agriculture

Article

The Negligible Effect of Toxic Metal Accumulation in the Flowers of Melliferous Plants on the Mineral Composition of Monofloral Honeys

Monika Tomczyk [1,*], Grzegorz Zaguła [2], Mateusz Kaczmarski [3], Czesław Puchalski [2] and Małgorzata Dżugan [1]

[1] Department of Chemistry and Food Toxicology, Institute of Food Technology and Nutrition, College of Life Sciences, University of Rzeszow, 1a Cwiklinskiej St., 35-601 Rzeszow, Poland
[2] Department of Bioenergetics, Food Analysis and Microbiology, Institute of Food Technology and Nutrition, College of Life Sciences, University of Rzeszow, 2D Cwiklinskiej St., 35-601 Rzeszow, Poland
[3] Department of Agriculture, The Jan Grodek State Vocational Academy in Sanok, 21 Mickiewicza St., 38-500 Sanok, Poland
* Correspondence: mwesolowska@ur.edu.pl

Abstract: The accumulation of heavy metals in plant pollen and nectar exposes pollinators to environmental contaminations. Although honeybees act as biofilters and impede the transfer of heavy metals to honey, possible antagonistic interactions could negatively affect the mineral composition of bee-processed nectar. The aim of this study was to assess the level of harmful metals (Cd, Pd, Hg, Al, Ni and Tl) in relation to essential macro- (K, Ca and Mg) and microelements (Mn, Fe, Zn, Cu and Se) in three melliferous plant species (n = 45)—rapeseed, dandelion, and goldenrod—using the ICP-OES method. Metal transferability to three types of monofloral honey (n = 45) produced from these plants was evaluated. Among the studied plants, goldenrod and dandelion were found to be Cd and Pb accumulators; however, regardless of the plant species, only traces of harmful metals were found in honey (<0.015 and <0.043 mg/kg, respectively). What is more, the adverse impact of accumulated toxic metals (Tl, Cd, Ni, Pb and Al) on Ca, Mg and K levels in plants was noted, though it was not reflected in honey. Our findings suggest that in moderately contaminated environments, toxic metals are not transferred to honey and do not disturb its beneficial mineral composition.

Keywords: heavy metals; minerals; interaction; plant; honey; translocation

check for updates

Citation: Tomczyk, M.; Zaguła, G.; Kaczmarski, M.; Puchalski, C.; Dżugan, M. The Negligible Effect of Toxic Metal Accumulation in the Flowers of Melliferous Plants on the Mineral Composition of Monofloral Honeys. *Agriculture* **2023**, *13*, 273. https://doi.org/10.3390/agriculture13020273

Academic Editors: Bartosz Piechowicz and Anna Koziorowska

Received: 20 December 2022
Revised: 18 January 2023
Accepted: 19 January 2023
Published: 22 January 2023

1. Introduction

Melliferous plants are the primary food source for bees, providing valuable biological products such as honey, pollen, nectar and propolis [1]. Bees collect nectar and pollen from flowering plants primarily to obtain necessary nutrients, such as proteins, carbohydrates, minerals and vitamins. In addition to their nutritional value, plant nectar and pollen are also raw materials used to produce honey and other bee products [2]. Moreover, when bees visit plants, they pollinate their flowers, thus contributing to fruit growth and seed formation, making the pollination function an essential ecosystem service [3]. The relationship between plants and pollinators is one of the most important engines of biodiversity on Earth [4,5]. In natural habitats, honeybees seem to be the most common pollinators, with an average of 13% of floral visits, with 5% of plant species being visited exclusively by *Apis mellifera* [6].

A good location for an apiary would be a place where plants grow in proximity in relatively large areas and are characterized by a long flowering period. Therefore, highly nectariferous crops, such as blue phacelia, common buckwheat, white melilot, dandelion, goldenrod, and rapeseed, are grown in Poland especially for beekeeping [7]. In addition to the level of availability of bee forage and beehive technology, the efficiency of honey production and its quality are greatly influenced by weather and environmental conditions. Honey and bee products are associated with being natural, healthy and clean; however, nowadays bee products are produced in an environment polluted by different sources of contamination (pesticides, heavy metals, bacteria, GMO, radioactivity) [8]. It is believed that *A. mellifera*, together with their products, are the most complete biosensors (bioindicator and bioaccumulator) that can provide a significant amount of environmental health data [9–13]. As each foraging bee is able to cover a distance of more than 3 km from the hive, moving from flower to flower, it comes into contact with a large number of pollutants [10,11,14]. However, it has been confirmed that bees act as a biofilter and retain most of the pollutants [10,11,14], thanks to which bee products are safe for consumers. Nevertheless, the possibilities of filtering pollutants by bees are limited, and high pollution levels may have a detrimental effect on the organism. Therefore, the level of contamination of melliferous plants should be controlled to ensure the health safety of bees as well as honey consumers [11,14].

