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Examination and comparison of certain heavy metals in honey

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Abstract

Given the importance of honeybees and their products, in addition to the fact that the products are considered a mirror of the environmental conditions surrounding the bees, which affect the health of individuals and the stability of the colony and affect the food chain that follows it. Random twelve honey samples from four countries, China, Lebanon, Egypt, and Saudi Arabia, were compared for four heavy elements: Lead, Cadmium, Molybdenum, and Cobalt. Using dried samples in a temperature-controlled muffle furnace at 550 °C, and determination of minerals by Atomic Absorption Spectrophotometer. The results obtained showed that the general residues of lead (67.17 mg/100 g) and molybdenum (72.52 mg/100 g) recorded a significant increase over the elements Cadmium (15.08 mg/100 g) and Cobalt (21.42 mg/100 g), which were equal in significance, and this was regardless of the countries. As for the total contamination with the four elements, honey samples taken from Saudi Arabia showed the highest significant increase (57.86 mg/100 g) compared to the rest of the countries, China, Lebanon, and Egypt, (35.73 mg/100 g, 41.72 mg/100 g, 40.89 mg/100 g), respectively. Mitigating these risks involves reducing environmental contamination, promoting practices that support bee health, and increasing awareness about the impact of heavy metals on pollinators.

Introduction:

Heavy metals can dissolve in various media, including water, soil, and biological tissues, depending on their chemical form, pH, temperature, and other environmental conditions. Many heavy metals can dissolve in water, especially in their ionic forms. For example, lead, cadmium, and copper can exist as cations in aqueous solutions. Factors like pH and the presence of complex agents (such as organic matter) can influence their solubility. For instance, acidic conditions often increase solubility (Dudka and Miller, 1999; Datta and Young, 2005; Peralta-Videa *et al*., 2009; Singh and Prasad, 2011, and Uddin *et al*., 2021).

Heavy metals can pose significant health and environmental risks due to their toxicity and persistence in the environment. Such exposure to heavy metals like lead, mercury, cadmium, and arsenic can lead to various health issues, including neurological damage, kidney damage, respiratory problems, reproductive issues, and increased risk of cancer (Leyssens *et al.*, 2017; Lauwerys and Lison, 1994, and Briffa *et al.*, 2020), which accumulate in the tissues of living organisms over time, leading to higher concentrations in the food chain. This can affect not only the organisms directly exposed but also predators higher up the chain, including humans, who contaminate soil and water, affecting plant growth and disrupting ecosystems (Maurya and Malik, 2019; Raj and Maiti, 2020; Mukherjee *et al.*, 2021; Agbugui and Abe, 2022, and Edo *et al.*, 2024).

Heavy metals can pose significant dangers to honeybees and their development. Heavy metals such as lead, cadmium, and mercury can be toxic to bees. Exposure can occur through contaminated nectar, pollen, or water sources. Toxic effects can lead to impaired foraging behavior, reduced reproductive success, and increased mortality rates. Exposure can affect the development of bee larvae and pupae. Sub-lethal concentrations may disrupt normal growth, leading to malformed or weaker individuals that are less capable of surviving and performing necessary tasks within the colony and causing Immune System Suppression, making them more susceptible to diseases and parasites, such as Nosema and Varroa mites. This can result in increased colony mortality and reduced overall health. Exposure to heavy metals can alter the foraging behavior of bees, reducing their ability to locate food sources effectively. This can impact the entire hive's food supply and survival, cause oxidative stress, and cause damage to DNA, which can lead to long-term health issues and reduced fitness of bee populations. As honeybees are vital pollinators, heavy metal contamination can indirectly affect agricultural ecosystems by reducing pollination efficiency, leading to lower crop yields and biodiversity loss. Heavy metals can accumulate in the bee body over time, leading to chronic toxicity even at low levels of exposure, which can further impact colony health and longevity (Zhelyazkova *et al.*, 2010; Moroń *et al.*, 2014; Burden, 2016; Polykretis *et al.*, 2016; Goretti *et al.*, 2020; Monchanin *et al.*, 2023, and Li *et al.*, 2024).

