

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/



CrossMark

The Impacts of Cadmium, an Environmental Pollutant, on Honeybees (Apis Mellifira,

Hymenoptera: Apidae): A Review

Ola El. Mohamed^{*1}, Mohamed M. El-Shazly¹, Mohamed E. Hashish², Mustafa M. Soliman¹

¹Department of Entomology, Faculty of Science, Cairo University, PO Box 12613, Giza, Egypt.

²Bee Research Department (B.R.D.), Plants Protection Research Institute (P.P.R.I.), Agriculture Research Centre (A.R.C.), Agriculture Ministry, Egypt.

Abstract

Cadmium (Cd) is a toxic trace metal that can harm humans and other organisms. One route through which this trace element enters the human body is via consuming contaminated honeybees' products. This review highlights the sources, biogeochemistry, toxicity, and remediation of Cd, with a focus on its impact on honeybees. Natural and anthropogenic activities release Cd into the environment, which is then transported through the atmosphere, soil, water, and trophic levels. Honeybees are particularly susceptible to Cd toxicity, which can mimic essential elements like zinc (Zn) and calcium (Ca), disrupting physiological and biochemical processes. Despite their ability to filter and purify nectar, honeybees can accumulate Cd in their bodies and products. This makes them act as potential bioindicators of Cd pollution, but uncertainties exist due to multiple exposure pathways and the variable accumulation of Cd in different bee products. Remediation strategies for Cdcontaminated soils include chemical, physical, and biological methods. These approaches aim to reduce Cd bioavailability and promote its immobilization or removal from the environment. Understanding the biogeochemistry and toxicity of Cd is crucial for developing effective strategies to protect honeybees and mitigate the risks associated with Cd contamination in the environment.

Keywords: cadmium; honeybees; pollution; biogeochemistry; toxicity; remediation.

1. Introduction

The scope of bioinorganic chemistry is currently expanding, especially through multidisciplinary environmental research. Thus, the biogeochemistry of an element includes, not only the exchange routes of the element among the living and the non-living components of the ecosystem, but also the impacts of anthropogenic activities on these cycles; in addition the biochemical bases of the element to transportations from the non-living to the living components of the ecosystem, and thence through multiple trophic levels of the food webs. During the past few decades, the field of biological inorganic chemistry has seen significant advancements in understanding the accumulation, transportation, metabolism, and toxicity of metal ions. These efforts have also led to attempts to reduce metal ion contamination in both natural and agricultural

ecosystems through the development of chemical remediation technologies.

A specific subset of metals and metalloids exhibits a propensity for high reactivity, often posing a threat of toxicity even at minimal concentrations. These elements enter the environment through various pathways, including both human activities (anthropogenic sources) and natural processes. Such chemicals penetrate soils, gain access to marine ecosystems, freshwater ecosystems, sediments. groundwater, and bio-accumulate in the successive trophic levels in the food webs. Persistent environmental pollutants, like Cd and other toxic elements, can remain in the environment for extended periods, posing long-term risks to living organisms even after the initial source of contamination is eliminated. These pollutants can migrate from contaminated soils into groundwater supplies. It can

*Corresponding author e-mail: <u>ola.elsayed.science@gmail.com</u>

Receive Date: 16 March 2024, Revise Date: 10 May 2024, Accept Date: 28 May 2024 DOI: 10.21608/EJCHEM.2024.272472.9384

^{©2024} National Information and Documentation Center (NIDOC)

also enter food chains through plant uptake from the soil, resulting in bioaccumulation and potential toxicity to wildlife and humans through the food web. [1]. Studies have shown that exposure to Cd^{2+} can inhibit the activity of antioxidant enzymes and disrupt the mitochondrial electron transport chain [2]. This disrupts cellular homeostasis, leading to an increase in intracellular levels of reactive oxygen species (ROS) [2]. The elevated ROS levels can cause damage to DNA strands, lipid peroxidation, and the formation of oxidatively modified proteins [3]. These cellular alterations can ultimately lead to dysfunction and necrotic cell death [3]. Additionally, Cd²⁺ has been implicated in the activation of various signalling pathways, potentially triggering proapoptotic (cell death) and/or adaptive cellular responses [4].

Cadmium has been called the "disseminated element" [5], due to its high mobility and widespread distribution, rendering it a potential contaminant in numerous ecosystems. This elevated mobility, coupled with Cd propensity to form strong complexes with S-containing proteins, poses a significant threat to a wide range of living organisms [6].

The biogeochemistry of an element involves its transportation among the atmosphere, lithosphere, hvdrosphere. and biosphere. Therefore. the biogeochemical cycling of Cd, as a toxic trace element, involves the biological, chemical, and geological aspects of the pathways by which it can be transported and circulated in nature. Cadmium originates from weathering of the bedrock, but its concentrations can be exacerbated by mining and land degradation or other operations [7–13]. Anthropogenic activities, particularly the rise in fossil fuel combustion and non-ferrous metal extraction since the Industrial Revolution, have demonstrably altered the biogeochemical cycle of Cd, significantly impacting its movement and circulation within the environment [14]. The geo-accumulation index (Igeo), introduced by Müller in 1969 [15], provides a valuable tool for evaluating environmental contamination. This index facilitates the assessment by comparing present-day concentrations of a pollutant to pre-industrial levels. The index has been used in some trace metal studies, e.g., [16–18]. This index was used in the evaluation of soil pollution by Cd in Egypt [19].

The trophic transfer of toxic metals and metalloids poses risks to both human and ecosystem health [20–23]. This is held true for bee products, where toxic metals enter the food chain through soil-

Egypt. J. Chem. 67, No. 11 (2024)

to-plant transfer mechanisms and are transferred to bee products through bee-to-bee product transfer mechanisms. The toxicity of Cd continues to be a significant public health concern as Cd enters the food chain and is consumed by humans; for instance, Itai-Itai, a chronic Cd poisoning disease, was first discovered in Japan. It causes renal tubular dysfunction, osteomalacia, and osteoporosis. This disease occurs as a result of the competition between Cd and other nutrients [24–25]. Furthermore, chronic exposure to Cd has been linked to various health concerns, including cardiac failure, glucose metabolism disorders, cerebral infarction, and breast and lung cancer [26]. The biochemical basis for Cd toxicity in humans has been revised and discussed in detail by several authors, e.g., [27].

Honeybee (Apis mellifera) is a cosmopolitan species; this insect is an important ecological and agricultural resource. In addition to their natural products that can be used as food and for medical purposes, honeybees are among the most widely worldwide, promoting available pollinators sustainability in agriculture and natural ecosystems. In addition to honey, the main edible product of honeybees, this insect produces a variety of honeybee products, including pollen, bee bread, royal jelly, bee venom, and propolis. The consumption of beehive products has gained increasing popularity in recent times. These products are characterized by their high nutritional value and/or bioactive properties [28]. Notably, several honeybees' products, including honey, propolis, and bee venom, are utilized in traditional medicine for the prevention of illness and facilitation of healing processes. Therefore, this insect has a significant influence on humans' life and the ecosystem as well. While Apis mellifera populations are large, there are concerns that the widespread commercialization of apiculture, together with environmental contamination and bee pathogens, has led to considerable issues for honeybee health [29].

Generally, honeybees contribute directly to global agriculture by an estimated amount of $\in 153$ billion per year [30, 31]. Consequently, from an economical point of view, the contribution of primary honeybee products (beehive or apian products), is very important [32–34]. However, honeybee populations are susceptible to several environmental threats, including toxic metal pollutants. Indeed, many publications confirmed that honeybees are prone to environmental stressors, including trace metals that affect the physiology and development of honeybees e.g., [35–37]. Information on the contamination of bee products is not only of great

importance to consumers but also in medicine. These products may be a tool for promising therapeutic and chemo-prophylactic strategies against COVID-19 (SARS-CoV2 [38–41]; other potential applications of honeybee venom are known in the treatment of arthritis, cancerous, and autoimmune diseases [42].

The current multidisciplinary review deals with the following topics:

- 1. Natural and anthropogenic sources of Cd pollution in the environment.
- 2. Biogeochemistry of Cd including atmospheric, River and irrigation systems, oceanic, soil and trophic transportation.
- 3. Toxicity of Cd against living organisms including toxicity to humans. Toxic effects on honeybees physiological, neurological, included immunological, and histopathological effects, as well as the effects of Cd on honeybee survival and development; besides the behavioural response and detoxification of Cd. The contamination of Cd to apian products and the reversal effects of royal jelly and propolis against Cd toxicity were reviewed.
- 4. The use of contaminated bees and beehive products as bioindicators of Cd toxicity in the environment, and the uncertainty created by these manipulations were discussed.
- 5. The rehabilitation of Cd-contaminated soils by physical, chemical, and biological remediation technologies in the areas of bee activities was reviewed.

2. Methods

The term "heavy metal" is inadequately used, especially in multidisciplinary studies; the International Union of Pure and Applied Chemistry discourages the use of this term, as no standardized definition currently exists [43]. Researchers should utilize only widely accepted terminology for consistency. Regarding "heavy metal," this phrase ought to be supplanted with "metal," "metalloid," or "trace metal" [43]. However, Pourret and Bollinger [44] deemed directly identifying or grouping the studied elements (as metals or metalloids) the optimal approach for clear description. In the present article, we shall use the chemical names and symbols of the elements. Trace metals and metalloid abbreviations used throughout this manuscript are those from the Periodic Table [45].

This article is a multidisciplinary approach outlines the interactions between cadmium (Cd) as a nonliving component of the global ecosystem, and honeybee. The selection of revised publications is based on the systematic and literature survey of the publications concerning the environmental sources, biogeochemistry and toxicity of Cd, and therefore, the impacts of this trace element on honeybees, as well as soil remediation of the foraging areas. The review process involved the popular academic search engines viz. Google Scholar, PubMed, Science Direct, Scopus, Springer, as well as official websites concerning the revised topics e.g., UN, FAW, WHO, etc.

2.1. Natural and anthropogenic sources of cadmium pollution in the environment 2.1.1. Natural sources of cadmium

Cadmium is not recovered as a principal product of any mine [46]. It naturally occurs in certain metalbearing ores and forms its own minerals as impurities in zinc (Zn), copper (Cu), lead (Pb), and base metal ores, which represent the main economic natural source of this element [47]. Cd is a relatively rare element in the earth crust, with an average concentration of 0.1-0.2 mg Cd/kg [48]. Cd abundance in the upper continental crust is about 0.098 ppm [49]. The concentration of Cd in the lithosphere was estimated to be roughly 650-fold lower than its Group 12 neighbour, Zn [50]. However, relatively high concentrations of Cd in nature can be found in marine sedimentary rocks owing to its high ability to accumulate in biota [14]. Levels as high as 300 Cd mg/kg have been recorded in marine sedimentary rocks [51]. Forest fires and volcanic eruptions constitute major natural sources of Cd, collectively releasing approximately 890 metric tons of Cd annually into the atmosphere [52]. Furthermore, the erosion and weathering of rocks are estimated to contribute an additional 15,000 metric tons of Cd per annum [53], which is ultimately transported by rivers to various environmental sinks, including oceans, groundwater, cultivated lands, plants, and other living organisms (Fig. 1).

2.1.2. Anthropogenic sources of cadmium

The Environment United Nations Programme (UNEP) [54] estimated global anthropogenic Cd emissions to be around 2,983 tons in the mid-1990s. While data from developed countries indicates a significant decrease in anthropogenic Cd emissions, averaging around 50% between 1990 and 2003, insufficient data hinders the assessment of emission trends in developing countries. Emissions primarily come from the production of non-ferrous metals and the combustion of fossil fuels [54].

Industrial processes including mining and smelting, particularly Zn [55], are the main sources of

Egypt. J. Chem. 67, No. 11 (2024)

Cd emissions to the atmosphere. Other sources include iron and steel production, oil and gas industries, cement production, as well as waste incineration [56]. Among the common sources are burning of vegetation, sea salt spray, and the production of marine biogenic aerosols [57-60]. Paints, plastic stabilizers, pigments, incineration of Cd-containing plastics, electroplating and phosphate fertilizers are also common sources of Cd pollution [61, 62]. Animal manure, sewage sludge (biosolids), compost, and phosphate fertilizer are also among the most common sources of Cd pollution [56, 61]. Phosphate fertilizers are one of the most common sources of Cd contamination in agricultural soils throughout the world, as Cd often occurs in high concentrations in the phosphate rocks which are used in the production of phosphate fertilizers [64, 65]. A recent review of fertilizers and pesticides as sources of heavy metal pollution has been given by Rashid et al. [66] (Fig. 1).

2.2. Biogeochemistry of cadmium 2.2.1. Cadmium chemistry

Cadmium is a member of Group 12 of the periodic table, (atomic number: 48, relative atomic mass: 112.41); it is like Zn and Hg in chemical and physical properties [67, 68]. Cadmium is a soft, silver-white metal in its elemental form. Its structure exhibits a slight elongation along the six-fold axis, a deviation from perfect hexagonal close packing [6]. Cadmium is quite volatile, with a melting point of 321°C and a boiling point of 767°C. Its heat of vaporization is 26.8 kcal/mol. [69].

Though Cd forms 27 minerals (10 sulfides, 7 sulfates, 4 arsenates, 2 phosphates, 1 oxide, 1 selenite, 1 carbonate, & native Cd) [53], it rarely occurs as a pure metal. Instead, it's typically found in complex oxides, sulfides, and carbonates associated with Zn, Pb, & Cu ores. It is rarely present in large quantities as chlorides and sulfates [70]. Cd may form a group of salts, and both its environment mobility and impacts depend mostly on the nature of these salts in combination with other elements such as chlorine (cadmium chloride), sulfur (cadmium sulfide) or oxygen (cadmium oxide) [46]. In aqueous solutions. Cd primarily exists as the divalent Cd^{2^+} ion. Its mobility is highly influenced by various factors, including pH, redox conditions, and ionic strength of the solution. Cadmium solubility tends to be enhanced under acidic conditions and when abundant sorbents like hydrous metal oxides, clays, and organic matter are present to facilitate release from solid phases. [71]. Unlike most metals, Cd

forms water-soluble complexes (e.g., $CdCl^+$, $Cd(SO_4)_2^{2^-}$) and binds to dissolved organic matter, resisting sorption and precipitation, making it highly mobile in the environment [71].

2.2.2. Geochemical transportation of cadmium

Despite being a heavy metal, Cd exhibits exceptional mobility in soil due to factors like competition and ligand-induced desorption, leading to its faster release into groundwater compared to other trace metals [71]. The element is being fluxed among the living and non-living compartments of the ecosystem. Thus, Cd released into the atmosphere can be deposited in terrestrial and aquatic environments and transported through trophic levels of organisms. Soil Cd can be washed out to the aquatic environments over time. Atmospheric Cd transport range varies from local to intercontinental, influenced by particle size, emission height, and meteorology for both natural and anthropogenic sources. Because Cd has a relatively short residence time in the atmosphere (days or weeks), this metal is mainly transported over local, national, or regional distances (Fig. 2). The biogeochemistry of Cd was revised and discussed in the Northwest African upwelling [72], Kuroshio-Oyashio Extension region, Japan [73], subtropical gyre of the South West Pacific Ocean [74], waters of small lakes in European Russia (from the tundra to deserts) and large river systems - Volga, Severnaya Dvina, Pechora [47], Angola Basin [75], the Indian and Pacific sectors of the Southern Ocean [76], the Amundsen Sea, [77], coastal Antarctica [78].

2.2.2.1. Atmospheric transportation

Due to its chemical properties, Cd readily participates in atmospheric transport, constituting a crucial aspect of the global Cd cycle [79]. Compared to other elements like mercury, Cd atmospheric residence time is considerably shorter. This is primarily because most airborne Cd is associated with fine particulate matter (less than 1 μ m) [48]. Cadmium chloride, cadmium sulfate, and cadmium oxide are the most prevalent forms of Cd found in ambient air [48]. Given its brief atmospheric lifespan (days to few weeks). Cd predominantly travels over local, national, or regional distances. Emission source and particle size significantly influence Cd atmospheric transport. While elevated Cd

Egypt. J. Chem. 67, No. 11 (2024)

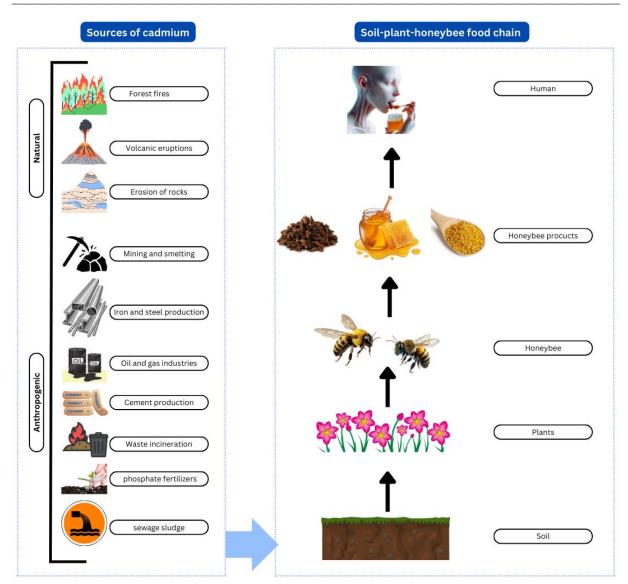


Fig. 1. Possible sources of cadmium input to honeybee and its product.

contamination can extend up to 30 km from the source [66], aerosols facilitate transport over much greater distances. Under specific conditions, air currents can carry Cd over hundreds or even thousands of kilometers, impacting human health and ecosystems far beyond the emission point [54]. Notably, combustion processes often release Cd as microscopic particles, contributing significantly to the overall atmospheric particulate matter burden [69]. Cd from atmospheric deposition concentrates in the upper humus soil layer [56] and appears to be easily available to plants [66]. However, the accumulation of atmospheric Cd on different organs of the plants (leaves, flowers, etc.) cannot be neglected.

2.2.2.2. Aquatic transportation

In natural environments, Cd primarily exists in the +2-oxidation state (Cd (II)). This valence state is virtually the only one observed in aquatic systems. [80]. Cadmium chloride and cadmium sulfate exhibit high solubility in water, whereas elemental Cd, cadmium oxide, and cadmium sulfide are almost insoluble [48].