The productivity of bee colonies and the quality of their honey directly depend on the natural conditions of the environment. They concern the floristic composition of melliferous plant species as well as climatic, soil and phenological factors [15]. Melliferous plants serve as an intermediate link for carrying metals from water, air, and above all, from soil, to human and animal organisms. Thus, the development of methods to protect food chains against unacceptable concentrations of toxic agents is a necessity [11,16]. Even when the concentration of heavy metals in the environment is below the minimum levels of risk to human health, it may still pose a significant threat to pollinator activity and survival. Air and soil contain heavy metals, mainly from industry, motorcars or other sources. Lead (Pb) and cadmium (Cd) are considered the most toxic heavy metals and are therefore the most intensively studied. Lead, which is present in the air, originates mainly from motor vehicle traffic. It can pollute the air and then directly pollute the nectar and honeydew; however, Pb is generally not transported by plants. On the other hand, Cd, which originates from the metal industry and incinerators, is transported from the soil to the plants and then, as a consequence, can contaminate the nectar and honeydew [8].

Until now, the research on this topic was concerned mostly with the transfer of heavy metals from plants to honey. However, the authors have not yet tried to assess the impact of plant contamination with heavy metals on the content of beneficial bioelements in plants and honey produced from their nectar. Therefore, the aim of the study was to find a correlation between the heavy metal contamination in essential macro- and microelements levels in both plant flowers and corresponding honeys, in order to find the possible antagonistic metal–metal interactions that could negatively affect the honey mineral content.

2. Materials and Methods

2.1. Collection of Samples

Material for the study consisted of 45 plant samples of 3 different species: rapeseed *Brassica napus L. var. napus* (n = 15), dandelion *Taraxacum officinale* Weber ex Wigg. (n = 15), and goldenrod *Solidago canadensis* L. (n = 15). Dandelion and goldenrod samples were collected from wild plant habitats located about 0–500 m radius around the apiary, whereas rapeseed plants were from the crop field where the hives had been placed. Plant and honey samples were collected in cooperation with owners of 15 small apiaries located in a rural area in the southeastern part of Poland during the 2019 beekeeping season. Samples in the form of fully developed inflorescences (10 per each sampling point) were collected manually, based on the beekeepers' advice, in the middle of their flowering season. For rapeseed, it was the end of April, for dandelion the beginning of May, and for goldenrod the beginning of September. Immediately after harvest, the plant material was dried at 60 °C in a laboratory convective dryer to a constant weight and then ground into powder using a laboratory mill. The obtained powder was later stored in tightly closed polyethylene bags in a desiccator until further analysis.

The honey samples of the three varieties were obtained from the same apiaries where the plants were collected. The honey variety was classified by a beekeeper according to nectar flow availability. Until analysis, honey samples were stored at room temperature in tightly closed glass jars.

2.2. ICP-OES Analysis

The contents of harmful elements (Cd, Pb, Hg, Al, Ni and Tl) as well as essential macro- (K, Ca and Mg) and microelements (Mn, Fe, Zn, Cu, Se) in plant flowers and honey samples were determined by optical emission spectrometry with inductively induced plasma (ICP-OES) using a Thermo iCAP 6500 spectrophotometer (Thermo Fisher Scientific Inc., Bridgewater, MA, USA) according to the procedure described by Dżugan et al. [10]. Before the determination, all tested samples were subjected to mineralization, which was performed using the microwave mineralizer Milestone Ethos Ultrawave-One (Milestone SRL, Sorisole, Italy) for approximately 45 min under pressure in Teflon containers. After cooling (approx. 45 min), the digested samples were transferred into sterile flasks with a capacity of 50 mL and supplemented with redistilled water to the mark. The detection threshold obtained for each element was no less than 0.01 mg kg^{-1} (with the assumed detection capacity of the measuring apparatus at a level exceeding 1 ppb). The curve-fit factor for the studied elements was above 0.99. All the analyses were made in replication for each sample. The targeted repeatability, expressed as the relative standard deviation (RSD), and the targeted recovery, were 20% and 97% to 102%, respectively. The method was validated using certified reference material (NIST–1515). In order to identify the relevant measurement lines and avoid possible interference, the method of adding an internal standard was applied. Yttrium and ytterbium ions (at concentrations of 2 and 5 mg dm^{-3}, respectively) were used as internal standards to verify the correctness of the test method. Their choice was based on the fact that these are ions that are not found in the matrix of the analyzed samples, which is the basis for their correct use. The results were expressed as mg per kg of dm for plants and mg per kg for honey.