Bee products can become contaminated with heavy metals through several pathways: contaminated forage bees collect nectar and pollen from flowers that may be growing in soil contaminated with heavy metals. This can occur near industrial sites, highways, or agricultural areas where heavy metals have been used in fertilizers or pesticides. Bees may come into contact with contaminated water sources, which can affect the quality of honey and other products. Industrial emissions or vehicle exhaust can settle on vegetation, affecting the plants that bees forage on. This can lead to the accumulation of heavy metals in nectar and pollen, while the use of certain beekeeping equipment and materials, such as painted hive boxes or contaminated wax, can introduce heavy metals into bee products. For example, older paints may contain lead, and some wax may be contaminated if sourced from polluted environments. Bees may be exposed to heavy metals through supplemental feeding. If beekeepers provide sugar syrups or pollen substitutes that are contaminated, these can introduce heavy metals into the hive, or during the processing, transport, or storage of bee products, contamination could occur if the materials used (Containers and transport vehicles) are contaminated with heavy metals. Over time, bees can accumulate heavy metals in their bodies, which may then be transferred to hive products like honey, beeswax, propolis, and royal jelly (Bogdanov, 2006; Roman, 2010; Zafeiraki *et al.*, 2022; Atarshchykova *et al.*, 2023, and Végh *et al.*, 2023).

This research aims to examine twelve honey samples from four countries: China, Lebanon, Egypt, and the Kingdom of Saudi Arabia, and compare them to the presence of four heavy elements: lead, cadmium, molybdenum, and cobalt.

Materials and methods

Twelve honey samples were collected from four countries; China, Lebanon, Egypt, and Saudi Arabia collected three replicates for each country stored under the same conditions at 4ºC until analysis according to the Central Laboratory, Horticulture Research Institute, Agricultural Research Center (ARC). Ash content, using a known weight of the dried sample, two grams were weighed in a porcelain crucible and placed in a temperature-controlled muffle furnace at 550ºC for several hours until a constant weight was obtained by A.O.A.C. (1990). The percentage of ash was calculated on a dry weight basis. The ash dissolved in HCL 0.1N for determination of minerals, lead (Pb), cadmium (Cd), molybdenum (Mo), cobalt (Co) by Atomic Absorption Spectrophotometer. Pyeunican SP1900, according to Brandifeld and Spincer (1965).

Statistical analysis: Obtained results were subjected to simple correlation, regression, and multiple regression using Procs Corr and Reg in SAS (Anonymous 2003).

Results and discussion

The obtained data in Table (1) shows the following: Lead, cadmium, molybdenum, and cobalt were recorded a value from honey samples collected from China, they were 41.23 mg/100 g, 13.01 mg/100 g, 39.59 mg/100 g, and 18.48 mg/100 g, respectively, and showed 78.80 mg/100g, 15.50 mg/100g, 86.73 mg/100g and 22.07 mg/100g, respectively, for honey samples collected from Lebanon, while honey samples collected from Egypt recorded 57.18 mg/100 g, 12.32 mg/100 g, 76.56 mg/100 g, and 17.50 mg/100 g, respectively, and honey samples collected from Saudi Arabia showed 82.43 mg/100 g for lead, 19.04 mg/100 g for cadmium, 102.93 mg/100 g for molybdenum, and 27.03 mg/100 g for the element cobalt. Accordingly, the levels of lead and molybdenum pollution in China, Lebanon, and Egypt were higher than the averages, with a significant difference from the other two elements, cadmium, and cobalt, while the honey samples collected from Saudi Arabia showed significant differences between the mean of the elements, the lowest of which was cobalt and the highest of which was molybdenum.

Table (1): Screening comparison of some heavy metals in honey collected from China, Lebanon, Egypt, and Saudi Arabia.