Cadmium mobility in aquatic environments is increased under conditions of low pH, low water hardness, low suspended particulate matter, high redox potential, and low salinity. Natural water systems exhibit a reduced bioavailability of cadmium (Cd) due to sorption onto suspended particles. Consequently, higher Cd concentrations are required to elicit biological responses [81]. In aquatic

Egypt. J. Chem. 67, No. 11 (2024)

environments, organisms tend to absorb Cd most readily directly from the water when it is present in its free ionic form [82]. Due to bioaccumulation within organisms, relatively high concentrations of Cd are observed in marine sedimentary rocks [14]. Dissolved Cd concentrations in river water typically range between less than 1 and 13.5 nanograms per Liter (ng/L) [83]. Notably, higher proportions of dissolved Cd are found in acidic waters. EU freshwater Cd concentrations have exhibited a general decline since the late 1970s. However, the rate of decrease has slowed since 1990 [81]. Several studies have highlighted the significance of major river systems as sources of various materials, including potentially harmful elements, delivered to coastal marine environments [84-88].

The average Cd concentration in seawater is reported to be around 0.1 µg/L or less [48]. Cd readily forms complexes with chloride ions. This complexation increases with increasing salinity [48]. Consequently, in typical seawater, Cd primarily exists as chloride species (CdCl⁺, CdCl₂⁻, CdCl₃⁻) with a minor fraction present as free Cd²⁺ ions (National Toxicology Program, 1991 as cited by ATSDR [70]). The complexation of Cd with chloride significantly influences its bioavailability, impacting its potential toxicity to marine organisms [70]. A marked bioaccumulation of Cd has been reported in large migrating mammals such as dolphins [89] and whales [90]. Therefore, a minor role in the biological intercontinental oceanic transfer of Cd cannot be excluded.

Macdonald et al. [91] highlight the crucial role of ocean currents in heavy metal transport, particularly in the Arctic Ocean. Their findings suggest that atmospheric deposition and land-based runoff (rivers, etc.) contribute minimally compared to the significant influx from ocean currents. Natural oceanographic processes lead to elevated Cd concentrations in the North Pacific, approximately five times higher than those observed in the North Atlantic [92]. Oceanic transport and response times to anthropogenic pollution far exceed those in the atmosphere. Unlike atmospheric pollutants with hemispheric transport timescales measured in days to weeks, ocean circulation patterns, such as the thermohaline circulation (estimated at 600 years for a single water molecule to complete the cycle) [93], significantly influence the movement and response of pollutants within the marine environment. This translates to a much slower large-scale response to anthropogenic inputs. The estimated residence time of Cd in the ocean is around 15,000 years [54]. This extended timeframe suggests that the current

Egypt. J. Chem. 67, No. 11 (2024)

anthropogenic contributions of Cd to surface waters are relatively insignificant compared to the vast oceanic reservoir of the element [53].

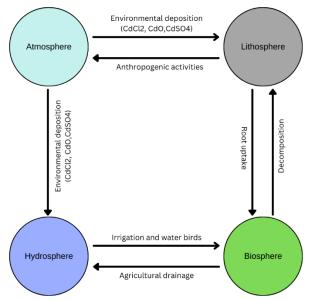


Fig. 2. Geochemical transportation of cadmium.

2.2.2.3. Soil transportation

Cadmium accumulates in the soil as a result of a combination of natural processes including rock weathering, volcanic activity, forest fires, erosion and deposition in river sediments, as well as anthropogenic activities, including mining and industrial activities, in addition to agricultural practices such as irrigation and fertilization that can result in Cd input into the soil (Fig. 1). He et al. [94] pointed out that the contribution of natural processes to soil Cd is 3 to 10-fold lower than that of Cadmium solubility anthropogenic activities. increases under acidic conditions [95]. Chloride readily forms soluble CdCl⁺ complexes, reducing Cd²⁺ adsorption onto soil particles. Unlike inorganic ligands, organic matter can enhance Cd²⁺ adsorption on kaolinite (a variable-charge mineral) by forming an adsorbed layer on its surface [96]. However, research indicates that critical limits for Cd contamination in agricultural soils vary based on texture [97]. Soils with higher clay content generally exhibit higher tolerance levels compared to those with lower clay content. The established critical limits are light-textured soils: 5.33 mg/kg, mediumtextured soils: 6.33 mg/kg and heavy-textured soils: 9.29 mg/kg. Regulations limit the Cd concentration in sewage sludge intended for land application to a range of 20-40 mg/kg dry matter [98]. Furthermore, the total Cd content in the soil after sludge application should not exceed 1-3 mg/kg. Cd accumulation in soil poses a risk of mobilization through leaching processes. This can contaminate groundwater or surface water resources [99, 100]. Toxic metals from soil also leached down to the groundwater reservoirs making it unfit for drinking purposes [1]. Kubier et al. [71] discussed the hydrogeochemistry of Cd in groundwater, exploring its reaction pathways within aquatic environments. It should be mentioned, however, that some elements cannot be transported from soil to plants; for instance, Pb is not transported by plants, while Cd is transported from the soil to plants and can then contaminate nectar and honeydew. Atmospheric deposition accounts for only minor cadmium contamination in honey, primarily in proximity to incineration facilities [101].

2.2.2.4. Trophic transportation

Toxic metals and metalloids transport from soil to plant; and subsequently to animals through food webs, and ultimately to human beings (Fig. 1). Thus, plants take up Cd, together with other nonbiodegradable metals and metalloids from contaminated soil and distribute it in successive trophic levels, where it is ingested by herbivorous animals, and subsequently higher trophic levels. The increased concentration of trace metals, due to their non-degradability is known as biomagnification, while the accumulation of heavy metals in living systems is known as bioaccumulation. The amount of the Cd compound identified analytically is not necessarily equivalent to the bioavailable amount [70].

Trophic transportation of Cd and other trace elements can be concluded from earlier studies; for example, Hunter and Johnson [102] found a much greater food chain transfer potential for Cd than for Cu irrespective of their concentration in the environment. The biogeochemistry of Cd in the terrestrial habitat, the soil-plant-insect system, was studied by Zhang et al. [103]. A general review of the transfer of metals and metalloids collectively (without specification of each metal separately) through terrestrial food webs was given by Gall et al. [104], while Chen et al. [105] examined the trophic transfer of Cd in various components of sovbeandodder parasitic. Singh et al. [106] reported that much pollinator diversity is being lost due to toxic metal exposure, which poses a serious threat to agriculture. Recently, Khan et al. [107] have evaluated the allocation and bioaccumulation of Cd through successive trophic levels from soil to cotton plants, cotton plants to herbivore pests, and herbivorous pests to a natural enemy predator. On the

other hand, Mochizuki et al. [108] reported that the ranges of the Cd contents in the kidneys and livers of 85 wild birds collected from 9 different prefectures in Japan were ND-174.4 and ND-21.2 μ g g-1 dry wt., respectively. However, Cd and other metals can be transported from water bodies in aquatic ecosystems to terrestrial ecosystems through avian tissue after death and decay of the predatory birds.

2.3. Toxicity of cadmium against living organisms

Metallic compounds cannot be easily degraded, even at low levels [109, 110, 111]. Owing to their toxicity, persistence in the atmosphere, and bioaccumulation potential in human body, these compounds pose significant environmental concerns [112]. Cadmium is a toxic transition metal that accumulates in cell tissues and has no mechanism for expelling from the body. Cd is ranked as the 7th most hazardous substance for living organisms [113]. The toxicity of Cd to living organisms can be explained based on its chemical properties; for example, Zn and Ca are essential metal ions in numerous biological processes in humans and other organisms, including honevbees. The ionic radius, identical charge, and similar chemical behavior of Cd to both Zn and Ca enable Cd to replace them, causing physiological and biochemical disorders. Studies have proposed that free Cd²⁺ ions exploit transporters meant for essential elements like Ca²⁺, iron (Fe²⁺), and Zn²⁺ to gain entry into cells [114]. Toxicological effects of Cd on humans were discussed by many authors, e.g., [115-126].

2.3.1. Cadmium has only one biological function

Although Cd is not generally considered a bio-essential metal; yet it has been indicated that this trace element can perform the physiological function of Zn, when ambient bioavailable Zn becomes depleted in the planktonic marine diatoms, Thalassiosira weissflogii [127–129], Phaeodactylum tricornutum and Pseudonitzschia delicatissima [130] as well as in the phytoplanktonic coccolithophoride Emiliania huxleyi [131–134]. This could be attributed to the chemical similarities of Cd to the divalent ions of Zn. Thus, only one well-defined biological function has been established for Cd. In marine diatoms, Cd can potentially replace Zn within the enzyme carbonic anhydrase, a crucial component of their photosynthetic machinery [135–137]. However, the biological mechanisms of Cd absorption by phytoplankton are poorly understood [129, 138-140].

Some marine plankton have evolved the ability to substitute Cd, a toxic non-essential metal, in place of the biologically essential element Zn in

Egypt. J. Chem. 67, No. 11 (2024)

certain physiological functions. This evolutionary adaptation demonstrates how these organisms have developed over millions of years to exhibit a diverse array of structural, metabolic, and physiological adaptations enabling them to thrive in a wide range of oceanic environments. On the other hand, phytoplankton can take up free Cd^{2+} ions through transporters originally designated for essential metals like Ca^{2+} , Fe^{2+} and Zn^{2+} [114]. This unintended cellular uptake is attributed to ionic mimicry. Due to their similar chemical properties, Cd^{2+} can bind to the active sites of membrane proteins specific to these essential elements, facilitating its entry into the cell.

2.3.2. Guideline values

Due to its long persistence in the human body (10-35 years), the safe monthly intake of cadmium is limited to 25 µg/kg body weight. Each member state of the European Community developed their procedures to determine a limit value, which ranged from 0.08 to 27 µg/L [119]. The recommended level for Cd in drinking water is set to 3 µg/L [122]. The Environmental Protection Agency of the United States set the maximum permissible level for Cd to 5 μ g/L, which is the same as in the European Union [56] and China [141]. In Denmark, the environmental quality criteria for Cd in groundwater is 0.5 µg/L; while it has been set at 10 µg/L in Japan and China [54, 71,142]. Some of the permissible limits for Cd in honey and beeswax, food, water, and soil are given in (Table 1).

2.3.3. Cadmium toxicity to honeybees

The toxicity of Cd to living organisms can be explained based on its chemical properties; for example, both Ca and Zn are essential nutritive elements in numerous biological processes, including the function and structure of many proteins in honeybees and other insects [143, 144]. The ionic radius, identical charge and similar chemical behavior of Cd to both Zn and Ca enable Cd to displace them if encountered, causing physiological, biochemical, and genetic disorders. Honeybees are exposed to environmental pollutants, including heavy metals while flying [145] and collecting food resources (water, pollen grains, and flower nectars) [146, 147]. Metals bio-accumulate in honevbee bodies [148, 149] and in their hive products [150, 151], impacting their survival [152], physiology [153], and behavior [154, 155]. However, atmospheric Cd may gain access to Arthropod bodies directly from the atmosphere to the tracheal system. It has been reported that accumulation of essential trace elements, e.g., Zn, can be checked through

homeostatic control mechanisms; in contrast to nonessential ones including Cd, where no homeostatic control can check accumulation of this element [102, 156]. Gekière et al. [157] Listed publications on the effects of 68 'trace metals and metalloids' on honeybees, bumblebees, stingless bees, and solitary bees.

2.3.3.1. Effects of Cd on survival and food consumption

The mortality of honeybees increases, and the growth rate decreases in larvae, pupae, and foragers, exposed to sublethal doses of Cd, in a dosedependent manner [152, 158]. The exposure to sugar syrup containing either CdO nanoparticles alone or a combined mixture of CdO and PbO nanoparticles resulted in a significant decrease in both the survival and feeding rates of the bees. [159].

2.3.3.2. Physiological effects of Cd

Cadmium exposure disrupts the physiological regulation of cellular signaling pathways, leading to subsequent dysfunction [160]. This disruption stems from two primary mechanisms: firstly, the substitution of essential Ca²⁺ ions with Cd²⁺ ions within signaling processes, and secondly, the replacement of Zn²⁺ ions in crucial enzymes and transcription factors [161, 162]. This Zn²⁺ substitution can trigger aberrant gene expression, potentially stimulating uncontrolled cell proliferation or inhibiting apoptosis [162]. Additionally, research by Nikolić et al. demonstrates that exposure to heavy metals like Cu, Pb and Cd significantly alters gene expression, enzyme activity, and cellular redox state [153]. Notably, the effects are metal-specific and dose-dependent. While both Cd and Cu exposure impacted the expression of genes encoding catalase and superoxide dismutase (antioxidant enzymes), Pb exposure solely induced the expression of superoxide dismutase genes [153].

2.3.3.3. Histopathological effects

Cadmium oxide (PbO) and nanoparticles of cadmium oxide (NPs) induced rupture of the midgut peritrophic membrane, in addition to common cytological alterations in epithelial cells, including irregular distribution or/and condensation of nuclear chromatin, mitochondrial swelling and lysis, and rough endoplasmic reticulum (rER) dilation, fragmentation, and vesiculation [163].

Matrices	(ppm) for Cd in food Area of application	, water and soil Value in ppm	Source
Honey and beeswax	Global	$0.25 \mu gg^{-1}$	WHO/FAO (Kebebe 2019) [311]
Honey	European Union	0.05–0.3.00 mg/kg	(EC) No. 1881/2006 as quoted from Šerevičienė et al. (2022) [312]; Bogdanov, 2006 [101]
Food (in general)	International European Union China	0.05-2.00 0.05-3.00 0.05	Joint FAO/WHO (2015) [313] Commission Regulation (EU 2015) [314] Li et al. (2006) [315]
Leafy vegetables	Global	0.2 mg kg ⁻¹	FAO/ WHO (1996) [316]
Root vegetables	Global	0.3 mg kg ⁻¹	FAO/ WHO (1996) [316]
Other vegetables	Global	0.1 mg kg ⁻¹	FAO/ WHO (1996) [316]
Drinking water	International European Union USA China	0.003 0.005 0.005 0.005	Joint FAO/WHO (2015) [313] European Commission (EU 2019) [317] US EPA (2017) [318] Ministry of Health, China (2006) [141]
Irrigation water	International USA	0.01 0.005- 0.01	Ayers RS, Westcot DW (1994) [319] US EPA (2006) [320]
Soil	International	0.9-3	de Vries et al. (2002) [321] WHO/FAO (2001) [322]
	Finland	120.0	Ministry of the Environment, Finland (2007) [323]
	UK	10-230	UK Environment Agency (2009) [324]
	USA	0.48	US EPA (2002) [325]
	China	0.3-0.6	Environmental Protection Ministry of China (2015) [326]

Table 1
Permissible limits (ppm) for Cd in food, water and soil

2.3.3.4. Neurotoxicity

Honeybee exposure to cadmium oxide nanoparticles (NPs) disrupts their nervous system by affecting the enzyme acetylcholinesterase (AChE). AChE, belonging to the Carboxyl/cholinesterases family, normally breaks down the neurotransmitter acetylcholine (ACh) into choline and acetate. However, CdO NPs inhibit AChE, leading to ACh accumulation. This excess ACh hyperstimulates receptors, disrupting neurotransmission and causing altered locomotor behavior in honeybees, as observed in other insect studies [164, 165]. A significant decrease in acetylcholinesterase activity was reported in honeybees treated with 0.001 and 0.01 mg L-1 CdCl2 [153]. Acetylcholinesterase activity in the heads of honeybees was inhibited by 3.8-, 3.0-, and 2.8-fold relative to control, respectively, in response to exposure to Cd or/and Pb oxide nanoparticles [159]. Furthermore, Cd exposure in honeybees triggered dysregulation of genes related to oxidative stress response and odor sensing, suggesting oxidative stress and reduced chemoreceptor expression, likely leading to impaired olfactory learning [166].

2.3.3.5. Immunological response and detoxification

Glutathione S-transferases (GSTs) constitute a diverse family of multifunctional enzymes found throughout various organisms [166]. They play a critical role in detoxification by catalyzing the conjugation of the tripeptide glutathione (GSH) with a wide range of electrophilic substrates. This conjugation process effectively reduces the reactivity and enhances the water solubility of these substrates [167]. Cd-induced genomic instability via a complex interplay of diverse mechanisms [168]. Various combinations alter xenobiotic detoxification gene expression. For example, a binary sublethal mixture of CdO and PbO nanoparticles in sugar syrup triggered a 13.6-fold increase in catalase expression compared to unexposed bees [159].

Exposure to Cu, Pb and Cd significantly alters gene expression patterns, enzyme activity levels, and the cellular redox state in bees. However, the specific effects depend on the particular metal involved and the dose to which the bees are exposed. Exposure to Cd and Cu altered expression of both catalase and superoxide dismutase genes, while Pb only affected superoxide dismutase [153]. Distinct microbial communities inhabit the honeybee gut and its products, actively supporting the host's health and nutrient availability. Moreover, it inhibits food spoilage and contributes to maintaining hygienic conditions within the hive [28]. The honeybee gut microbiome is actively involved in bee protection against infectious diseases [169], as well as in the degradation of pollen wall polysaccharides [31, 170]. In addition to the detoxification of pollutants and toxic plant compounds [31, 171]. Moreover, the honeybee microbiome is essential for honey and bee bread production during maturation [169, 170, 172-175].

Research suggests a degree of resilience in the honeybee microbiome regarding Cd exposure. Notably, certain bee-associated bacterial strains exhibit the ability to bioaccumulate Cd [176]. This phenomenon might offer a protective mechanism for bees against metal and metalloid contamination. Additionally, these bacterial strains potentially possess genes involved in the detoxification of such chemicals [176]. In vitro studies with liquid cultures demonstrated the capacity of specific bee-associated bacteria to remove Cd from the surrounding medium [176].

2.3.3.6. Behavioral response to Cd exposure

Chronically exposed honeybees displayed significantly impaired olfactory learning and lower head weight compared to controls [166], highlighting Cd's impact on this vital foraging behavior crucial for plant-bee interactions [36].

