/kg) in Salah al-Din near the fertilizer and pesticide production plants. **Dhahir & Hemed (2015)** reported that cadmium concentrations in Iraqi honey samples ranged between 0.210 to 0.894 mg/kg. **Alisawi (2013)** in his study of Iraqi honey, indicated that the cadmium concentration ranged between 0.208 to 0.571 mg/kg, he explained that the high concentration of this element in honey in some governorates may be due to the large number of materials containing its compounds, such as plastic waste that is spread widely, waste of used and damaged batteries, the frequent circulation of dyes, and even the smoke of many cigarettes that contains significant levels of cadmium, the results of the study of **Mahmoudi et al. (2015)** in fertilizer production areas and **Bartha et al. (2020)**, near the industrial waste collection areas, the cadmium concentration in honey samples was 0.131 and 0.125 mg/kg, respectively, for the two studies, while the percentage of cadmium contamination in Ethiopian honey samples increased to 3.021 mg/kg in areas close to phosphate fertilizer production plants (**Nega et al., 2020**).

Lead is a non-essential element in the human body, and it is known that its accumulation in the tissues and organs of the body can cause neurotoxicity, anemia, and danger to the liver and kidneys, as well as other serious symptoms (**Public Health England 2019**), lead concentrations in honey samples under study ranged between 2.492 to 4.657 mg/kg as shown in the (Table 2), significant differences were recorded at ($P\leq0.05$) between the concentrations of the samples, and all of them were higher than the acceptable limits approved by **European Commission Regulation (2006)** of 0.5 mg/kg, the highest concentration of lead was 4.657 mg/kg in sample S_3 in Babylon, near a power plant, followed by the other samples that were collected from areas near a complex for the production of petrochemicals, waste treatment plants, oil production and refining sites, as well as those areas near plants for the production of fertilizers and pesticides, as shown in (Figure 2), which shows the rates of lead contamination of honey samples, both of **Chandrama et al. (2014)** and **Salama et al. (2014)**, pointed out the high concentration of lead in honey produced in contaminated areas similar to what was mentioned above, reaching 4.22 and 5.14 mg/kg respectively, while the concentrations of lead were low in all Iraqi honey samples, according to the study conducted by the two researchers. **Dhahir & Hemed (2015)** it reached 0.108-0.820 mg/kg, while **Alisawi (2013)**, when he studying honey pollution in the areas of Najaf governorate in Iraq, stated that

all samples were contaminated with varying concentrations of lead, ranging from 2.64 to 10.37 mg/kg, he pointed that the reason for this significant increase in the levels of this element in Iraqi bee honey in the environment of Najaf governorate, whether in the air, soil or water, is due to the increase in industrial and consumer activity of the population, because lead can be found in any part of our environment, most cars depend on gasoline containing a high percentage of lead, which volatilizes into the air, the air and many of our household waste, according to what was confirmed by the **United States Environmental Protection Agency (1992)**, contains this toxic element, such as house and car paint, book and newspaper papers, printer ink, water pipes, metal tanks, fertilizers, pesticides, and even some children's toys, the high levels of this pollution were recorded in **Alisawi (2013)** study in Kufa, and the high concentration of lead may be due to the proximity of the apiary from which the honey was collected from the Kufa cement factory, and the southeast winds that blow in the summer over the place where bees fly can carry the smoke of the factory to the nectar collection area.

Nickel is one of the elements with low levels when it is present in the environment, increased exposure to it can cause a range of health effects on the respiratory system such as inflammation, lung fibrosis and tumors **(European Commission 2001)**, the joint committee of experts between **FAW-WHO Organization, (2003)** on food additives determined that the level of nickel taken daily, whether through water, food or air, does not exceed 5 mg/kg of body weight, as can be seen from the (Table 2) and (Figure 3), cadmium concentrations in all honey samples in this study were within the acceptable limits approved by these organizations, and ranged between 0.023 mg/kg in sample S_3 and 0.002 mg/kg in sample S_1, **Dhahir & Hemed (2015)** indicated that the concentration of nickel 0.117 - 0.440 mg/kg in Iraqi honey samples was higher than what was found in this study, and the results of the studies of **Oroian et al. (2016)**; **Nega et al. (2020)**; **Mahmoudi et al. (2015)** approach to what was recorded by this study, it recorded low cadmium concentrations of 0.026 mg/kg in Romania, 0.009 mg/kg in Ethiopia and 0.087 mg/kg in Iran, respectively, for honey samples collected from its production sites near industrial areas.

Iron is one of the vital essential minerals that have an important role in the activities of the human body, and it is the basis for the formation of hemoglobin in the blood and is necessary in the process of cellular respiration through the bloodstream **(Abu-Almaaly 2019)**, so, its percentage in foods should be within the acceptable limits and according to the body's need. The **Codex Standard Alimentarius (1982)**, set the upper limit for iron concentration, which is present in sweet nutrients such as honey, at 1.5 mg/kg, referring to (Table 2), the honey samples under study recorded rates for this element ranging from 1.863 to 0.521 mg/kg (Figure 4), and thus most of the samples are within the acceptable limits of iron concentration, except for the sample S_2, which was collected near the waste collection and burning areas, which rose slightly from acceptable limits for iron, **Spiric et al. (2019)** and **Oroian et al. (2016)** indicated that iron concentrations were high in honey samples collected in areas close to waste collection and treatment plants and petrochemical industry complexes, reaching 3.94 and 2.51 mg/kg, respectively, while the study of **Dhahir & Hemed (2015)** recorded very low iron concentrations in Iraqi honey samples were 0.002-0.034 mg/kg.

Table (2): Concentration of heavy metals in local honey samples.