Country	Rep.	Elements (mg/100g)				
		Lead (Pb)	Cadmium (Cd)	Molybdenum (Mo)	Cobalt (Co)	Mean
China	1	41.23	13.01	39.59	18.48	28.08
	2	76.43	14.59	52.67	20.71	41.10
	3	72.97	12.92	47.83	18.35	38.02
	Mean	63.54 a	13.51 b	46.70 a	19.18 b	35.73 b
Lebanon	1	57.88	11.14	36.21	15.82	30.26
	2	59.91	19.75	68.74	28.04	44.11
	3	78.80	15.50	86.73	22.07	50.78
	Mean	65.53 a	15.46 b	63.89 a	21.98 b	41.72 b
Egypt	1	46.26	12.79	59.05	18.16	34.07
	2	50.77	10.89	92.69	15.47	42.46
	3	74.51	13.29	77.95	18.88	46.16
	Mean	57.18 a	12.32 b	76.56 a	17.50 b	40.89 b
Saudi Arabia	1	76.62	19.58	108.30	27.80	58.08
	2	83.26	18.93	101.10	26.87	57.54
	3	87.40	18.61	99.38	26.42	57.95
	Mean	82.43 b	19.04 d	102.93 a	27.03 c	57.86a
Mean		67.17 a	15.08 b	72.52 a	21.42 b	

Total pollution with the four elements in the three countries, China (35.73 [b]), Lebanon (41.72 [b]), and Egypt (40.89 [b]), showed no significant differences with the heavy elements under investigation, but Saudi Arabia showed the highest means with significant differences (57.86[a]) in pollution rates with the same elements.

In general, the results showed that environmental pollution in general is caused by the elements lead (67.17 mg/100 g) and molybdenum (72.52 mg/100 g), with non-significant differences observed between them. Both the elements (Cadmium and cobalt) were non-significant, with average means of 15.08 mg/100 g and 21.42 mg/100 g, respectively.

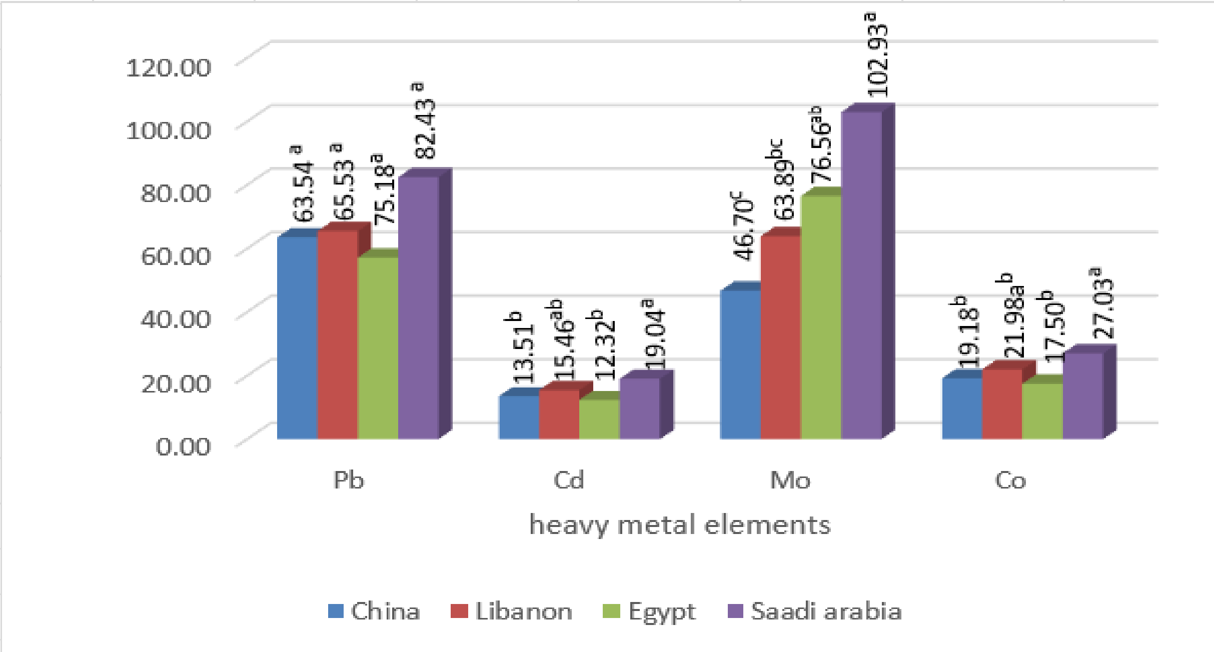

Figure (1): Comparison of pollution levels of each element between China, Lebanon, Egypt, and Saudi Arabia.