Concerning the feeding behavioral response of the honeybee to toxic metal-contaminated plants; several studies indicate that restrained bees will ingest solutions containing selenium (Se) or Cd [154]. Interestingly, they do not exhibit any behavioral signs of aversion to these solutions. In contrast, Cu seems to be palatable to bees at specific concentrations [154]. Electrophysiological studies [177] revealed no evidence of specific mechanisms in honeybees enabling selective detection of toxic metals (arsenic and Pb) compared to Zn, which is essential for biological functions. The overall, cellular, and behavioral responses of honeybees to these metals did not support such selective detection capabilities.

Burden et al. [154] investigated the discriminatory gustatory responses of bees towards different metals. Their findings revealed that bees readily rejected sucrose solutions containing Cu upon antennal contact, while solutions containing Cd were not. Interestingly, Cd ingestion did not affect the bees' sensitivity to sucrose. These observations suggest distinct mechanisms underlying the detection of each metal and the potential pathways of metalinduced toxicity. However, the challenge lies in the chemical similarity between Zn, a crucial trace element for bees and other organisms, and Cd. Notably, even at the highest reported concentrations, Cd did not deter feeding behavior, and copper-laced nectar was readily consumed following proboscis contact, as documented in the same study by Burden et al. [154]. Honeybees seem unable to sense certain toxicants through their antennae or proboscis. For instance, they readily ingest sucrose contaminated with even fatal Se levels [178]. Similarly, Cd showed

Egypt. J. Chem. 67, No. 11 (2024)

no rejection or impact on sucrose sensitivity [154]. This leaves them vulnerable to undetected or unrecognized harmful xenobiotics like Se and Cd.

2.3.4. Cadmium in honeybee products

Understanding the contamination levels of bee products is crucial not only for consumer safety but also for medical applications. Notably, the degree of contamination can vary significantly within different bee products, even when collected from the same apiary. Cadmium, for instance, poses a particular concern. Once absorbed by plant roots, it is transported through the vascular system into nectar and pollen. This process leads to bioaccumulation in pollinators, subsequently impacting bee products like honey, propolis, beeswax, and others [152]. Research by Leita et al. [179] demonstrates this phenomenon, highlighting a positive correlation between the Cd content in honey and the Cd levels found in Trifolium pratense L. flowers foraged by bees near a heavily trafficked highway. Studies conducted in Switzerland [101, 180] have revealed a descending trend in the level of contamination across various bee products: bees > propolis > comb > wax > honey. This phenomenon is likely attributed to the filtering process employed by bees during honey production. It is also possible that Pb and Cd are partially removed during the comb melting process used to obtain pure beeswax. It is noteworthy that Gabriel et al. [181] developed a novel method for determining Cd residue in bee products like propolis and pollen. This technique, known as square wave anodic stripping voltammetry (SWASV), utilizes a lab-made Bismuth Bulk Electrode (BiBE).

2.3.4.1. Propolis

Propolis is a complicated material that has many biologically active compounds valuable to the human organism, e.g., lipids and wax, bio-elements, vitamins, proteins, and other compounds [182, 183, 184]. Bees leverage propolis, a resinous substance collected from plants, to construct and repair their hives. It seals openings, smooths internal walls, and acts as a protective barrier against external threats and weather. The contamination of propolis by Cd has been documented, e.g., Roman and Popiela-Pleban [185]. Worker bees do not perform purification steps while processing raw materials into propolis. Consequently, the mineral and trace element composition of propolis directly reflects the natural abundance of these elements in the bees' surrounding environment. [186, 187].

2.3.4.2. Honey

Nectar is a sugary liquid secreted by specialized plant structures called nectaries [188, 189]. This aqueous solution contains a complex blend of nutrients, including sugars, amino acids, organic acids, proteins, fats, vitamins, and minerals. Forager bees create beebread by combining pollen with nectar and their own glandular secretions [190]. This fermented mixture is a highly nutritious food source, particularly for young bees. Upon returning to the hive, beekeepers can carefully harvest and market beebread for its potential health benefits [191].

The collected nectar is stored at the bottom of the esophagus in the honey stomach before being transported to the hive. During transportation to the hive, the nectar undergoes transformation via enzymatic treatment. This chemical transformation is based on the hydrolysis of sucrose, a biochemical process catalyzed by an invertase enzyme. This is followed by the nectar loads transfer from "bee nectar collectors" to "food-storing bees". Honeybees transform nectar into honey through a ripening process. Food-storing bees regurgitate and deposit nectar in honeycomb cells, where it undergoes further conversion of sucrose to glucose and fructose, accompanied by water evaporation. This process, lasting 1-3 days, is finalized by capping the nectarfilled cells with beeswax [192, 193]. Contamination of honey with Cd was reported by earlier authors, e.g., [186, 194–198].

Trace elements and metalloids in honey have high nutritive values; however, at high concentrations, they may cause serious health problems. Cd levels have been measured in honey in different countries; e.g., Egypt [199, 200, 201], Turkey [202], Poland [203, 204, 205], Spain [206], New Zealand [207], Italy [208], Russia [209], Romania [210], and Iran [211]. Historical records indicate significant variations in Cd contamination in honey across different regions. levels Concentrations range from a low of 4.4 µg/kg in Spain to a concerning high of 390 µg/kg in Iran. Due to the potential health risks associated with Cd exposure, a recent Romanian study conducted a complex risk assessment analysis to evaluate the safety of honey consumption from three distinct regions within the country. [212].

2.3.4.3. Beeswax

Numerous studies have reported that metal contamination levels are lower in honey compared to those observed in the bodies of bees and the surrounding environment [101, 213]. This observation has led to the suggestion that bees possess the ability to filter and purify nectar, thereby removing these contaminants during the process of honey production [214, 215]. Specifically, Dżugan et al. [216] have defined bees as "biofilters" that prevent the penetration of elements into bee products, particularly honey. Recently, Borsuk et al. [217] conducted research to investigate the mechanism of nectar purification by bees. Their findings indicated that Cd and certain other elements were partially immobilized or metabolized in the bee fat body, with the residues being excreted through feces from the gut. Furthermore, Ullah et al. [218] determined and compared heavy metal levels in honey, beeswax, and bees obtained from apiaries located in different regions of Pakistan, subsequently estimating the risk level for those residing in areas where honey consumption is prevalent.

Intensive beekeeping relies on beeswax foundations, but the practice of recycling wax can lead to decades-long accumulation of toxic metals. Tlak Gajger et al. [219] analyzed beeswax samples during foundation production and found metal concentrations (mg kg⁻¹) in the final comb products ranging as follows: As 0.01-0.88; Cd 1.26-3.55; Pb 82.5-171; and Hg 0.29-1.46.

2.3.4.4. Bee pollen

Pollen, rich in lipids, proteins, vitamins, and minerals, is crucial for honeybee growth, development, and reproduction [220]. It fuels hypopharyngeal gland and body fat development in young workers, essential for brood rearing and winter survival [221]. Bees collect and transport pollen on their hind leg structures called corbiculae [222]. Bee pollen is an antioxidant and antimicrobial bee product; used in apitherapy. Its structure contains various enzymes, co-enzymes, steroids, vitamins, antibiotics, mineral substances, and flavonoids [101, 223]. Despite its therapeutic value, bee pollen may be contaminated with environmental pollutants, including Cd. The Cd concentration of bee pollen has been reported by several authors [186, 224–226]. The average concentration of Cd ranged between 2 µg/kg [227] and 2965 µg/kg [150]. Vegh et al. [228] conducted a risk assessment for the most common pesticide-active substances, including Cd in bee pollen.

2.3.4.5. Royal Jelly

Young worker bees produce royal jelly, a secretion from their hypopharyngeal glands. royal jelly nourishes drone and worker bee larvae for their first three days and the queen throughout her life. Unlike worker and drone larvae, which receive royal jelly along with honey and pollen, the queen bee

Egypt. J. Chem. 67, No. 11 (2024)

exclusively consumes royal jelly [28, 228, 229]. It has been reported that the amount of Pb, Zn, and Cd accumulated in royal jelly [179, 231]. The royal jelly is initially fed to all larvae (not just queens), therefore its contamination with toxic metals can potentially affect all members of the colony directly [232]. However, as will be discussed later, royal jelly has a protective role against Cd-induced genotoxicity and oxidative stress in mice, due to its antioxidant effects [113].

2.3.4.6. Honeybee venom

Honeybee venom is a defensive secretion produced by specialized glands and delivered externally through a stinger. The reported lethal dose (LD50) for humans is approximately 2.8–3.5 mg/kg, equivalent to the venom from 400–1500 stingers. The LD50 for intravenous administration in mice is 0.6 mg/kg. Dried bee venom presents as a very fine, lightly yellow powdered substance. It exhibits partial solubility in water, forming an opalescent solution. The composition of bee venom has been extensively documented by several authors [233–236]. Honeybee venom harbors traces of substances bees encounter, including environmental toxins like Cd. Choinska et al. [237] developed a method to measure specific heavy metals, including Cd, in bee venom.

2.3.5. Reversal Effects of Royal Jelly and Propolis Against Cadmium Toxicity

Propolis and royal jelly are essential natural products that possess a wide array of active biological properties. These properties encompass antioxidant, anti-inflammatory, antibacterial. antitumor. immunomodulatory, and anti-infertility effects, as documented by several researchers [238-241]. Furthermore, Royal jelly and propolis exhibit potential in alleviating the toxic effects of Cd. Cavuşoğlu et al. [242] suggest that the antioxidant properties of royal jelly act against Cd-induced genotoxicity and oxidative stress in mice. Amr et al. [113] concluded that Honeybee products like propolis and royal jelly may alter Cd absorption, increase excretion, and mitigate oxidative stress, potentially preparing the organism against harmful effects.

2.4. Honeybees and apian products as bioindicators of cadmium pollution

Due to a specific lipid-based chemical composition, Cd is one of the main toxic heavy metals in environmental pollution that can contaminate beehive products. Thus, combs and the inside of the hives can also be contaminated as a consequence of the order and social activity of

Egypt. J. Chem. 67, No. 11 (2024)

foragers and house bees [196]. It has been suggested that there is a close correlation between the level of metal accumulation in soil and plants and their content in bee products. The beehive products have been regarded as bio-indicators of a polluted environment by earlier and recent authors e.g., [186, 187, 203, 224, 243-247]. However, honeybees can filter and purify nectar to remove these contaminants during honey production; honeybees were defined as "biofilters" that prevent elements from penetrating bee products, especially honey. Lower heavy metal content in honey compared to bees suggests effective "filtering" by bees. [179, 198, 248]. Thus, honey concentrates metals well below typical detection limits [249], rendering it unreliable as an environmental indicator. Research by Borsuk et al. [217] suggests that bees can partially immobilize or metabolize certain elements, including Cd, within their fat bodies. Residues are then excreted through the gut. In another study, Costa et al. [250] explored the use of honeybees as bioindicators for atmospheric Pb and Cd levels. Their study suggests bees could serve as alternative tools for monitoring environmental pollution by these metals. In the Netherlands, Van der Steen et al. [251] found air metal concentrations too low and variable to link them to bee metal levels, suggesting honeybees are not reliable air pollution indicators compared to mechanical devices. Furthermore, Beeswax foundations can be recycled [252], accumulating toxic metals in these foundations for decades.

The absence of interdependencies in metal accumulation between consecutive products is likely attributable to the accidental exposure of bees and plants to contamination. Furthermore, it is noteworthy that different plant species and plant organs may exhibit varying concentrations of metals [253]. Honeybees primarily collect nectar and pollen from the same plant species. However, at any given time, a colony utilizes less than half of the plant genera they encounter for both nectar and pollen collection. This limited overlap in plant use raises concerns about the accuracy of bee products (like honey) as indicators of specific metal contamination in the environment. Different plant species accumulate these pollutants at different rates. Recently, DNA-metabarcoding by Leponiemi et al. [190] revealed floral sources of honey and pollen, showing workers leverage similar plants for both, yet use less than half the plant genera per colony for both nectar and pollen simultaneously. Finally, it can be suggested that there is a high level of uncertainty if the honeybees and/or beehive products as environmental bioindicators for Cd pollution for the following reasons: The use of honeybees or apian products as bio-indicators for environmental

555

pollution by trace element creates a high level of uncertainty due to the following reasons: i) trace elements may gain access to internal organs from the atmosphere via spiracles and direct contact with contaminated bodies, as well as from the collected nectar, ii) bees remove contaminants from nectar and honey by metabolizing and immobilizing metals in their fat bodies. The residues are then excreted in the bees' faeces during honey production., iii) bee workers use mostly the same plants for both nectar and pollen, while different plant species and plant organs may contain different concentrations of metals, iv) the lack of interdependences in metal accumulation between the consecutive products probably reflects accidental exposure of bees and plants to contamination, v) as a beekeeping practice, wax may be recycled, and heavy metals can accumulate in wax foundations for decades.

2.5. Remediation of cadmium

The rehabilitation of soils contaminated with toxic metals, in the areas of bee activities, should be considered to avoid the toxicity of this element against honeybees and their beehive products. Common remediation strategies include soil excavation and replacement, chemical precipitation, physicochemical adsorption, biosorption, phytoremediation, etc. [254-256]. Remediation technologies of Cd include digging and filling [257], frozen soil remediation technology [258], vitrification technology also referred to as melting and solidification technology [259], electro-kinetic remediation [260-262], Lime/volcanic ash solidification [263], stabilization technology [264-266], Cement-based binders [267, 268], the plastic material containment method [263, 269], chemical solidification technology [270, 270], Adsorption and coordination [272, 273], chemical complexion mechanism [274, 275], Chemical extraction technology [276, 277]; in addition to bioremediation technologies including soil invertebrates repair technology [278], phytoremediation, and microbial remediation. Generally, remediation procedures can be classified into 4 major categories: physical remediation, Chemical remediation, Electrokinetic remediation, and biological remediation.

2.5.1. Physical remediation

Soil removal and isolation may be applied for seriously contaminated soil with a small area; while adding a huge amount of clean soil to the polluted soil surface or blending the clean soil with it [255, 279, 280].

Egypt. J. Chem. **67**, No. 11 (2024)

2.5.2. Chemical remediation

Contaminated soil can be cleaned by soil leaching, using certain reagents, thereby removing heavy metal complexes and dissolved iron adsorbed on solidphase particles. The removed heavy metals are then recovered from the extraction solution [255]. Contaminated soil can be cleaned also by fixation and adsorption using clay minerals, for example, bentonite, zeolite, and so forth [281]. On the other hand, the removal of Cd(II) ions from polluted solutions has been studied in Egypt by Swelam et al.[282], who have compared adsorption and coagulation techniques in the removal of Cd(II) ions from polluted solutions, using Moringa oleifera Seeds; while a nano-magnetite could be used in laboratory as an eco-friendly sorbent (without the usage of surfactants during the synthesis) for removing Pb(II), Cd(II) and Cr(III) from both Nile river water and wastewater[283].

2.5.3. Electrokinetic remediation

Electrokinetic (EK) migration is a synonymous term for EK remediation, which selfexplanatorily describes the fundamental principles underlying this technology [284]. The application of EK remediation for the treatment of heavy metals in soil has gained increasing attention, serving as both a remediation approach and a resource recovery method [284-287]. The process involves the application of a direct current voltage to generate an electric field gradient across the sides of an electrolytic tank containing the contaminated soil. The pollutants present in the soil are transported to the processing chamber and concentrated at the two poles of the electrolytic cell through mechanisms as electromigration, electroosmosis, or such electrophoresis, thereby facilitating the reduction of pollution. This method has demonstrated efficacy in the treatment of low-permeability soils [255, 288]. Electrokinetic remediation has been widely studied for Cd and other metals at both laboratory and field scales. In situ application of these methods has been investigated [255, 256, 289]. However, heavy metals immobilized within the soil matrix pose a persistent risk due to the potential for environmental disturbances, and phytoremediation techniques for the uptake of these contaminants are characterized by inefficient and prolonged treatment timelines. A comprehensive review of the electrokinetic remediation of Cd has been provided by Zongping et al. [284]. The integration of EK remediation and other remediation strategies has also been investigated [290-292].

2.5.4. Bioremediation

Two major technologies are used in bioremediation: Phytoremediation and Microbial remediation.

2.5.4.1. Phytoremediation

Phytoremediation was defined as "a set of techniques or processes where plants are used for extracting. containing, degrading/destroying or restraining contaminants from the medium (soil, water or sediments)" [293]. However, other definitions [294–299] reflect the concept. Phytoremediation can both immobilize heavy metals mainly in the plant rhizosphere and uptake heavy [299]. aboveground Phytoremediation metals leverages the power of plants and their associated microbial communities to remediate and cleanse environments contaminated with heavy metals. This environmentally friendly technology plays a crucial role in safeguarding both the environment and public health. Saxena et al. [300] explored the potential of phytoremediation as a sustainable approach for managing heavy metal contamination in soil. This technique involves planting specific plant species, like those belonging to the Cruciferae family (e.g., genera Brassica and Alyssum) in the contaminated soil [255, 288, 301]. Plants employed in phytoremediation are termed "hyperaccumulators." These hyperaccumulators have the unique ability to concentrate heavy metals in their aboveground tissues at significantly higher levels compared to the surrounding soil or neighboring non-accumulating It's important to note that plants [302, 303]. hyperaccumulators represent an extreme example within the broader category of accumulator plants [304]. They are hyper-tolerant to the toxic metals, which they accumulate in their organs. For Cd hyperaccumulator plant species can accumulate greater than 100 mg kg-1 dry weight [304, 305]. These authors suggested also quantitative values for other metals. The plant hyper-accumulators of Cd include Azolla pinnata Rai [306], Eleocharis acicularis Sakakibara et al. [307] and Rorippa globosa Wei et al. [308]. Generally, the choice of a plant species for remediation of a specific pollutant should be based on some criteria. Thus, the plant species must have A fully developed system to secret a substantial quantity of catalyst for degradation of the xenobiotics, a tolerance to the xenobiotics at a degree found in soil, a quick growth rate, and a comparatively high biomass [309].

2.5.4.2. Microbial remediation

Microbial remediation, on the other hand, involves the use of several microorganisms (bacteria, archaea, and fungi) to carry out the absorption, deposition, oxidation, and reduction of heavy metals in the soil [255, 288, 310]. However, just like other nonessential toxic metals, Cd is non-biodegradable; such chemicals accumulate in the environment and may be transported to living organisms through the food webs. Thus, Cd taken by microorganisms will eventually re-accumulate in the soil after death of microorganisms. Conversely, in phytoremediation applications, hyperaccumulator plants can be removed from the soil and dumped away or recycled.