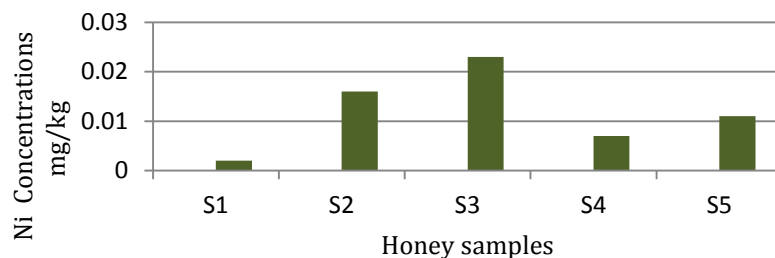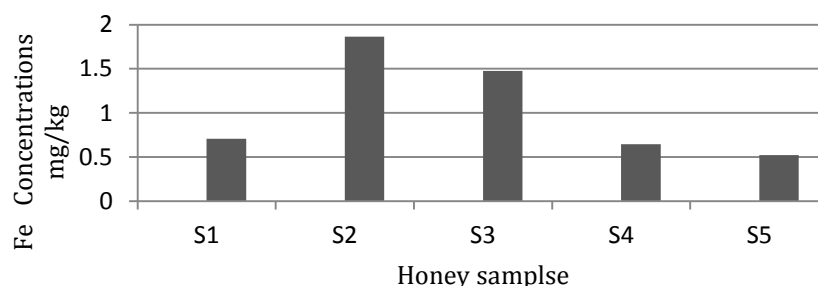| Samples	Heavy metals (mg/kg)							
	Cd	Range	Pb	Range	Ni	Range	Fe	Range
S_1	0.132 ±0.06 a	0.108-0.125	3.637 ±0. 14 b	2.974-4.185	0.002 ±0.0007 b	0.001-0.003	0.707 ±0.08 b	0.496-0.871
S_2	0.095 ±0.02 ab	0.087-0.102	3.566 ±0.11 b	3.104-4.211	0.016 ±0.003 a	0.011-0.025	1.863 ±0.10 a	1.753-2.023
S_3	0.073 ±0.01 b	0.059- 0.094	4.657 ±0.17 a	3.975-5.201	0.023 ±0.006 a	0.019-0.032	1.476 ±0.08 a	1.284-1.729
S_4	0.074 ±0.02 b	0.054 - 0.098	2.492 ±0.07 c	2.334 -2.718	0.007 ±0.001 b	0.004 -0.012	0.645 ±0.08 b	0.488-0.914
S_5	0.126 ±0.04 ab	0.098 -0.143	3.558 ±0.12 b	3.243-4.015	0.011±0.002 ab	0.009-0.013	0.521±0.07 b	0.398-0.752
LSD value	0.0559 *	---	0.892 *	---	0.0113 *	---	0.568 *	---
Means having with the different letters in same column differed significantly. * ($P \leq 0.05$). The result is an average of three samples.								
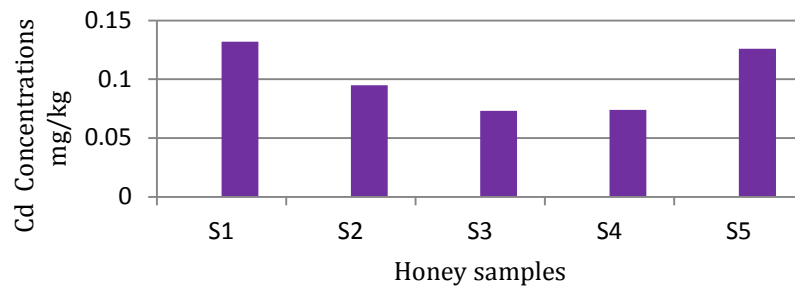
Figure (1): Cadmium concentrations in honey samples.
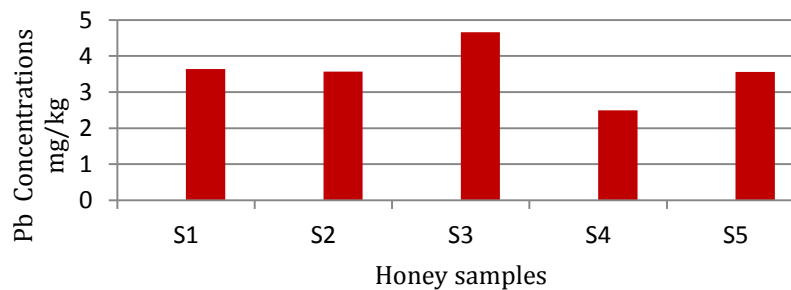
Figure (2): Lead concentrations in honey samples.

Figure (3): Nickel Concentrations in Honey Samples.

Figure (4): Iron concentrations in honey samples.

CONCLUSION

The results of this study showed that the local honey samples contained varying concentrations of heavy metals according to the areas of their collection. The concentrations of cadmium were S1>S5>S2>S4>S3 in descending order, the highest concentration was recorded in honey samples in Baghdad near the Petrochemical Production Complex, while the highest concentrations of lead were recorded in Babylon near the power plant, followed by the rest of the samples in descending order S3>S1>S5>S2>S4. The concentrations of nickel in the Babylon honey samples were also higher than the rest of the governorates S3>S2>S5>S4>S1, honey samples from Karbala near the waste treatment complex recorded the highest concentrations of iron S2>S3>S1>S4>S5. From these results, it is clear that the pollution caused by industrial areas, waste treatment places and power plants has a significant impact on the surrounding environment as a whole, whether plants, animals or humans, and honey apiaries should not be located in places close to industrial and commercial areas.

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