In comparison of pollution levels of each element between China and Lebanon, as shown in Figure (1), all pollution values for lead appear to have no significant differences between honey samples collected from the three countries under investigation which recorded 63.54 mg/100 g, 65.53 mg/100 g and 75.18 mg/100 g, respectively, while the differences were significant between Saudi Arabia and other three countries (China, Lebanon and Egypt) in cadmium and cobalt residue in honey samples Egypt recorded the lowest mean value with non-significant difference 12.32 mg/100g and 17.50 mg/100 g, respectively. Saudi Arabia honey samples recorded the highest mean value with a non-significant difference (19.04 and 27.03 mg/100 g, respectively). Molybdenum residue in honey samples showed the highest significant difference between Saudi Arabia samples with both Lebanon and China samples (102.93 mg/100 g, 63.89 mg/100g and46.70 mg/100 g, respectively), also there was a significant difference between honey samples between Egypt and China with means 76.56 mg/100 g and 46.70 mg/100 g, respectively.

Heavy metal residues represent an important reflection of the level of pollution of the production environment, which includes the tools and equipment used in honey production, such as hive paint, materials from which honey extractors and Buckets are made, and also the environment surrounding the apiary and the surplus crop.

Lead (Pb) can be found in various sources, both natural and anthropogenic (Human-made). Older homes and buildings may have lead-based paint, which can deteriorate and create lead dust or chips, lead pipes, fixtures, and solder used in plumbing systems can leach lead into drinking water, especially if the water is acidic or has low mineral content, while soil can become contaminated with lead from industrial activities, leaded gasoline (Historically), or the deterioration of lead-based paint, certain industries, such as battery manufacturing, metal smelting, and construction, can expose workers to lead, some imported toys, jewellery, and cosmetics may contain lead, particularly if they are not regulated, and some traditional remedies and cosmetics may contain lead as an ingredient. Also, lead can be released into the air from industrial emissions, particularly from factories and power plants that process lead or burn fossil fuels, and some hobbies including activities such as shooting (lead bullets) or making stained glass can expose individuals to lead (Kumar and Pastore, 2007; Yost and Weidenhamer, 2008; Lekouch *et al*., 2001; Tiffany-Castiglioni *et al*., 2001; Petrović, 2014; Chowdhury *et al*., 2018; Jarvis *et al*. 2018; Al Kindi and Ali, 2020; Kilic *et al*., 2021; Filippelli and Finkelman, 2021; Salles *et al*., 2021; Triantafyllidou *et al*., 2021; Wilson, 2021; Asante-Duah, 2002; Hatam *et al*., 2023; Jurowski, 2023 and Hettiarachchi *et al*., 2024). Reducing exposure involves an awareness of these sources and taking steps to minimize risk, such as proper home maintenance, using lead-safe practices in renovation, and ensuring water quality testing.