3. Conclusions

This review article highlights the major aspects of Cd biogeochemistry and toxicity against honeybees. The main conclusions are: 1) Cadmium is a toxic heavy metal with no known biological function, except for its potential replacement of Zn in some marine plankton. Its presence in the environment is mainly from anthropogenic sources such as mining, fossil fuel combustion, and industrial activities; 2) The biogeochemical cycling of Cd involves transportation through the atmosphere, systems. soil. aquatic and Cadmium can bioaccumulate and biomagnified in organisms and trophic levels; 3) Cadmium is toxic to most organisms including humans and honeybees. Its mechanisms of toxicity include displacement of essential metals like Ca and Zn, and induction of oxidative stress; 4) Honeybees and bee products can accumulate Cd from the environment. However, their reliability as bioindicators of Cd pollution is limited due to factors like nectar filtering by bees and wax recycling practices; and 5) Remediation of Cd contaminated soils is necessary to protect honeybees. Strategies like phytoremediation using hyperaccumulator plants, microbial bioremediation, chemical stabilization, and electrokinetic remediation show promise. In summary, this review integrates research across multiple disciplines to highlight cadmium's environmental behavior, toxicity mechanisms, and impacts on an ecologically and economically vital insect species - the honeybee. A better understanding of these interactions can inform efforts to monitor and rehabilitate environments affected by Cd pollution.

4. Conflicts of interest

There are no conflicts to declare.

5. References

- [1] Schreck, E. et al. 2013. "Influence of Fine Process Particles Enriched with Metals and Metalloids on Lactuca Sativa L. Leaf Fatty Acid Composition Following Air and/or Soil-Plant Field Exposure." Environmental Pollution 179: 242-249.
- [2] Wang, Y. D., J. Fang, S. S. Leonard, and K. M. K. Rao. 2004. "Free Radical Biology and Medicine." Free Radical Biology and Medicine 36:1434–1443.

Egypt. J. Chem. 67, No. 11 (2024)

https://doi.org/10.1016/j.freeradbiomed.2004.03. 024.

- [3] Waisberg, M., P. Joseph, B. Hale, and D. Beyersmann. 2003. "Toxicology." Toxicology 192: 95–117. https://doi.org/10.1016/S0300-483X(03)00305-6.
- [4] Cuypers, Ann, Michelle Plusquin, Tony Remans, Marijke Jozefczak, Els Keunen, Heidi Gielen, Kelly Opdenakker, et al. "Cadmium Stress: An Oxidative Challenge." BioMetals 23, no. 5 (April 2, 2010): 927–40. https://doi.org/10.1007/s10534-010-9329-x.
- [5] Brewers, J. M., B. J. Barry, and D. J. MacGregor. 1987. "Distribution and Cycling of Cadmium in the Environment." In Cadmium in the Aquatic Environment, edited by J. O. Nriagu and J. B. Sprague, 1-18. New York: John Wiley & Sons.
- [6] Traina, S. J. 1999. "The Environmental Chemistry of Cadmium." In Cadmium in Soils and Plants, edited by M. J. McLaughlin and B. R. Singh, 17-37. Dordrecht: Springer Netherlands. https://doi.org/10.1007/978-94-011-4473-5_2.
- [7] Takijima, Y., and Katsumi, F. 1973. "Cadmium Contamination of Soils and Rice Plants Caused by Zinc Mining III. Effects of Water Management and Applied Organic Manures on the Control of Cd Uptake by Plants." Soil Science and Plant Nutrition 19 (1): 29-38.
- [8] Mortvedt, J. 1985. "Plant Uptake of Heavy Metals in Zinc Fertilizers Made From Industrial By-Products1." Journal of Environmental Quality 14.
- [9] Smolders, A., Lock, R., der Velde, G., Medina Hoyos, R., and Roelofs, J. 2003. "Effects of Mining Activities on Heavy Metal Concentrations in Water, Sediment, and Macroinvertebrates in Different Reaches of the Pilcomayo River, South America." Archives of Environmental Contamination and Toxicology 44 (3): 314-323.
- [10] Yang, Q.W., Lan, C.Y., Wang, H.B., Zhuang, P., and Shu, W.S. 2006. "Cadmium in Soil–Rice System and Health Risk Associated with the Use of Untreated Mining Wastewater for Irrigation in Lechang, China." Agricultural Water Management 84 (1): 147–152.
- [11] Oporto, C., Vandecasteele, C., and Smolders, E. 2007. "Elevated Cadmium Concentrations in Potato Tubers Due to Irrigation with River Water Contaminated by Mining in Potos[], Bolivia." Journal of Environmental Quality 36: 1181-1186.
- [12] Zhai, L., Liao, X., Chen, T., Yan, X., Xie, H., Wu, B., and Wang, L. 2008. "Regional Assessment of Cadmium Pollution in Agricultural Lands and the Potential Health Risk Related to Intensive Mining Activities: A Case Study in Chenzhou City, China." Journal of Environmental Sciences 20 (6): 696–703.
- [13] Sun, H., Li, Y., Ji, Y., Yang, L., Wand, W., and Li, H. 2010. "Environmental Contamination and Health Hazard of Lead and Cadmium around Chatian Mercury Mining Deposit in Western Hunan Province, China." Transactions of Nonferrous Metals Society of China 20 (2): 308-314.
- [14] Cullen, J.T., and M.T. Maldonado. 2013."Biogeochemistry of Cadmium and Its Release to the Environment." In Cadmium: From Toxicity to

Essentiality, edited by Astrid Sigel, Helmut Sigel, and Roland K.O. Sigel, 31-62. Dordrecht: Springer Netherlands.

- [15] Müller, G. 1969. "Index of Geoaccumulation in Sediments of the Rhine River." GeoJournal 2:108-118.
- [16] Ji, Y.Q., Y.C. Feng, J.H. Wu, T. Zhu, Z.P. Bai, and C.Q. Duan. 2008. "Using Geoaccumulation Index to Study Source Profiles of Soil Dust in China." Journal of Environmental Sciences 20:571-578.
- [17] Loska, K., D. Wiechula, and I. Korus. 2004. "Metal Contamination of Farming Soils Affected by Industry." Environment International 30:159-165. https://doi.org/10.1016/S0160-4120(03)00157-0.
- [18] Li, Z., Z. Ma, T.J. van der Kuijp, Z. Yuan, L. Huang. 2014. "A Review of Soil Heavy Metal Pollution from Mines in China: Pollution and Health Risk Assessment." Science of The Total Environment 468–469: 843-853. https://doi.org/10.1016/j.scitotenv.2013.08.090.
- [19]H.S. Mekky, E.A. Abou El-Anwar, S.A. Salman, A.A. Elnazer, W. Abdel Wahab and A.S. Asmoay.,2019.
 "Evaluation of Heavy Metals Pollution by Using Pollution Indices in the Soil of Assiut District, Egypt." *Egypt.J.Chem.* 1673 1683.
- [20] El-Shazly M. M, Omar W. A, Edmardash Y. A, Ibrahim M. S, Elzayat E. I, El-Sebeay I. I, Abdel Rahman K. M, Soliman M. M., 2016. "Area reduction and trace element pollution in Nile Delta wetland ecosystems." African Journal of Ecology.
- [21] El-Shazly M. M, Elzayat E, Omar W. A, El-Sebeay I. I. A, Edmardash Y. A, Soliman M. M, Abdel Rahman K. M, Ibrahim M. S., 2016.
 "Water cytotoxicity and dioxins bioaccumulation in an Egyptian delta wetland ecosystem." African Journal of Aquatic Science 1-8.
 [22] El-Shazly, M. M. 2019. "The impact of some
- [22] El-Shazly, M. M. 2019. "The impact of some anthropogenic activities on river Nile delta wetland ecosystems." Global Journal of Ecology 001–007. https://doi.org/10.17352/gje.000008.
- [23] Soliman M. M., El-Shazly M. M., Abd-El-Samie E., Fayed H., 2019. "Variations in heavy metal concentrations among trophic levels of the food webs in two agroecosystems." African Zoology 54:21–30.
- [24] Aoshima, K. 2016. "Itai-itai disease: renal tubular osteomalacia induced by environmental exposure to cadmium - historical review and perspectives." Soil Science and Plant Nutrition 62: 319-326.
- [25] Arain, M.B., T.G. Kazi, J.A. Baig, H.I. Afridi, L. Sarajuddin, K.D. Brehman, H. Panhwar, S.S. Arain, and N. Talpur. 2015. "Co-exposure of arsenic and cadmium through drinking water and tobacco smoking: risk assessment on kidney dysfunction." Environmental Science and Pollution Research 22: 350-357.
- [26] Khan, M.A., S. Khan, A. Khan, and M. Alam. 2017. "Soil contamination with cadmium, consequences and remediation using organic amendments." Science of the Total Environment 601: 1591-1605.

Egypt. J. Chem. 67, No. 11 (2024)

- [27] Lavoie, Michel. "Cadmium: From Toxicity to Essentiality. Metal Ions in Life Sciences, Volume 11. Edited by Astrid Sigel, Helmut Sigel, and Roland K. O. Sigel. Dordrecht (The Netherlands) and New York: Springer. \$239.00. Xxxvi + 560 p.; Ill.; Index. ISBN: 978-94-007-5178-1 (Hc); 978-94-007-5179-8 (Eb). 2013." The Quarterly Review of Biology 90, no. 2 (June 2015): 225– 26. https://doi.org/10.1086/681486.
- [28] Tsadila, C.; Amoroso, C.; Mossialos, D. 2023.
 "Microbial Diversity in Bee Species and Bee Products: Pseudomonads Contribution to Bee Well-Being and the Biological Activity Exerted by Honey Bee Products: A Narrative Review." Diversity 15 (10): 1088. https://doi.org/10.3390/d15101088
- [29] Nowak, A., D. Szczuka, A. Górczy nska, I. Motyl, and D. Kr egiel. 2021. "Characterization of Apis mellifera Gastrointestinal Microbiota and Lactic Acid Bacteria for Honeybee Protection----A Review." Cells 10: 701. https://doi.org/10.3390/cells10030701.
- [30] Ribière, C., C. Hegarty, H. Stephenson, P. Whelan, and P.W. O'Toole. 2019. "Gut and Whole-Body Microbiota of the Honey Bee Separate Thriving and Non-Thriving Hives." Microbial Ecology 78: 195-205. https://doi.org/10.1007/s00248-018-1287-9.
- [31] Papp, M., L. Békési, R. Farkas, L. Makrai, M.F. Judge, G. Maróti, D. Tozsér, and N. Solymosi. 2022. "Natural Diversity of the Honey Bee (Apis mellifera) Gut Bacteriome in Various Climatic and Seasonal States." PLoS ONE 17: e0273844. https://doi.org/10.1371/journal.pone.0273844.
- [32] Dai, P., Z. Yan, S. Ma, Y. Yang, Q. Wang, C. Hou, Y. Wu, Y. Liu, and Q. Diao. 2018. "The Herbicide Glyphosate Negatively Affects Midgut Bacterial Communities and Survival of Honey Bee during Larvae Reared in Vitro." Journal of Agricultural and Food Chemistry 66: 7786-93. https://doi.org/10.1021/acs.jafc.8b02212.
- [33] Romero, S., A. Nastasa, A. Chapman, W.K. Kwong, and L.J. Foster. 2019. "The Honey Bee Gut Microbiota: Strategies for Study and Characterization." Insect Molecular Biology 28: 455-72. https://doi.org/10.1111/imb.12567.
- [34] Ricigliano, V.A., S.T. Williams, and R. Oliver. 2022. "Effects of Different Artificial Diets on Commercial Honey Bee Colony Performance, Health Biomarkers, and Gut Microbiota." BMC Veterinary Research 18: 52. https://doi.org/10.1186/s12917-022-03151-5.
- [35] Di, Ning, Kai Zhang, Kristen R. Hladun, Michael Rust, Ying-Fei Chen, Zi-Zhen Zhu, Tong-Xian Liu, and John T. Trumble. 2020.
 "Joint effects of cadmium and copper on Apis mellifera forgers and larvae." Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology 237: 108839. https://doi.org/10.1016/j.cbpc.2020.108839.
- [36] Klein, Stanislav, Amélie Cabirol, Jean-Marc Devaud, Andrew B. Barron, and Mathieu Lihoreau. 2017. "Why bees are so vulnerable to environmental stressors." Trends in Ecology & Evolution 32: 268-78. https://doi.org/10.1016/j.tree.2016.12.009.

- [37] Gizaw, G., Y. Kim, K. Moon, J.B. Choi, Y.H. Kim, and J.K. Park. 2020. "Effect of environmental heavy metals on the expression of detoxification-related genes in honey bee Apis mellifera." Apidologie 51: 664-74. https://doi.org/10.1007/s13592-020-00716-3.
- [38] Lima, W.G., Brito, J.C.M., and da Cruz Nizer, W.S. 2020. "Phytother Res."
- [39] Evain, L. 2020. "Future of Food." Journal of Food and Agriculture Society 8: 79.
- [40] Yang, Wei, Fu-Liang Hu, and Xiao-Feng Xu. 2020. "Bee Venom and SARS-CoV-2." Toxicon 181: 69-70.
- [41] Kumar, V., Dhanjal, J.K., Bhargava, P., Kaul, A., Wang, J., Zhang, H., Kaul, S.C., Wadhwa, R., and Sundar, D. 2020. "J Biomol Struct Dyn."
- [42] Mannle, H., Hübner, J., and Münstedt, K. 2020. "Toxicon," 187, 279.
- [43] Pourret, Olivier. 2018. "On the Necessity of Banning the Term 'Heavy Metal' from the Scientific Literature." Sustainability 10 (8): 2879. https://doi.org/10.3390/su10082879.
- [44] Pourret, Olivier, and J.C. Bollinger. 2018.
 "'Heavy Metal'—What to Do Now: To Use or Not to Use?" Science of the Total Environment 610: 419-420. https://doi.org/10.1016/j.scitotenv.2017.08.043.
- [45] Silberberg, M., and P. Amateis. 2021. Chemistry: The Molecular Nature of Matter and Change. 9th ed. New York: McGraw Hill.
- [46] OŠPAR. 2002. "Cadmium." Hazardous Substances Series. OSPAR Commission, London.
- [47] Moiseenko, T.I., and Gashkina, N.A. 2018.
 "Biogeochemistry of Cadmium: Anthropogenic Dispersion, Bioaccumulation, and Ecotoxicity." Geochemistry International 56 (8): 798-811.
- [48] EC. 2001. "Ambient Air Pollution by As, Cd and Ni Compounds. Position paper." Working Group on Arsenic, Cadmium and Nickel Compounds. European Commission, Directorate-General Environment.
- [49] McLennan, S.M. 2001. "Relationships between the trace element composition of sedimentary rocks and upper continental crust." G-cubed 2. https://doi.org/10.1029/2000GC000109.
- [50] Rudnick, R.L., and Gao, S. 2003. In Treatise on Geochemistry, edited by H.D. Holland and K.K. Turekian, 1-64. Pergamon, Oxford.
 [51] Fergusson, J.E. 1990. The Heavy Elements:
- [51] Fergusson, J.E. 1990. The Heavy Elements: Chemistry, Environmental Impact, and Health Effects.
- [52] Hayat, M.T., M. Nauman, N. Nazir, S. Ali, and N. Bangash. 2019. "Environmental hazards of cadmium: past, present, and future." In Cadmium Toxicity and Tolerance in Plants: from Physiology to Remediation, edited by M. Hasanuzzaman, M.N.V. Prasad, and M. Fujita, 163-83. Academic Press. https://doi.org/10.1016/B978-0-12-814864-8.00007-3.
- [53] Yaciuk, Pablo A., Fernando Colombo, Karina L. Lecomte, Georgina De Micco, Ana E. Bohé. 2022. "Cadmium sources, mobility, and natural attenuation in contrasting environments (carbonate-rich and carbonate-poor) in the Capillitas polymetallic mineral deposit, NW

Argentina." Applied Geochemistry 136: 105152. https://doi.org/10.1016/j.apgeochem.2021.105152

[54] UNEP. 2010. "Chemicals Branch, DTIE: Final Review of Scientific Information on Cadmium." United Nations Environment Programme, December.

https://wedocs.unep.org/20.500.11822/27636.

- [55] Cook, N.J., C.L. Ciobanu, A. Pring, W. Skinner, M. Shimizu, L. Danyushevsky, B. Saini-Eidukat, and F. Melcher. 2009. "Trace and minor elements in sphalerite: a LA-ICPMS study." Geochemical Cosmochimica Acta 73: 4761-91. https://doi.org/10.1016/j.gca.2009.05.045.
- [56] Alloway, B.J., and Steinnes, E. 1999. "Anthropogenic Additions of Cadmium to Soils." In Cadmium in Soils and Plants, edited by M.J. McLaughlin and B.R. Singh, 97-123. Dordrecht: Springer Netherlands.
- [57] Nriagu, J.O. 1990A. Environment 32: 7-33.
- [58] Nriagu, J.O. 1990B. Environment 333: 134-139.
- [59] Nriagu, J.O. 1996. Science 272: 223-224.
- [60] Pacyna, J.M., and Pacyna, E.G. 2001. Environmental Reviews 9: 269-298.
- [61] Salem, H.M., E.A. Eweida, and A. Farag. 2000. "Heavy Metals in Drinking Water and Their Environmental Impact on Human Health." In Proceedings of the 5th International Conference on Environmental Hazard, Cairo University, Egypt, 542-556.
- [62] Pulford, I., and C. Watson. 2003.
 "Phytoremediation of Heavy Metal-Contaminated Land by Trees—A Review." Environment International 29:529-540. https://doi.org/10.1016/S0160-4120(02)00152-5
- https://doi.org/10.1016/S0160-4120(02)00152-5. [63] Adriano, D.C. 2001. Trace elements in terrestrial environments: Biogeochemistry, bioavailability, and risks of metals. 2nd ed. New York, NY: Springer-Verlag.
- Springer-Verlag.
 [64] Chaney, R. 2012. "Food Safety Issues for Mineral and Organic Fertilizers." In Advances in Agronomy, edited by Donald Sparks, 51-116. Vol. 117. Academic Press.
- [65] Roberts, T.L. 2014. "Cadmium and Phosphorous Fertilizers: The Issues and the Science." Procedia Engineering 83: 52-59.
- [66] Rashid, Abdur, Brian J. Schutte, April Ulery, Michael K. Deyholos, Soum Sanogo, Erik A. Lehnhoff, and Leslie Beck. "Heavy Metal Contamination in Agricultural Soil: Environmental Pollutants Affecting Crop Health." Agronomy 13, no. 6 (May 31, 2023): 1521.

https://doi.org/10.3390/agronomy13061521.

- [67] Nriagu, J.O. 1980. In Cadmium in the Environment, Part I: Ecological Cycling, edited by J.O. Nriagu, 35-70. New York: John Wiley & Sons.
- [68] Rehkamper, M., Wombacher, F., Horner, T.J., and Xue, Z. 2011. In Handbook of Environmental Isotope Geochemistry, edited by M. Baskaran, Springer Berlin Heidelberg, Berlin, Heidelberg, 1-64.
- [69] Cotton, F. A., and G. Wilkinson. 1966. Advanced Inorganic Chemistry: A Comprehensive Text. 2nd ed. New York: John Wiley & Sons.

- [70] ATSDR. 1999. "Toxicological profile for cadmium." U.S. Department of Health and Human Services. Public Health Service. Agency for Toxic Substances and Disease Registry.
- [71] Kubier, Arthur, Richard T. Wilkin, and Thomas Pichler. 2019. "Cadmium in soils and groundwater: A review." Applied Geochemistry 108: 104388.
- [72] Auger, P.A., E. Machu, T. Gorgues, N. Grima, and M. Waeles. "Comparative Study of Potential Transfer of Natural and Anthropogenic Cadmium to Plankton Communities in the North-West African Upwelling." Science of The Total Environment 505 (February 2015): 870–88. https://doi.org/10.1016/j.scitotenv.2014.10.045.
- [73] Yang, S.-C., Zhang, J., Sohrin, Y., and Ho, T.-Y. 2018. "Cadmium Cycling in the Water Column of the Kuroshio-Oyashio Extension Region: Insights from Dissolved and Particulate Isotopic Composition." Geochimica et Cosmochimica Acta 233.
- [74] George, Ejin, Claudine H. Stirling, Melanie Gault-Ringold, Michael J. Ellwood, and Rob Middag. "Marine Biogeochemical Cycling of Cadmium and Cadmium Isotopes in the Extreme Nutrient-Depleted Subtropical Gyre of the South West Pacific Ocean." Earth and Planetary Science Letters 514 (May 2019): 84–95. https://doi.org/10.1016/j.epsl.2019.02.031.
- [75] Guinoiseau, D.; Galer, S. J. G.; Abouchami, W.; Frank, M.; Achterberg, E. P.; Haug, G. H. 2019.
 "Importance of Cadmium Sulfides for Biogeochemical Cycling of Cd and Its Isotopes in Oxygen Deficient Zones---A Case Study of the Angola Basin." Global Biogeochemical Cycles 33(12): 1746.
- [76] Janssen, David J., Matthias Sieber, Michael J. Ellwood, Tim M. Conway, Pamela M. Barrett, Xiaoyu Chen, Gregory F. de Souza, Christel S. Hassler, and Samuel L. Jaccard. 2020. "Trace metal and nutrient dynamics across broad biogeochemical gradients in the Indian and Pacific sectors of the Southern Ocean." Marine Chemistry 221: 103773. https://doi.org/10.1016/j.marchem.2020.103773.
- [77] Cloete, R., J.C. Loock, N.R. Horner, S. Fietz, T.N. Mtshali, H. Planquette, and A.N. Roychoudhury. 2021. "Winter Biogeochemical Cycling of Dissolved and Particulate Cadmium in the Indian Sector of the Southern Ocean (GEOTRACES GIpr07 Transect)." Frontiers in Marine Science 8: 656321. doi:10.3389/fmars.2021.656321.
- [78] Tian, H.-A., van Manen, M., Wille, F., Jung, J., Lee, S., Kim, T.-W., Aoki, S., Brussaard, C.P.D., Reichart, G.-J., Conway, T.M., and Middag, R. 2023. "The Biogeochemistry of Zinc and Cadmium in the Amundsen Sea, Coastal Antarctica." Marine Chemistry 249: 104223.
- [79] Laws, E. A. 1993. Aquatic Pollution: An Introductory Text. 2nd ed. New York: John Wiley & Sons.
- [80] Baes, C. F., and R. E. Mesmer. 1976. The Hydrolysis of Cations. Malabar, FL: Robert E. Krieger Publishing Company.
- [81] ECB. 2005. "Risk Assessment: Cadmium metal/Cadmium oxide." Final, but not adopted

Egypt. J. Chem. 67, No. 11 (2024)

version of December 2005. European Chemicals

- Bureau, Ispra, Italy. [82] AMAP. 1998. "Assessment report: Arctic pollution issues." Arctic Monitoring and Assessment Programme, Oslo.
- [83] IPCS. 1992. "Cadmium environmental aspects." Environmental Health Criteria 135. International Programme on Chemical Safety, Geneva, Switzerland.
- [84] Martin, J. M., and M. Meybeck. 1979. "Elemental Mass-Balance of Material Carried by Major World Rivers." Marine Chemistry 7: 173-206.
- [85] Meybeck, M., L. Laroche, H. H. Durr, and J. P. M. Syvitski. 2003. "Global Variability of Daily Total Suspended Solids and Their Fluxes in Rivers." Global and Planetary Change 39: 65-93.
- [86] Scoullos, M. J., and A. S. Pavlidou. 2003. "Determination of the Lability Characteristics of Lead, Cadmium and Zinc in a Polluted Brackish-Marine Mediterranean Interface System." Water, Air, and Soil Pollution 147: 203-227.
- [87] Shumilin, E., A. Meyer-Willerer, A. J. Marmolejo-Rodriguez, O. Morton-Bermea, M. A. Galicia-Perez, E. Hernandez, and G. Gonzalez-Hernandez. 2005. "Iron, Cadmium, Chromium, Copper, Cobalt, Lead, and Zinc Distribution in the Suspended Particulate Matter of the Tropical Marabasco River and Its Estuary, Colima, Bulletin of Environmental Mexico." Contamination and Toxicology 74: 518-525.
- [88] Thevenot, D. R., Daniel, R., Moilleron, R., Lestel, L., Gromaire, M.C., Rocher, V., Cambier, P., Bonte, P., Colin, J. L., de Ponteves, C., and Meybeck, M. 2007. "Critical Budget of Metal Sources and Pathways in the Seine River Basin (1994-2003) for Cd, Cr, Cu, Hg, Ni, Pb and Zn.' Science of the Total Environment 375: 180-203.
- [89] Lahaye, V., P. Bustamante, W. Dabin, O. Van Canneyt, F. Dhermain, C. Cesarini, G. J. Pierce, and F. Caurant. 2006. "New Insights from Age Determination on Toxic Element Accumulation in Striped and Bottlenose Dolphins from Atlantic and Mediterranean Waters." Marine Pollution Bulletin 52: 1219-1230.
- [90] Frodello, J. P., D. Viale, and B. Marchand. 2002. "Metal Levels in a Cuvier's Beaked Whale (Ziphius cavirostris) Found Stranded on a Mediterranean Coast, Corsica." Bulletin of Environmental Contamination and Toxicology 69: 662-666.
- [91] Macdonald, R.W., Barrie, L.A., Bidleman, T.F., Diamond, M.L., Gregor, D.J., Semkin, R.G., Strachan, W.M.J., Li, Y.F., Wania, F., Alaee, M., Alexeeva, L.B., Backus, S.M., Bailey, R., Bewers, J.M., Gobeil, C., Halsall, C.J., Harner, T., Hoff, J.T., Jantunen, L.M.M., Lockhart, W.L., Mackay, D., Muir, D.C.G., Pudykiewicz, J., Reimer, K.J., Smith, J.N., Stern, G.A., Schroeder, W.H., Wagemann, R., and Yunker, M.B. 2000. "Contaminants in the Canadian Arctic: 5 Years of Progress in Understanding Sources, Occurrence and Pathways." Science of the Total Environment 254: 93-234.

- [92] Bruland, K.W., and R.P. Franks. 1983. "Mn, Ni, Cu, Zn and Cd in the Western North Atlantic." In Trace Metals in Sea Water, edited by C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg, 395-414. Boston, MA: Springer.
- [93] Toggweiler, J.R. and Key, R.M. 2001. "Thermohaline Circulation." In Encyclopedia of Ocean Sciences, edited by Elsevier. www.sciencedirect.com.
- [94] He, S., He, Z., Yang, X., Stoffella, P.J., and Baligar, V.C. 2015. "Soil Biogeochemistry, Plant Physiology, and Phytoremediation of Cadmium-Contaminated Soils." In D. L. Sparks, ed., 135-225
- [95] U.S. EPA. 1999. "Contaminant persistence and mobility factors." The Class V Underground Injection Control Study, Appendices E. United States Environmental Protection Agency, Office of Ground Water and Drinking Water.
- [96] Adriano, D.C., N.S. Bolan, J. Vangronsveld, and W.W. Wenzel. 2005. "Heavy metals." In Encyclopedia of Soils in the Environment, 175-82
- [97] Sukarjo, Sukarjo, Ina Zulaehah, and Wahyu Purbalisa. 2019. "The Critical Limit of Cadmium in Three Types of Soil Texture with Shallot as an Indicator Plant." In AIP Conference Proceedings 040012. 2120. (July): no. 1 https://doi.org/10.1063/1.5115650.
- [98] Ballabio, Cristiano, Arwyn Jones, Luca Montanarella, and Gergely Toth. 2023. Cadmium in the Soils of the EU: Analysis of LUCAS Soils Data for the Review of Fertilizer Directive. Luxembourg: Publications Office of the European Union. https://doi.org/10.2760/635857. JRC106056.
- [99] Kemi. 2000. "Assessment of Risks to Health and the Environment in Sweden from Cadmium in Fertilizers." National Chemicals Inspectorate, Solna, Sweden.
- [100] Louekari, K., Mäkelä-Kurtto, R., Pasanen, J., Virtanen, V., Sippola, J. and Malm, J. 2000. "Cadmium in Fertilizers. Risks to Human Health and the Environment." Publications 4/2000. Ministry of Agriculture and Forestry in Finland, Helsinki, Finland.
- [101] Bogdanov, S. 2006. "Contaminants of Bee Products." Apidologie 37 (1): 1-18. https://doi.org/10.1051/apido:2005043.
- [102] Hunter, Bruce A., and M.S. Johnson. 1982. "Food Chain Relationships of Copper and Cadmium in Contaminated Grassland
- Ecosystems." Oikos 38 (1): 108-17. [103] Zhang, ZS, Lu, XG, Wang, QC, and Zheng, DM. 2009. "Mercury, Cadmium and Lead Biogeochemistry in the Soil-Plant-Insect System in Huludao City." Bulletin of Environmental Contamination and Toxicology 83 (2): 255-9. https://doi.org/10.1007/s00128-009-9688-6
- [104] Gall, J.E., Boyd, R.S., and Rajakaruna, N. 2015. "Transfer of Heavy Metals through Terrestrial Food Webs: A Review." Food Webs: Terrestrial А Review.' Environmental Monitoring and Assessment 187: 201
- [105] Chen, Bin J.W. and Jianxu Xu. 2021. "Trophic Transfer without Biomagnification of Cadmium

in a Soybean-Dodder Parasitic System." Plants 10: 2690. https://doi.org/10.3390/plants10122690.

- [106] Singh, Sumit, Diksha Diksha, Evani Mahajan, and Satwinder Sohal. 2022. "Effect of Heavy Metals on Insects." In Appraisal of Metal (Loids) in the Ecosystem, edited by V. Kumar, A. Sharma, and R. Setia, 361-390. Elsevier, Amsterdam.
- [107] Khan, M.M., Fan, Z.-Y., Wang, X.-M., and Qiu, B.-L. 2024. "Distribution and Accumulation of Cadmium in Different Trophic Levels Affecting Serangium Japonicum, the Predatory Beetle of Whitefly Bemisia Tabaci, Biologically, Physiologically and Genetically: An Experimental Study Muhammad Musa Khan." Journal of Hazardous Materials 465: 133244.
- [108] Mochizuki, M., Hondo, R., Kumon, K. et al. 2002. "Cadmium Contamination in Wild Birds as an Indicator of Environmental Pollution." Environmental Monitoring and Assessment 73: 229-235.
- [109] Domingo, J. L. 1994. Developmental Toxicity in "Metal-Induced in Mammals: A Review." Journal of Toxicology and Environmental Health 42: 123-141. https://doi.org/10.1080/15287399409531868.
- [110] Saulnier, A., J. Bleu, A. Boos, I. El Masoudi, P. Ronot, S. Zahn, M. Del Nero, and S. Massemin. 2020. "Consequences of Trace Metal Cocktail Exposure in Zebra Finch (Taeniopygia guttata) and Effect of Calcium Supplementation." Ecotoxicology and Environmental Safety 193: 110357.

- https://doi.org/10.1016/j.ecoenv.2020.110357. [111] Tchounwou, P. B., C. G. Yedjou, A. K. Patlolla, and D. J. Sutton. 2012. "Heavy Metal Toxicity and the Environment." In Molecular, Clinical and Environmental Toxicology, edited by A. Luch, 133-164. Basel: Springer Basel. https://doi.org/10.1007/978-3-7643-8340-4_6.
- [112] Mitra, S., A J Chakraborty, A M Tareq, T B Emran, Nainu Firzan, A Khusro, M Abubakr Idris, Mayeen Uddin Khandaker, Hamid Osman, Fahad A Alhumaydhi, and Jesus Simal-Gandara. 2022. "Impact of Heavy Metals on the Environment and Human Health: Novel Therapeutic Insights to Counter the Toxicity." Journal of King Saud University - Science 34 (3): 101865

https://doi.org/10.1016/j.jksus.2021.101865.

- [113] Âmr, A., A. Abd Ěl-Wahed, H. R. El-Seedi, S. A. M. Khalifa, M. Augustyniak, L. M. El-Samad, A. E. Abdel Karim, and A. El Wakil. 2022. "UPLC-MS/MS Analysis of Naturally Derived Apis mellifera Products and Their Promising Effects against Cadmium-Induced Adverse Effects in Female Rats." Nutrients 15 (1): 119. https://doi.org/10.3390/nu15010119.
- [114] Thévenod, Frank. "Catch Me If You Can! Novel Aspects of Cadmium Transport in Mammalian Cells." BioMetals 23, no. 5 (March 5, 2010): 857-75. https://doi.org/10.1007/s10534-010-9309-1
- [115] Zalups, R.K. 2000. "Evidence for Basolateral Uptake of Cadmium in the Kidneys of Rats."

Toxicology and Applied Pharmacology 164 (1): 15-23. https://doi.org/10.1006/taap.1999.8854.

- [116] Paustenbach, D., B. Finley, F. Mowat, and B. Kerger. 2003. "Human Health Risk and Exposure Assessment of Chromium (VI) in Tap Water." Journal of Toxicology and Environmental Health, Part (14): 1295-1339. А 66 https://doi.org/10.1080/15287390306417.
- [117] Bernard, A. 2004. "Renal Dysfunction Induced by Cadmium: Biomarkers of Critical Effects." (5): 519-523. Biometals 17 https://doi.org/10.1023/B:BIOM.0000045731.756 02.b9.
- [118] Prozialeck, W. C., J. R. Edwards, and J. M. Woods. 2006. "The Vascular Endothelium as a Target of Cadmium Toxicity." Life Sciences 79 1493-1506. (16): https://doi.org/10.1016/j.lfs.2006.06.011.
- [119] EC. 2010. Commission Staff Working Document Accompanying the Report from the Commission in Accordance with Article 3.7 of the Groundwater Directive 2006/118/ EC on the Establishment of Groundwater Threshold Values. European Commission, 43.
- [120] Pan, J.L., J.A. Plant, and N. Voulvoulis. 2010. "Cadmium levels in Europe: implications for human health." Environmental Geochemistry and Health 32: 1-12.
- [121] Hajeb, P., J.J. Sloth, S. Shakibazadeh, N.A. Mahyudin, L. Afsah-Hejri, and N.A. Jinap. 2014. "Toxic elements in food: occurrence, binding, and reduction approaches." Comprehensive Reviews in Food Science and Food Safety 13: 457-472.
- [122] WHO. 2011. Guidelines for Drinking Water Quality, 4th ed. Geneva: World Health Quality, 4th ed. Geneva: Organization.
- [123] Meravi, N., and S. K. Prajapati. 2013. "Effects of Heavy Metals/Metalloids Contamination of Soils on Micronucleus Induction in Tradescantia pallida." Environmental Skeptics and Critics 2 (2): 58-62.
- [124] Briffa, J., E. Sinagra, and R. Blundell. 2020. "Heavy metal pollution in the environment and their toxicological effects on humans." Heliyon 6 e04691. (9)https://doi.org/10.1016/j.heliyon.2020.e04691.
- [125] Ozyigit, A. H., and B. N. Genc. 2020. "Cadmium in Plants, Humans and the Environment." Frontiers in Life Sciences and
- Related Technologies 1 (1): 12-21. [126] Phan, Rachel. 2022. "Affinity of Cadmium
- Versus Zinc for the Carbonic Anhydrase Active Site." Honors Theses 82. Belmont University. https://repository.belmont.edu/honors_theses/82.
- [127] Sunda, W.G., and Huntsman, S.A. 1995. "Cobalt and Zinc Interreplacement in Marine Phytoplankton: Biological and Geochemical Implications." Limnology and Oceanography 40 (8)
- [128] Sunda, W.G., and Huntsman, S.A. 1998. "Interactions among Cu2+, Zn2+, and Mn2+ in Controlling Cellular Mn, Zn, and Growth Rate in the Coastal Alga Chlamydomonas." Limnology and Oceanography 43 (6).