Cadmium (Cd) is released into the environment industries such as mining, smelting, and manufacturing, particularly in the production of batteries and pigments, commonly used in rechargeable nickel-cadmium (NiCd) batteries, which can leach cadmium into the environment if not disposed of properly; tobacco plants can absorb cadmium from the soil; smoking can expose individuals to cadmium through inhalation, and certain foods, particularly shellfish, organ meats, and leafy vegetables, can accumulate cadmium from contaminated soil or water. Some phosphate fertilizers and certain pesticides may contain cadmium, leading to soil and crop contamination. Cadmium can be found in some ceramics, jewellery, and paints, and it is used in electroplating and coatings for metal parts to enhance corrosion resistance (Yamagata, 1979; Jackson and Macgillivray, 1995; Gimeno-García *et al.*, 1996; Piadé *et al*., 2015; Huang *et al*., 2010; Pizzol *et al*., 2014; Bošković-Rakočević *et al*., 2017; Prokopowicz *et al*., 2019; Wang *et al*., 2019; Blumbergs *et al*., 2021, and Shao *et al*., 2013). To minimize exposure, it's important to be aware of these sources, ensure proper disposal of batteries and industrial waste, and choose foods from reputable sources that monitor for contamination.

Molybdenum (Mo) is a trace element essential for certain biological processes, but it can also be found in various sources in the environment; it is found in soil, rocks, and minerals, often present in molybdenite, which is the primary ore for extracting molybdenum. Molybdenum is an essential micronutrient for plants, and it can be taken up from soil by crops. It is especially important for legumes, which use it to fix nitrogen. Some fertilizers contain molybdenum, particularly those formulated for crops that require higher levels of this micronutrient. Molybdenum is used in steel and metal alloys to enhance strength and resistance to corrosion and wear. It is also used in electrical contacts and filaments; activities related to mining and processing molybdenum can release it into the environment. Molybdenum can lead to its presence in wastewater, which may affect nearby water sources, and it is present in small amounts in various foods, including legumes, grains, nuts, and leafy vegetables (Chongpraditnun *et al*., 1997; Kaiser *et al*., 2005; Bandyopadhyay *et al*., 2008; Mao *et al*., 2018; Pushpakumara *et al*., 2018 and, Chen *et al*., 2019). While molybdenum is essential in small amounts, excessive exposure can lead to health issues, so it's important to maintain a balance.

Cobalt (Co) is a trace element found in various sources, both natural and human made. Here are some common sources of cobalt exposure: Cobalt is widely used in the production of superalloys, batteries (especially lithium-ion batteries), and catalysts in chemical processes. It can be released into the environment during the mining and processing of cobalt ores, as well as from the extraction of copper and nickel. Cobalt is a critical component in rechargeable batteries, particularly in electric vehicles and portable electronics. Improper disposal of batteries can lead to cobalt contamination. It is used in various alloys for tools, dental materials, and jet engines, which can release cobalt during wear or when machined. Cobalt compounds are used in some pigments and dyes, including those found in ceramics and paints.

It is present in small amounts in certain foods, particularly in animal products such as meat and dairy, as well as in some seafood. Cobalt can be released into the air and water from industrial emissions, potentially leading to localized contamination. While cobalt is necessary for health in trace amounts (as part of vitamin B12), excessive exposure can lead to health issues, including respiratory problems and skin sensitization (Schrauzer, 1968; Hawkins, 2001; Yebra-Biurrun and Cancela-Pérez, 2007; Pellissier and Clavier, 2014; Al-Imam *et al*., 2016; Ferron, 2016; Lu *et al*., 2016; Vaicelyte *et al*., 2020; Wolf *et al*., 2021; Grosgogeat *et al*., 2022, and Lehel *et al*., 2023).

Therefore, the presence of residues of heavy elements indicates the use of contaminated or coated tools containing these elements, or it indicates the activity of industrial processes in these countries, or it may indicate that countries depend on imported honey. Acidic soils can increase the solubility of certain heavy metals (Like lead, cadmium, and arsenic), making them more likely to be absorbed by plants or enter the food chain. Mitigating heavy metals risks involves reducing environmental contamination, promoting practices that support bee health, and increasing awareness about the impact of heavy metals on pollinators. Preventing contamination involves monitoring environmental sources of heavy metals, using safe beekeeping practices, and ensuring that bee products are tested for contaminants before being sold or consumed. Understanding how heavy metals dissolve in different media is crucial for assessing their environmental impact, potential health risks, and strategies for remediation, managing and mitigating heavy metal pollution can be complex and costly, often requiring extensive monitoring and remediation efforts.

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