- [129] Morel, F.M.M., and Price, N.M. 2003. "The Biogeochemical Cycles of Trace Metals in the Oceans." Science 300: 944-947.
- [130] Kellogg, M.M., McIlvin, M.R., Vedamati, J., Twining, B.S., Moffett, J.W., Marchetti, A., Moran, D.M., and Saito, M.A. 2020. "Efficient Zinc/Cobalt Inter-Replacement in Northeast Pacific Diatoms and Relationship to High Surface Dissolved Co:Zn Ratios." Limnology and Oceanography 65 (11):
- Oceanography 65 (11): [131] Sunda, W.G., and Huntsman, S.A. 2000. "Effect of Zn, Mn, and Fe on Cd Accumulation in Phytoplankton: Implications for Oceanic Cd Cycling." Limnology and Oceanography 45 (7).
- [132] Sunda, W.G., and Huntsman, S.A. 2005. "Effect of CO2 Supply and Demand on Zinc Uptake and Growth Limitation in a Coastal Diatom." Limnology and Oceanography 50 (4).
- [133] Saito, M.A., Goepfert, T.J., and Ritt, J.T. 2008.
 "Some Thoughts on the Concept of Colimitation: Three Definitions and the Importance of Bioavailability." Limnology and Oceanography 53 (1):
- [134] Xu, Y., and F.M.M. Morel. 2013. "Cadmium in Marine Phytoplankton." In Cadmium: From Toxicity to Essentiality, edited by Astrid Sigel, Helmut Sigel, and Roland K.O. Sigel, 413-38. Metal Ions in Life Sciences 11. Dordrecht: Springer. https://doi.org/10.1007/978-94-007-5179-8 16.
- [135] Lane, T.W., Saito, M.A., George, G.N., Pickering, I.J., Prince, R.C., and Morel, F.M.M. 2005. "Biochemistry: A Cadmium Enzyme from a Marine Diatom." Nature 435: 42.
- [136] Park, H., Song, B., and Morel, F.M.M. 2007. "Diversity of the Cadmium-Containing Carbonic Anhydrase in Marine Diatoms and Natural Waters." Environmental Microbiology 9: 403-413.
- [137] Xu, Y., Feng, L., Jeffrey, P.D., Shi, Y., and Morel, F.M.M. 2008. "Structure and Metal Exchange in the Cadmium Carbonic Anhydrase of Marine Diatoms." Nature 452: 56–61.
- [138] Finkel, Z.V., Quigg, A.S., Chiampi, R.K., Schofield, O.E., and Falkowski, P.G. 2007.
 "Phylogenetic Diversity in Cadmium: Phosphorus Ratio Regulation by Marine Phytoplankton." Limnology and Oceanography 52: 1131-1138.
- Limnology and Oceanography 52: 1131-1138.
 [139] Horner, T.J., Lee, R.B.Y., Henderson, G.M., and Rickaby, R.E.M. 2013. "Nonspecific Uptake and Homeostasis Drive the Oceanic Cadmium Cycle." Proceedings of the National Academy of Sciences 110: 2500-2505.
- [140] Twining, B.S., and Baines, S.B. 2013. "The Trace Metal Composition of Marine Phytoplankton." Annual Review of Marine Science 5: 191–215.
- [141] Ministry of Health of China. 2006. National Standard of the People's republic of China: Standard for Drinking Water Quality, GB 5749-2006 Standardization Administration of China, 16.
- [142] Li, F., Z.Z. Qiu, J.D. Zhang, W.C. Liu, C.Y. Liu, and G.M. Zeng. 2017. "Investigation, pollution mapping and simulative leakage health risk assessment for heavy metals and metalloids

Egypt. J. Chem. 67, No. 11 (2024)

in groundwater from a typical brownfield, Middle China." International Journal of Environmental Research and Public Health 14: 768.

- Research and Public Health 14: 768. [143] Clark, Edgar W. 1958. "A Review of Literature on Calcium and Magnesium in Insects." Annals of the Entomological Society of America 51 (2): 142-54. https://doi.org/10.1093/aesa/51.2.142.
- [144] Leipart, V., Ø. Enger, D.C. Turcu, O. Dobrovolska, F. Drabløs, Ø. Halskau, and G.V. Amdam. 2022. "Resolving the zinc binding capacity of honey bee vitellogenin and locating its putative binding sites." Insect Molecular Biology 31 (6): 810-20. https://doi.org/10.1111/imb.12807.
- [145] Thimmegowda, G. G., S. Mullen, K. Sottilare, A. Sharma, S. S. Mohanta, A. Brockmann, P. S. Dhandapany, and S. B. Olsson. 2020. "A Field-Based Quantitative Analysis of Sublethal Effects of Air Pollution on Pollinators." Proceedings of the National Academy of Sciences 117: 20653-20661. https://doi.org/10.1073/pnas.2009074117.
- [146] Gutiérrez, M., R. Molero, M. Gaju, J. van der Steen, C. Porrini, J. A. Ruiz. 2020. "Assessing Heavy Metal Pollution by Biomonitoring Honeybee Nectar in C'ordoba (Spain)." Environmental Science and Pollution Research 27: 10436-10448. https://doi.org/10.1007/s11356-019-07485-w.
- [147] Roman, A. 2007. "Content of Some Trace Elements in Fresh Honeybee Pollen." Polish Journal of Food and Nutrition Sciences 57: 475-478.
- [148] Balestra, V., G. Celli, and C. Porrini. 1992.
 "Bees, Honey, Larvae and Pollen in Biomonitoring of Atmospheric Pollution." Aerobiologia 8: 122-126. https://doi.org/10.1007/BF02291339.
- [149] Goretti, E., M. Pallottini, R. Rossi, G. La Porta, T. Gardi, B. T. Cenci Goga, A. C. Elia, M. Galletti, B. Moroni, C. Petroselli, R. Selvaggi, and D. Cappelletti. 2020. "Heavy Metal Bioaccumulation in Honey Bee Matrix, an Indicator to Assess the Contamination Level in Terrestrial Environments." Environmental Pollution 256: 113388. https://doi.org/10.1016/j.envpol.2019.113388.
- [150] Satta, A., M. Verdinelli, L. Ruiu, F. Buffa, S. Salis, A. Sassu, and I. Floris. 2012. "Combination of Beehive Matrices Analysis and Ant Biodiversity to Study Heavy Metal Pollution Impact in a Post-Mining Area (Sardinia, Italy)." Environmental Science and Pollution Research 19: 3977-3988. https://doi.org/10.1007/s11356-012-0921-1.
- [151] Zhou, X., M. P. Taylor, P. J. Davies, and S. Prasad. 2018. "Identifying Sources of Environmental Contamination in European Honey Bees (Apis mellifera) Using Trace Elements and Lead Isotopic Compositions." Environmental Science & Technology 52 (2): 991-1001.
 - https://doi.org/10.1021/acs.est.7b04084.
- [152] Di Noi, A., S. Casini, T. Campani, G. Cai, and I. Caliani. 2012. "Review on Sublethal Effects of Environmental Contaminants in Honey Bees (Apis mellifera), Knowledge Gaps and Future

Perspectives." International Journal of Environmental Research and Public Health 18: 1863. https://doi.org/10.3390/ijerph18041863.

- [153] Nikolić, T.V., D. Kojić, S. Orčić, E.L. Vukašinović, D.P. Blagojević, and J. Purać. 2019. "Laboratory bioassays on the response of honey bee (Apis mellifera L.) glutathione S-transferase and acetylcholinesterase to the oral exposure to copper, cadmium, and lead." Environmental Science and Pollution Research International 26 (7): 6890-97. https://doi.org/10.1007/s11356-018-3950-6.
- [154] Burden, C.M., M.O. Morgan, K.R. Hladun, et al. 2019. "Acute sublethal exposure to toxic heavy metals alters honey bee (Apis mellifera) feeding behavior." Scientific Reports 9: 4253. https://doi.org/10.1038/s41598-019-40396-x. [155] Chicas-Mosier, A. M., B. A. Cooper, A. M.
- Melendez, M. Pérez, D. Oskay, C. I. Abramson. 2017. "The Effects of Ingested Aqueous Aluminum on Floral Fidelity and Foraging Strategy in Honey Bees (Apis mellifera)." Ecotoxicology and Environmental Safety 143: 80-86.

https://doi.org/10.1016/j.ecoenv.2017.05.008.

- [156] Wieser, W., Dallinger, R., and Busch, G. 1977. "The Flow of Copper Through a Terrestrial Food Chain. II. Factors Influencing the Copper Content of Isopods." Oecologia (Berlin) 30: 265-272.
- [157] Gekière, A., M. Vanderplanck, D. Michez, and D. 2023. "Trace Metals with Heavy Consequences on Bees: A Comprehensive Review." Science of the Total Environment 895: 165084.

- https://doi.org/10.1016/j.scitotenv.2022.165084. [158] Hladun, Kristen R., Ning Di, Tong-Xian Liu, and John T. Trumble. 2016. "Metal contaminant accumulation in the hive: consequences for whole-colony health and brood production in the honey bee (Apis mellifera L.)." Environmental Toxicology and Chemistry 35: 322-29.
- [159] AL Naggar, Y., K. Dabour, S. Masry, A. Sadek, E. Naiem, and J.P. Giesy. 2020. "Sublethal effects of chronic exposure to CdO or PbO nanoparticles or their binary mixture on the honey bee (Apis mellifera L.)." Environmental Science and Pollution Research 27: 19004-19015.
- [160] Thévenod, Frank. "Cadmium and Cellular Signaling Cascades: To Be or Not to Be?" Toxicology and Applied Pharmacology 238, no. (August 2009): 221 - 39. 1. https://doi.org/10.1016/j.taap.2009.01.013.
- [161] Antonio, M. T., L. Corredor, and M. L. Leret. 2003. "Toxicology Letters." Toxicology Letters 331–340. 143: https://doi.org/10.1016/j.toxlet.2003.09.008.
- [162] López, E., C. Arce, M. J. Oset-Gasque, and S. Cañadas. 2006. "Free Radical Biology and Medicine." Free Radical Biology and Medicine 940-951. $40 \cdot$ https://doi.org/10.1016/j.freeradbiomed.2005.10. 042
- [163] Dabour, K., Y. Al Naggar, S. Masry, E. Naiem, and J.P. Giesy. 2019. "Cellular alterations in midgut cells of honey bee workers (Apis mellifera L.) exposed to sublethal concentrations of CdO or PbO nanoparticles or their binary

Egypt. J. Chem. 67, No. 11 (2024)

mixture." Science of the Total Environment 651: 1356-1367.

- [164] Čolović, M.B., D.Z. Krstić, T.D. Lazarević-Pašti, A.M. Bondžić, and V.M. Vasić. 2013. "Acetylcholinesterase inhibitors: pharmacology and toxicology." Current Neuropharmacology 11: 315-35.
- [165] Jensen, C.S., L. Garsdal, and E. Baatrup. 1997. Acetylcholinesterase inhibition and altered locomotor behavior in the carabid beetle Pterostichus cupreus. A linkage between biomarkers at two levels of biological complexity." Environmental Toxicology and Chemistry 16: 1727-32.
- [166] Li, Zhiyong, Yan Qiu, Jiao Li, Kai Wan, Huiling Nie, Song Su. 2022. "Chronic Cadmium" Exposure Induces Impaired Olfactory Learning and Altered Brain Gene Expression in Honey Bees (Apis mellifera)." Insects 13: 988. https://doi.org/10.3390/insects13110988.
- [167] Hayes, J.D., J.U. Flanagan, and I.R. Jowsey. 2005. "Glutathione transferases." Annual Review of Pharmacology 45: 51-88.
- [168] Hesketh, H., E. Lahive, A. Horton, et al. 2016. Standard Testing "Extending Period in Honeybees to Predict Lifespan Impacts of Pesticides and Heavy Metals Using Dynamic Energy Budget Modelling." Scientific Reports 6: 37655. https://doi.org/10.1038/srep37655
- [169] de Sousa, L.P. 2021. "Bacterial Communities of Indoor Surface of Stingless Bee Nests." PLoS ONE 16: e0252933. ONE https://doi.org/10.1371/journal.pone.0252933
- [170] Bonilla-Rosso, G. and P. Engel. 2018. 'Functional Roles and Metabolic Niches in the Honey Bee Gut Microbiota." Current Opinion in 43: Microbiology 69-76. https://doi.org/10.1016/j.mib.2018.01.009.
- [171] Donkersley, P., G. Rhodes, R.W. Pickup, and K.C. Jones. 2018. "Bacterial Communities Associated with Honeybee Food Stores Are Correlated with Land Use." Ecology and 4743-56. Evolution 8: https://doi.org/10.1002/ece3.4039.
- [172] Lee, F.J., D.B. Rusch, F.J. Stewart, H.R. Mattila, and I.L.G. Newton. 2015. "Saccharide Breakdown and Fermentation by the Honey Bee Gut Microbiome." Environmental Microbiology 796-815. https://doi.org/10.1111/1462-17: 2920.12526.
- [173] Kafantaris, I., G.D. Amoutzias, and D. Mossialos. 2020. "Foodomics in Bee Product Research: A Systematic Literature Review." European Food Research and Technology 247: 309-31. https://doi.org/10.1007/s00217-020-03535-3.
- [174] Degrandi-Hoff Man, G., B. Eckholm, and K.E. Anderson. 2011. "Honey Bee Health: The Potential Role of Microbes." In Honey Bee Colony Health: Challenges and Sustainable Solutions, edited by D. Sammataro and J. Yoder, CRC 1-12. Boca Raton, FL: Press. https://doi.org/10.1201/b10994-2
- [175] Leonhardt, S.D. and M. Kaltenpoth. 2014. "Microbial Communities of Three Sympatric Australian Stingless Bee Species." PLoS ONE 9:

564

e105718.

https://doi.org/10.1371/journal.pone.0105718.

- [176] Rothman, J.A., L. Leger, J.S. Kirkwood, and Q.S. McFrederick. 2019. "Cadmium and Selenate Exposure Affects the Honey Bee Microbiome and Metabolome, and Bee-Associated Bacteria Show Potential for Bioaccumulation." Applied and Environmental Microbiology 85 (21): e01411-19. https://doi.org/10.1128/AEM.01411-19.
- [177] Monchanin, Coline, Maria Gabriela de Brito Sanchez, Loreleï Lecouvreur, Océane Boidard, Grégoire Méry, Jérôme Silvestre, Gaël Le Roux, David Baqué, Arnaud Elger, Andrew B. Barron, Mathieu Lihoreau, and Jean-Marc Devaud. 2022. "Honey Bees Cannot Sense Harmful Concentrations of Metal Pollutants in Food." 297: 134089. Chemosphere https://doi.org/10.1016/j.chemosphere.2021.1340 89.
- [178] Hladun, K.R., B.H. Smith, J.A. Mustard, R.R. Morton, and J.T. Trumble. 2012. "Selenium toxicity to honey bee (Apis mellifera L.) pollinators: Effects on behaviors and survival." PLoS ONE 7: e3448. https://doi.org/10.1371/journal.pone.0034484
- https://doi.org/10.1371/journal.pone.0034484. [179] Leita, L., G. Muhlbachova, S. Cesco, R. Barbattini, C. Mondini, and I. Benfenati. 1996. "Investigation of the use of honey bees and honey bee products to assess heavy metals contamination." Environmental Monitoring and Assessment 43: 1-9.
- [180] Bogdanov, S., A. Imdorf, J. Charrière, J. Fluri, and V. Kilchenmann. 2003. "The Contaminants of the Bee Colony." Swiss Bees Research Center. Accessed March 4, 2023. http://www.alp.admin.ch/themen/00502/00503/00 513/index.html?lang=en&download=M3wBPgD B/...en%20--.
- [181] Krepper, Gabriela, Paula B. Resende de Cerqueira, Marcelo F. Pistonesi, María S. Di Nezio, and María E. Centurión. 2016.
 "Determination of Cadmium Residues in Bee Products Using a 'Lab-Made' Bismuth Bulk Electrode." International Journal of Environmental Analytical Chemistry 96(14): 1331-1340.
- [182] Bankova, V. S., S. L. Castro, and M. C. Marcucci. 2000. "Propolis: Recent Advances in Chemistry and Plant Origin." Apidologie 31: 3-15.
- [183] De Castro, S. L. 2001. "Propolis: Biological Properties and Pharmacological Activities. Therapeutic Uses of This Bee-Product." Annual Review of Biomedical Sciences 3: 49-83.
- [184] Marcucci, M. C. 1995. "Propolis: Chemical Composition, Biological Properties and Therapeutic Activity." Apidologie 26: 83-99.
- Therapeutic Activity." Apidologie 26: 83-99.
 [185] Roman, A., and Popiela-Pleban, E. 2012.
 "Contamination of Propolis Used as a Dietary Supplement." Potravinarstvo 6 (2): 50-52.
- [186] Conti, M.E. and F. Botre. 2001. "Honeybees and their products as potential bioindicators of heavy metals contamination." Environmental Monitoring and Assessment 69: 267-82. https://doi.org/10.1023/A:1010719107006.

Egypt. J. Chem. **67**, No. 11 (2024)

- [187] Roman, A. 1997. "Bees and Their Products as Pollution Bioindicator in the Copper (LGOM) and Lime-Cement (Opole) Industry Areas." In Scientific Exercise Books of Agricultural University in Wroclaw, 323: 175-193.
- [188] Bertazzini, M., P. Medrzycki, L. Bortolotti, L. Maistrello, and G. Forlani. 2010. "Amino acid content and nectar choice by forager honeybees (Apis mellifera L.)." Amino Acids 39: 315-18. https://doi.org/10.1007/s00726-009-0444-4.
 [189] Nicolson, S.W. 2011. "Bee food: The
- [189] Nicolson, S.W. 2011. "Bee food: The chemistry and nutritional value of nectar, pollen and mixtures of the two." African Zoology 46: 197-204. https://doi.org/10.3377/004.046.0201.
- [190] Leponiemi, M., D. Freitak, M. Moreno-Torres, et al. 2023. "Honeybees' foraging choices for nectar and pollen revealed by DNA metabarcoding." Scientific Reports 13: 14753. https://doi.org/10.1038/s41598-023-42102-4.
- [191] Thakur, M., and V. Nanda. 2020. "Composition and functionality of bee pollen: A review." Trends in Food Science & Technology 98: 82-106. https://doi.org/10.1016/j.tifs.2020.02.001.
- [192] Ball, D.W. 2007. "The chemical composition of honey." Journal of Chemical Education 84: 1643. https://doi.org/10.1021/ed084p1643.
- [193] Sveč njak, L., S. Prd un, J. Rogina, D. Bubalo, and I. Jerković. 2017. "Characterization of Satsuma mandarin (Citrus unshiu Marc.) nectartohoney transformation pathway using FTIR-ATR spectroscopy." Food Chemistry 232: 286-94.

https://doi.org/10.1016/j.foodchem.2017.03.146.

- [194] Uren, A., A. Serifoglu, and Y. Sarikahya. 1998.
 "Distribution of elements in honeys and effect of a thermoelectric power plant on the element contents." Food Chemistry 61: 185-90. https://doi.org/10.1016/S0308-8146(97)00130-7.
 [195] Fakhim-Zadeh, K. 1998. "Investigation of
- [195] Fakhim-Zadeh, K. 1998. "Investigation of selected heavy metals (Cd, Pb, Cu and Zn) in honey bees, honey and pollen in Finland." PhD diss., University of Helsinki.
- [196] Devillers, J., J.C. Doré, C. Viel, M. Marenco, F. Poirier-Duchêne, N. Galand, and M. Subirana. 2002. "Typology of French acacia honeys based on their concentrations in metallic and nonmetallic elements." In Honey Bees: Estimating the Environmental Impact of Chemicals, edited by J. Devillers and M.H. Pham-Delègue, 248-68. London: Taylor & Francis.
- [197] Conti, M.E., S. Saccares, F. Cubadda, R. Cavallina, and C.A. Tenoglio. 1998. "Il miele nel Lazio: Indagine sul contenuto in metalli in tracce e radionuclidi." Journal of Food Science and Nutrition 27: 107-19.
- [198] Porrini, C., S. Ghini, S. Girotti, A.G. Sabatini, E. Gattavecchia, and G. Celli. 2002. "Use of honey bees as bioindicators of environmental pollution in Italy." In Honey Bees: Estimating the Environmental Impact of Chemicals, edited by J. Devillers and M.H. Pham-Delègue, 186-247. London: Taylor & Francis.
- [199] Rashed, M.N., and Soltan, M.E. 2004. "Major and Trace Elements in Different Types of Egyptian Mono-Floral and Non-Floral Bee

Honeys." Journal of Food Composition and Analysis 17 (6): 725-735.

- [200] Rashed, M.N., El-Haty, M.T.A., and Mohamed, S.M. 2009. "Bee Honey as Environmental Indicator for Pollution with Heavy Metals." Toxicology and Environmental Chemistry 91 (3): 389-403.
- [201] Malhat, F., Kasiotis, K.M., Hassanin, A.S., and Shokr, S.A. 2019. "An MIP-AES Study of Heavy Metals in Egyptian Honey: Toxicity Assessment and Potential Health Hazards to Consumers." Journal of Elementology 24 (2): 473-488.
- Journal of Elementology 24 (2): 473-488.
 [202] Altunatmaz, S. S., A. Sancak, F. Ekici, and Z. Konuskan. 2019. "Levels of Chromium, Copper, Iron, Magnesium, Manganese, Selenium, Zinc, Cadmium, Lead and Aluminium of Honey Varieties Produced in Turkey." Food Science and Technology (Campinas) 39 (Suppl. 2): 392-97. doi:10.1590/fst.19718.
- [203] Przybyłowski, P., and Wilczynska, A. 2001. "Honey as an Environmental Marker." Food Chemistry 74: 289-291.
- [204] Roman, A. 2010. "Levels of Copper, Selenium, Lead, and Cadmium in Forager Bees." Polish Journal of Environmental Studies 19 (3): 663-69.
- [205] Dzugan, M., Zagula, G., Wesolowska, M., Sowa, P., and Puchalski, C. 2017. "Levels of Toxic and Essential Metals in Varietal Honeys from Podkarpacie." Journal of Elementology 22 (3): 1039-1048.
- [206] Frias, I., Rubio, C., Gonzalez-Iglesias, T., Gutierrez, A.J., Gonzalez-Weller, D., and Hardisson, A. 2008. "Metals in Fresh Honeys from Tenerife Island, Spain." Bulletin of Environmental Contamination and Toxicology 80 (1): 30-33.
- [207] Vanhanen, L.P., Emmertz, A., and Savage, G.P. 2011. "Mineral Analysis of Mono-floral New Zealand Honey." Food Chemistry 128 (1): 236-40.
- https://doi.org/10.1016/j.foodchem.2011.02.064
- [208] Buldini, P.L., S. Cavalli, A. Mevoli, and J.L. Sharma. 2001. "Ion Chromatographic and Voltammetric Determination of Heavy and Transition Metals in Honey." Food Chemistry 73 (4): 487-95. doi:10.1016/S0308-8146(01)00132-7
- [209] Eskov, E.K., Eskova, M.D., Dubovik, V.A., and Vyrodov, I.V. 2015. "Content of Heavy Metals in Melliferous Vegetation, Bee Bodies, and Beekeeping Production." Russian Agricultural Sciences 41 (5): 396-398.
- Agricultural Sciences 41 (5). 576 576 [210] Szilárd Bartha, Ioan Taut, Gyozo Goji, Ioana Andra Vlad and Florin Dinulica. 2020. "Heavy Metal Content in Polyfloral Honey and Potential Health Risk. A Case Study of Cops, a Mica, Romania." International Journal of Environmental Research and Public Health 2020.
- [211] Akbari B., Gharanfoli F., Khayyat M.H., Khashyarmanesh, Z., Rezaee, R., and Karimi, G. 2012. "Determination of Heavy Metals in Different Honey Brands from Iranian Markets." Food additives & contaminants: Part B 5 (2): 105-11. doi:10.1080/19393210.2012.664173.
- [212] Mititelu, Magdalena, Denisa Ioana Udeanu, Anca Oana Docea, Aristidis Tsatsakis, Daniela Calina, Andreea Letitia Arsene, Mirela

Egypt. J. Chem. 67, No. 11 (2024)

Nedelescu, Sorinel Marius Neacsu, Bruno Ștefan Velescu, and Manuela Ghica. 2023. "New method for risk assessment in environmental health: The paradigm of heavy metals in honey." Environmental Research 236, no. 1: 115194. https://doi.org/10.1016/j.envres.2022.115194.

- [213] Erbilir, F., and O. Erdoğrul. 2005. "Determination of Heavy Metals in Honey in Kahramanmaraş City, Turkey." Environmental Monitoring and Assessment 109: 181-187. https://doi.org/10.1007/s10661-005-5848-2.
- [214] Losfeld, G., J.B. Saunier, and C. Grison. 2014. "Minor and Trace-elements in Apiary Products from a Historical Mining District (Les Malines, France)." Food Chemistry 146: 455-459.
- [215] Conti, M.E., S. Canepari, M.G. Finoia, G. Mele, and M.L. Astolfi. 2018. "Characterization of Italian Multifloral Honeys on the Basis of Their Mineral Content and Some Typical Quality Parameters." Journal of Food Composition and Analysis 74: 102-113.
- [216] Dźugan, M., M. Wesołowska, G. Zaguła, M. Kaczmarski, M. Czernicka, and C. Puchalski. 2018. "Honeybees (Apis mellifera) as a Biological Barrier for Contamination of Honey by Environmental Toxic Metals." Environmental Monitoring and Assessment 190 (3): 101. https://doi.org/10.1007/s10661-018-6492-5.
- [217] Borsuk, G., A. Sulborska, E. Stawiarz, et al. 2021. "Capacity of Honeybees (Apis mellifera) to Remove Heavy Metals from Nectar and Excrete the Contaminants from Their Bodies." Apidologie 52: 1098-1111. https://doi.org/10.1007/s13592-021-00890-6.
- [218] Ullah, R., F.A. Jan, H. Gulab, et al. 2022. "Metals Contents in Honey, Beeswax and Bees and Human Health Risk Assessment Due to Consumption of Honey: A Case Study from Selected Districts in Khyber Pakhtunkhwa, Pakistan." Archives of Environmental Contamination and Toxicology 82: 341-54. https://doi.org/10.1007/s00244-021-00910-z.
- [219] Gajger, I. T., Marina Kosanović, Nina Bilandžić, Marija Sedak, and Bruno Čalopek. 2016. "Variations in Lead, Cadmium, Arsenic, and Mercury Concentrations during Honeybee Wax Processing Using Casting Technology." Archives of Industrial Hygiene and Toxicology 67: 223-228.
- [220] Danner, N., A. Keller, S. Härtel, and I. Steffan-Dewenter. 2017. "Honey bee foraging ecology: Season but not landscape diversity shapes the amount and diversity of collected pollen." PLoS ONE 12: e0183716. https://doi.org/10.1371/journal.pone.0183716.
- [221] Hoover, S.E. and L.P. Ovinge. 2018. "Pollen Collection, Honey Production, and Pollination Services: Managing Honey Bees in an Agricultural Setting." Journal of Economic Entomology 111: 1509-16. https://doi.org/10.1093/jee/toy118.
- [222] Vieira, K.I.C., H. Azevedo Werneck, J.E. Santos Júnior, D.S. Silva Flores, J.E. Serrão, L.A.D.O. Campos, and H.C. Resende. 2020. "Bees and the environmental impact of the rupture of the fundão dam." Integrated

Environmental Assessment and Management 16: 631-35. https://doi.org/10.1002/ieam.4239.

- [223] Pascoal, A., Rodrigues, S., Teixeira, A., Feas, X., and Estevinho, L. M. 2014. "Biological Activities of Commercial Bee Pollens: Antimicrobial, Antimutagenic, Antioxidant and Anti-Inflammatory." Food and Chemical Toxicology 63: 233-239.
 [224] Roman, A. 2009. "Concentration of Chosen
- [224] Roman, A. 2009. "Concentration of Chosen Trace Elements of Toxic Properties in Bee Pollen Loads." Polish Journal of Environmental Studies 18 (2): 265-272.
- [225] Nascimento, N. O., H. A. Halini, F. Ataide, A. T. Abreu, and Y. Antonini. 2018. "Pollen storage by stingless bees as an environmental marker for metal contamination: Spatial and temporal distribution of metal elements." Sociobiology 65: 259-270.

https://doi.org/10.13102/sociobiology.v65i2.2078

- [226] Belina-Aldemita, M. D., V. Fraberger, M. Schreiner, K. J. Domig, and S. D'Amico. 2020. "Safety aspects of stingless bee pot-pollen from the Philippines." Bodenkultur: Journal of Land Management, Food and Environment 71: 87-100. https://doi.org/10.2478/ boku-2020-0009.
- https://doi.org/10.2478/ boku-2020-0009.
 [227] Oliveira, F. A., A. T. Abreu, N. Oliveira Nascimento, R. E. Santos Froes-Silva, Y. Antonini, H. A. Nalini, and J. C. Lena. 2017. "Evaluation of matrix effect on the determination of rare earth elements and As, Bi, Cd, Pb, Se and in in honey and pollen of native Brazilian bees (Tetragonisca angustula -- jataí) by Q-ICP-MS." Talanta 162: 488-494. https://doi.org/10.1016/i.talanta.2016.10.058.
- https://doi.org/10.1016/j.talanta.2016.10.058. [228] Vegh, R., M. Csoka, C. Soros, and L. Sipos. 2021. "Food safety hazards of bee pollen - A review." Trends in Food Science & Technology 114: 490-509. https://doi.org/10.1016/j.tifs.2021.07.014.
- [229] Melliou, E. and I. Chinou. 2014. "Chemistry and bioactivities of royal jelly." In Studies in Natural Products Chemistry, vol 43, 261-90. Amsterdam: Elsevier. https://doi.org/10.1016/B978-0-444-63294-4.00008-7.
- [230] Vezeteu, T.V., O. Bobi s, R.F.A. Moritz, and A. Buttstedt. 2016. "Food to some. poison to others---honeybee royal jelly and its growth inhibiting effect on European Foulbrood bacteria." MicrobiologyOpen 6: e00397. https://doi.org/10.1002/mbo3.397.
- [231] Ayestaran, A., M. Giurfa, and M. G. de Brito Sanchez. 2010. "Toxic but Drank: Gustatory Aversive Compounds Induce Post-Ingestional Malaise in Harnessed Honeybees." PLoS One 5 (10): e15000. https://doi.org/10.1371/journal.pone.0015000.
- [232] Di, N., K. R. Hladun, K. Zhang, T.-X. Liu, J. T. Trumble, and B. H. Smith. 2016. "Laboratory Bioassays on the Impact of Cadmium, Copper and Lead on the Development and Survival of Honeybee (Apis mellifera L.) Larvae and Foragers." Chemosphere 152: 530-38. https://doi.org/10.1016/j.chemosphere.2016.02.06 0.

[233] Haberman, E. 1972. "Bee and wasp venoms." Science 177: 314-322.

- [234] Schumacher, M.J., Tveten, M.S., and Egen, N.B. 1994. "J Allergy Clin Immun," 93, 831.
 [235] Meier, J., and White, J. 1995. Handbook of
- [235] Meier, J., and White, J. 1995. Handbook of Clinical Toxicology of Animal Venoms and Poisons. New York: Informa HealthCare.
- [236] MDI Biological Laboratory and North Carolina State University. 2017. "Comparative Toxicogenomics Database Adolapin."
- [237] Choinska, M., V. Hrdlička, I. Šestěková, T. Navrátil, and L. Baldrianová. 2021 "Voltammetric Determination of Heavy Metals in Honey Bee Venom Using Hanging Mercury Drop Electrode and PLA/Carbon Conductive Filament for 3D Printer." Monatshefte Für Chemie -Chemical Monthly 152 35-41. (1): doi:10.1007/s00706-020-02725-z.
- [238] Pasupuleti, V. R., L. Sammugam, N. Ramesh, and S. H. Gan. 2017. "Honey, Propolis, and Royal Jelly: A Comprehensive Review of Their Biological Actions and Health Benefits." Oxidative Medicine and Cellular Longevity 2017: 1259510. https://doi.org/10.1155/2017/1259510.
- [239] Noh, S., A. Go, D. B. Kim, M. Park, H. W. Jeon, and B. Kim. 2020. "Role of Antioxidant Natural Products in Management of Infertility: A Review of Their Medicinal Potential." Antioxidants 9 (9): 957. https://doi.org/10.3390/antiox9090957.
- [240] Yosri, N., A. A. A. El-Wahed, R. Ghonaim, O. M. Khattab, A. Sabry, M. A. A. Ibrahim, M. F. Moustafa, Z. Guo, X. Zou, A. F. M. Algethami et al. 2021. "Anti-Viral and Immunomodulatory Properties of Propolis: Chemical Diversity, Pharmacological Properties, Preclinical and Clinical Applications, and In Silico Potential against SARS-CoV-2." Foods 10 (8): 1776. https://doi.org/10.3390/foods10081776.
- [241] Salama, S., Q. Shou, A. A. Abd El-Wahed, N. Elias, J. Xiao, A. Swillam, M. Umair, Z. Guo, M. Daglia, K. Wang et al. 2022. "Royal Jelly: Beneficial Properties and Synergistic Effects with Chemotherapeutic Drugs with Particular Emphasis in Anticancer Strategies." Nutrients 14 (12): 4166. https://doi.org/10.3390/nu14124166.
- [242] Cavuşoğlu, K., K. Yapar, and E. Yalçin. 2009. "Royal jelly (honey bee) is a potential antioxidant against cadmium-induced genotoxicity and oxidative stress in albino mice." Journal of Medicinal Food 12 (6): 1286-92. https://doi.org/10.1089/jmf.2008.0203.
- [243] Celli, G. and B. Maccagnani. 2003. "Honey bees as bioindicators of environmental pollution." Bulletin of Insectology 56: 137-39.
- [244] Roša, J. 2006. "Tannins and Microelements in the Cells of Silver Fir Tree Needles (Abies Alba Mill.) and the Microelements in Bee Honey as Indicators of the Silver Fir Forests Condition in the Area of Gorski Kotar." Sumarski List 130: 493-509.
- [245] Yazgan, S., Horn, H., and Isengard, H.D. 2006. "Honey as Bioindicator by Screening the Heavy Metal Content of the Environment." Deutsche Lebensmittel-Rundschau 102:192-7.

- [246] Pisani, A., Protano, G., and Riccobono, F. 2008. "Minor and Trace Elements in Different Honey Types Produced in Siena County (Italy)." Food Chemistry 107:1553-1560.
- [247] Naccari, C., Macaluso, A., Giangrosso, G., Naccari, F., and Ferrantelli, V. 2014. "Risk Assessment of Heavy Metals and Pesticides in Honey from Sicily (Italy)." Journal of Food Research 3:107-17.
- [248] Porrini, C., Celli, G., Radeghieri, P., Marini, S., and Maccagnani, B. 2000. "Studies on the Use of Honeybees (*Apis Mellifera* L.) as Bioindicators of Metals in the Environment." Insect Social Life 3: 153-159.
- [249] Conti, M.E., M.L. Astolfi, M.G. Finoia, L. Massimi, and S. Canepari. 2022. "Biomonitoring of element contamination in bees and beehive products in the Rome province (Italy)." Environmental Science and Pollution Research International 29 (24): 36057-74. https://doi.org/10.1007/s11356-021-18072-3.
- [250] Costa, A., M. Veca, M. Barberis, L. Cicerinegri, and F.M. Tangorra. 2021. "Predicting Atmospheric Cadmium and Lead Using Honeybees as Atmospheric Heavy Metals Pollution Indicators." Italian Journal of Animal Science 20 (1): 850-58. doi:10.1080/1828051X.2021.1929523.
- [251] Van der Steen, J.J.M., J. de Kraker, and T. Grotenhuis. 2015. "Assessment of the Potential of Honeybees (Apis mellifera L.) in Biomonitoring of Air Pollution by Cadmium, Lead and Vanadium." Journal of Environmental Protection 6: 96-102. http://dx.doi.org/10.4236/jep.2015.62011
- http://dx.doi.org/10.4236/jep.2015.62011. [252] Alkassab, Abdulrahim T., David Thorbahn, Malte Frommberger, Gabriela Bischoff, and Jens Pistorius. 2022. "Effect of contamination and adulteration of wax foundations on the brood development of honeybees." Apidologie 51 (4): 642-51. https://doi.org/10.1007/s13592-020-00749-2.
- [253] Formicki, G., A. Greń, R. Stawarz, B. Zyśk, and A. Gał. 2013. "Metal Content in Honey, Propolis, Wax, and Bee Pollen and Implications for Metal Pollution Monitoring." Polish Journal of Environmental Studies 22 (1): 99-106.
- [254] Wang, Ying, Dongmei Jia, Rongfu Sun, Huijuan Zhu, and Dongsheng Zhou. 2008.
 "Adsorption and Cosorption of Tetracycline and Copper(II) on Montmorillonite as Affected by Solution pH." Environmental Science & Technology 42 (9): 3254-3259. https://doi.org/10.1021/es702641a.
- [255] Su, C., Jiang, L., and Zhang, W. 2014. "A Review on Heavy Metal Contamination in the Soil Worldwide: Situation, Impact and Remediation Techniques." Environmental Skeptics and Critics 3 (2): 24-38.
- [256] Li, C., K. Zhou, W. Qin, C. Tian, M. Qi, X. Yan, and W. Han. 2019. "A Review on Heavy Metals Contamination in Soil: Effects, Sources, and Remediation Techniques." Soil and Sediment Contamination: An International Journal 28:380-394.

https://doi.org/10.1080/15320383.2019.1592108.

- [257] Chen, Y.J., L.N. Fang, and J.Y. Yang. 2014. "The Cropland Pollution in China: Status and Countermeasures." Chinese Journal of Agricultural Resources and Regional Planning 35: 1-5.
- [258] Zhao, Jinglian. 2006. Principles and Technology of Environmental Remediation. Beijing: Chemical Industry Press.
- [259] Smith, L.A., Means, J.L., Chen, A., et al. 1995. Remedial Options for Metals-Contaminated Sites. Boca Raton, FL.
- [260] Probstein, R.F., and Hicks, R.E. 1993. "Removal of Contaminants from Soils by Electric Fields." Science 260: 498-503.
- [261] Suer, Y.B., Gitye, K., and Allard, B. 2003. "Speciation and Transport of Heavy Metals and Macroelements during Electroremediation." Environmental Science and Technology 37: 177-181.
- [262] Gomes, H.I., Dias-Ferrira, C., Ribero, A.B. 2012. "Electrokinetic Remediation of Organochlorines in Soil: Enhancement Techniques and Integration with Other Remediation Technologies." Chemosphere 87: 1077-1090.
- [263] Tang, X. and Ni, Y. 2021. "Review of Remediation Technologies for Cadmium in Soil." E3S Web of Conferences 233: 010.
- [264] Environmental Protection Agency. 2009. Technology Performance Review: Selecting and Using Solidification/Stabilization Treatment for Site Remediation. Washington: EPA.
- [265] Hao, Hanzhou, Chen, Tongbin, Jin, Menggui, et al. 2011. "Research Progress of Heavy Metal Contaminated Soil Stabilization/Solidification Technology." Chinese Journal of Applied Ecology 22(3): 816-824.
- [266] Du, Yanjun, Jin Fei, Liu Songyu, et al. 2011. "Research Progress on Solidification/Stabilization of Contaminated Sites in Heavy Metal Industry." Rock and Soil Mechanics 32 (1): 116-124.
- [267] Malviya, R., and Chaudhary, R. 2006. "Leaching Behavior and Immobilization of Heavy Metals in Solidified/Stabilized Products." Journal of Hazardous Materials 137: 207-217.
- [268] Chen, Q.Y., M. Tyrer, C.D. Hills, X.M. Yang, and P. Carey. 2009. "Immobilisation of Heavy Metal in Cement-Based Solidification/Stabilisation: A Review." Waste Management 29: 390-403. doi:10.1016/j.wasman.2008.03.019.
- [269] Simeonova, A., Petkov, A., and Balgaranova, J. 2006. "Stabilization of Sludge from Electroplating of Plastic Materials for Safe Disposal and Utilization." Journal of the University of Chemical Technology and Metallurgy 41: 107-110.
- [270] Sun, Pengcheng, Huang, Zhanbin, Tang, Ke, et al. 2014. "Research Progress in Chemical Solidification of Soil Heavy Metal Pollution Control." Environmental Engineering 32 (1): 158-161.
- [271] Li, Ning, Ren, Bozhi, Zhou, Yingying, et al. 2017. "Research on Soil Heavy Metal Pollution Hazards and Remediation Methods." Guangzhou Chemical Industry 45 (9): 30-32.

- [272] Yang, Xiuli, and Wang, Xuejie. 2002. "Chemical Treatment and Restoration of Soil Contaminated by Heavy Metals." Journal of Zhejiang Education Institute 2002 (2): 55-61.
- [273] Li, Jianrui, Xu, Yingming, Lin, Dasong, et al. 2014. "Research Progress in In-Situ Passivation Remediation of Heavy Metal Pollution in Farmland." Journal of Ecological Environment 23 (4): 721-728.
- [274] Sun, Fusheng. 2015. "Study on the Content of Heavy Metals and Their Complexing Mechanism in Soil with Long-Term Located Fertilization." Dissertation, Nanjing Agricultural University.
- Dissertation, Nanjing Agricultural University.
 [275] Wu, Xue, Zhao, Li, and Ding, Lin. 2017. "The Application of Organic Amendments in the Remediation of Heavy Metal Contaminated Soil." Southern Agriculture 11 (12): 119-122.
 [276] Peng, Da. 2018. "Chemical Extraction
- [276] Peng, Da. 2018. "Chemical Extraction Technology in the Remediation of Heavy Metal Contaminated Soil." Environmental Governance and Development (25): 53-54.
 [277] Qi, Miao. 2019. "Chemical Extraction
- [277] Qi, Miao. 2019. "Chemical Extraction Technology in the Remediation of Heavy Metal Contaminated Soil." Regional Management (4): 67-68.
- [278] Li, J.R., and Xu, Y.M. 2017. "Immobilization Remediation of Cd-Polluted Soil with Different Water Conditions." Journal of Environmental Management 193: 607-612.
- [279] Zheng, XS, Lu, AH, Gao, X, et al. 2002. "Contamination of Heavy Metals in Soil Present Situation and Method." Soils and Environmental Science 11 (1): 79–54.
- [280] Nyiramigisha et al. 2021. "Reviews in Agricultural Science," 9, 271-282.
 [281] Wang, XZQ. 2004. "The Ecological Process,
- [281] Wang, XZQ. 2004. "The Ecological Process, Effect and Remediation of Heavy Metals Contaminated Soil." Ecological Science 23 (3): 278–281.
- [282] A. A. Swelam, Sherif S. S. and A. I. Hafez.2019. "Removal Comparative Study for Cd(II) Ions from Polluted Solutions by Adsorption and Coagulation Techniques Using Moringa Oleifera Seeds." *Egypt.J.Chem.* 1499 – 1517.
- [283] Shimaa M. Ali, A. Galal, Nada F. Atta, Yassmin Shammakh.2017." Toxic Heavy Metal Ions Removal from Wastewater by Nano-Magnetite: Case Study Nile River Water." *Egypt.J.Chem.* 601- 612.
- [284] Cai, Zongping, Yan Sun, Yanghong Deng, Xiaojie Zheng, Shuiyu Sun, Martin Romantschuk, and Aki Sinkkonen. 2021. "In Situ Electrokinetic (EK) Remediation of the Total and Plant Available Cadmium (Cd) in Paddy Agricultural Soil Using Low Voltage Gradients at Pilot and Full Scales." Science of the Total Environment 785: 147277. https://doi.org/10.1016/j.scitotenv.2021.147277.
- [285] Acar, Y.B., R.J. Gale, A.N. Alshawabkeh, R.E. Marks, S. Puppala, M. Bricka, and R. Parker. 1995. "Electrokinetic Remediation: Basics and

Egypt. J. Chem. 67, No. 11 (2024)

Technology Status." Journal of Hazardous Materials 40:117-137. https://doi.org/10.1016/0304-3894(94)00066-P.

[286] Kim, B.K., K. Baek, S.H. Ko, and J.W. Yang. 2011. "Research and Field Experiences on Electrokinetic Remediation in South Korea." Separation and Purification Technology, Elsevier, 116–123.

https://doi.org/10.1016/j.seppur.2011.03.002.

- [287] Ottosen, L. M. 2014. "Electrokinetics in the Removal of Metal Ions from Soils." In Encyclopedia of Applied Electrochemistry, edited by G. Kreysa, K.-i. Ota, and R. F. Savinell, 742– 746. New York, NY: Springer New York. https://doi.org/10.1007/978-1-4419-6996-5 87.
- [288] Kamari, A. 2011. "Chitosans as Soil Amendments for the Remediation of Metal Contaminated Soil." PhD diss., University of Glasgow.
- [289] Wang, L., L. Huang, H. Xia, H. Li, X. Li, and X. Liu. 2019. "Application of a Multi-Electrode System with Polyaniline Auxiliary Electrodes for Electrokinetic Remediation of Chromium-Contaminated Soil." Separation and Purification Technology 224:106-112. https://doi.org/10.1016/j.seppur.2019.05.019.
- [290] Lee, K.-Y., K.-R. Kim, B.-T. Lee, J.-Y. Kim, K.-W. Kim, and S.-O. Kim. 2009. "Evaluation on the Feasibility of Microbially Enhanced Electrokinetic Removal of Multiple Heavy Metals from Tailing Soil." Separation Science and Technology 44: 2322–2340. https://doi.org/10.1080/01496390902983653.
- [291] Selvi, A., A. Rajasekar, J. Theerthagiri, A. Ananthaselvam, K. Sathishkumar, J. Madhavan, and P.K.S.M. Rahman. 2019. "Integrated Remediation Processes toward Heavy Metal Removal/Recovery from Various Environments—A Review." Frontiers in Environmental Science 7. https://doi.org/10.3389/fenvs.2019.00066.
- [292] He, Chiquan, Anni Hu, Feifei Wang, Pu Zhang, Zhenzhen Zhao, Yanping Zhao, and Xiaoyan Liu. "Effective Remediation of Cadmium and Zinc Co-Contaminated Soil by Electrokinetic-Permeable Reactive Barrier with a Pretreatment of Complexing Agent and Microorganism." Chemical Engineering Journal 407 (March 2021): 126923.

https://doi.org/10.1016/j.cej.2020.126923.

- [293] EPA. 2000. Introduction to Phytoremediation. EPA/600/R-99/107. National Risk Management Research Laboratory. http://www.cluin.org/download/remed/introphyto .pdf.
- [294] Rodriguez, L., F. J. Lopez-Bellido, A. Carnicer, F. Recreo, A. Tallos, and J. M. Monteagudo. 2005. "Mercury Recovery from Soils by Phytoremediation." In Book of Environmental Chemistry, 197-204. Berlin: Springer.
- [295] Tangahu, B. V., S. R. Sheikh Abdullah, H. Basri, M. Idris, N. Anuar, and M. Mukhlisin. 2011. "A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants through Phytoremediation." International Journal of

Chemical Engineering 2011: 939161. https://doi.org/10.1155/2011/939161.

- [296] Ismail, S. 2012. "Phytoremediation: A Green Technology." Iranian Journal of Plant Physiology 3 (1): 567-576.
- [297] Cameselle, C., R. A. Chirakkara, and K. R. Reddy. 2013. "Electrokinetic-Enhanced Phytoremediation of Soils: Status and Opportunities." Chemosphere 93 (4): 626-636. https://doi.org/10.1016/j.chemosphere.2013.06.01
- [298] Abioye, O. P., U. J. J. Jah, and S. A. Aransiola. 2017. "Phytoremediation of Soil Contaminants by Biodiesel Plant Jatropha curcas." In Phytoremediation Potential of Bioenergy Plants, edited by K. Bauddh, 55-73. Singapore: Springer.
- [299] Ali, H., E. Khan, and M.A. Sajad. 2013. "Phytoremediation of Heavy Metals—Concepts and Applications." Chemosphere 91:869-881. https://doi.org/10.1016/j.chemosphere.2013.01.07 5.
- [300] Saxena, G., D. Purchase, S. I. Mulla, G. D. Bharagava. Saratale, Ν 2019 R. "Phytoremediation of Heavy Metal-Contaminated Eco-Environmental Sites: Concerns, Field Studies, Sustainability Issues, and Future Prospects." In Reviews of Environmental Contamination and Toxicology Volume 249, edited by P. de Voogt, 133-186. Cham: Springer Publishing. International https://doi.org/10.1007/398 2019 24
- [301] Xin, QG, Pan, WB, and Zhang, TP. 2003. "On Phytoremediation of Heavy Metal Contaminated Soils." Ecological Science 22 (3): 275–279.
- [302] Memon, A.R., D. Aktoprakligil, A. Ozdemir, and A. Vertii. 2001. "Heavy Metal Accumulation and Detoxification Mechanisms in Plants." Turkish Journal of Botany 25: 111-121.
- Turkish Journal of Botany 25: 111-121. [303] Memon, A.R., and P. Schröder. 2009. "Implications of Metal Accumulation Mechanisms to Phytoremediation." Environmental Science and Pollution Research 16: 162-175. https://doi.org/10.1007/s11356-008-0044-5.
- [304] Ent, Antony van der, Alan J. M. Baker, Roger D. Reeves, A. Joseph Pollard, and Henk Schat. 2012. "Hyperaccumulators of Metal and Metalloid Trace Elements: Facts and Fiction." Plant and Soil 362 (1-2): 319–34. https://doi.org/10.1007/s11104-012-1287-3.
- [305] Baker, A.J.M, and R.R. Brooks. 1989. "Terrestrial Higher Plants Which Hyperaccumulate Metallic Elements - A Review of Their Distribution, Ecology and Phytochemistry." Biorecovery 1: 81-126.
- [306] Řai, P. K. 2008. "Phytoremediation of Hg and Cd from Industrial Effluents Using an Aquatic Free Floating Macrophyte Azolla pinnata." International Journal of Phytoremediation 10: 430-439.

https://doi.org/10.1080/15226510802378368.

[307] Sakakibara, M., Y. Ohmori, N.T.H. Ha, and S. Sano. 2011. "Phytoremediation of Heavy Metal Contaminated Water and Sediment by Eleocharis acicularis." Clean - Soil, Air, Water 39: 735-741. https://doi.org/10.1002/clen.201000202.

- [308] Wei, S., Q. Zhou, and U.K. Saha. 2008. "Hyperaccumulative Characteristics of Weed Species to Heavy Metals." Water, Air, and Soil Pollution 192: 173-181. https://doi.org/10.1007/s11270-008-9615-7.
- [309] Aransiola, S.A., U.J.J. Ijah, O.P. Abioye, and J.D Bala. 2019. "Microbial-Aided Phytoremediation of Heavy Metals Contaminated Soil: A Review." European Journal of Biological Research 9 (2): 104-125. https://doi.org/10.5281/zenodo.3244176.
- [310] Fred T, Davies J, Jeffrey DP et al. 2001. "Mycorrhizal Fungi Enhance Accumulation and Tolerance of Chromium in Sunflower (Helianthus Annuus)." Journal of Plant Physiology 158 (7): 777-786.
- [311] Kebebe D. 2019. "Study on pesticide residues and heavy metals levelsin honey samples collected from Walmara District of Oromia special zone, Ethiopia." Scientific Journal of Food Science & Nutrition 5: 1-5.
- [312] Šerevičienė, V., A. Zigmontienė, and D. Paliulis. 2022. "Heavy Metals in Honey Collected from Contaminated Locations: A Case of Lithuania." Sustainability 14: 9196. https://doi.org/10.3390/su14159196.
- [313] FAO/WHO. 2015. p. 59. Available: 10.13140/RG.2.1.4910.2560
- [314] Commission Regulation (EU) 2015/1006. http://data.europa.eu/eli/reg/2015/1006/oj/eng.
- [315] Li, J., Z.M. Xie, J.M. Xu, and Y.F. Sun. 2006.
 "Risk assessment for safety of soils and vegetables around a lead/zinc mine." Environmental Geochemistry and Health 28: 37-44. https://doi.org/10.1007/s10653-005-9009-x.
 [316] FAO and WHO. 1996. "Codex General
- [316] FAO and WHO. 1996. "Codex General Standard for Contaminants and Toxins in Foods." Joint Food Standards Programme, Codex Alimentarious Commission, Rome, Italy.
 [317] European Commission. 2019. "Proposal for a
- [317] European Commission. 2019. "Proposal for a Directive of the European Parliament and of the Council on the quality of water intended for human consumption (COM/2017/0753)."
- [318] US EPA. 2017. "Drinking water regulations (Safe Drinking Water Act)." https://www.epa.gov/dwreginfo/drinking-waterregulations.
- [319] Ayers, R.S. and D.W. Westcot. 1994. Water Quality for Agriculture. Food and Agriculture Organization of the United Nations, Rome. http://www.fao.org/3/t0234e/T0234E06.htm#ch5. 5.
- [320] US EPA, Office of Water. 2006. Memorandum on Management of Aerators during Collection of Tap Samples to Comply with the Lead and Copper Rule.
- [321] de Vries, W., G. Schütze, S. Lots, M. Meili, P. Römkens, L. de Temmerman, et al. 2003. "Critical limits for cadmium, lead and mercury related to ecotoxicological effects on soil organisms, aquatic organisms, plants, animals and humans." In Proceedings of the expert meeting on critical limits for heavy metals and methods for their application, Berlin, 2-4 December 2002 Held under the UN/ECE Convention on Long- Range Transboundary Air Pollution. Edited by G. Schütze, U. Lorent, and

T. Spranger, 29-78. UBA-Texte 47/03. Berlin: Umweltbundesamt.

- [322] FAO/WHO Codex Alimentarius Commission. 2001. "Food additives and contaminants." Food Standards Programme, ALINORM 10/12A. Joint FAO/WHO.
- [323] Ministry of the Environment, Finland. 2007. "Government Decree on the assessment of soil contamination and remediation needs (214/2007)."
- [324] UK Environment Agency. 2009. "Soil guideline values for arsenic, cadmium, mercury and lead in soil (SC050021)."
 [325] US EPA. 2002. "Supplemental guidance for
- [325] US EPA. 2002. "Supplemental guidance for developing soil screening levels for superfund sites." Office of Solid Waste and Emergency Response, Washington, D.C. http://www.epa.gov/superfund/health/conmedia/s oil/index.htm.
- [326] Environmental Protection Ministry of China. 2015. "Standards of soil environmental quality of agricultural land." Office of Environmental Protection Ministry of China, Beijing, China.