2.3. Translocation Factor (TF)

Honey contamination with toxic metals transferred from plants was also expressed as translocation factor (TF) based on the following formula proposed by Romeh [17]:

$$TF = \text{concentration of element in honey} / \text{concentration of element in plant}$$

2.4. Statistical Analysis

All data were analyzed using analysis of variance (ANOVA). Significant differences among the means ($p < 0.05$) were determined using Tukey's multiple range test. Spearman's rank-order correlations between individual elements' concentrations were calculated. Principal components analysis (PCA) was applied as a pattern recognition unsupervised classification method. Analyses were performed using Statistica 13.1 software.

3. Results and Discussion

3.1. Heavy Metals and Mineral Nutrients in Plant

Harmful elements such as Cd, Pb, Hg, Al, Ni and Tl, as well as macro- (K, Ca and Mg) and microelements (Mn, Fe, Zn, Cu and Se), were determined in flower parts of three different melliferous plant species (Table 1). The concentration of Cd and Pb in plant inflorescences ranged from 0.167 to 0.575 and from 0.030 to 0.635 mg/kg, respectively. The content of toxic metals tested in plant inflorescences decreased in the following order: Al > Ni > Cd > Pb > Tl. Among the studied plants, goldenrod and dandelion were found to be Cd and Pb accumulators, as they were more polluted than rapeseed plants. Additionally, dandelion was extremely polluted by Al. Rapeseed seems to be the least susceptible to the accumulation of harmful metals among the tested plants. Measured levels of Cd, Pb, Al and Ni were consistently lower in rapeseed than dandelion or goldenrod.

Table 1. The concentration of elements in tested melliferous plant inflorescences and honey samples (mg/kg).

Element		Rapeseed (n = 15) (*Brassica napus L. var. napus*)		Dandelion (n = 15) (*Taraxacum officinale*)		Goldenrod (n = 15) (*Solidago canadensis*)	
		Plant	Honey	Plant	Honey	Plant	Honey
harmful elements							
Cd	mean ± SD	0.168 ± 0.100 [a]	0.009 ± 0.008 [b]	0.410 ± 0.262 [a]	0.015 ± 0.014 [b]	0.575 ± 0.323 [a]	0.007 ± 0.006 [b]
	min-max	0.040–0.370	n.d.–0.019	0.060–0.940	n.d.–0.038	0.070–1.040	n.d.–0.019
Pb	mean ± SD	0.030 ± 0.053 [b]	0.024 ± 0.037 [b]	0.561 ± 0.291 [a]	0.044 ± 0.043 [b]	0.635 ± 0.167 [a]	0.037 ± 0.031 [b]
	min–max	n.d.–0.180	n.d.–0.095	0.130–0.890	n.d.–0.112	0.370–0.830	n.d.–0.093
Hg	mean ± SD min–max	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Al	mean ± SD	41.51 ± 19.50 [bc]	0.414 ± 0.307 [d]	321.81 ± 155.32 [a]	1.819 ± 2.094 [cd]	103.21 ± 40.84 [ab]	0.590 ± 0.386 [d]
	min–max	21.38–83.04	n.d.-0.850	156.74–593.14	0.154–7.519	31.86–157.25	0.120–1.569
Ni	mean ± SD	0.668 ± 1.501	0.200 ± 0.168	1.141 ± 1.804	0.132 ± 0.153	0.388 ± 0.366	0.255 ± 0.236
	min–max	n.d.-5.370	n.d.-0.483	n.d.-5.480	n.d.-0.429	n.d.-0.910	n.d.-0.635
Tl	mean ± SD	0.267 ± 0.218 [ab]	0.155 ± 0.254 [b]	0.247 ± 0.426 [ab]	0.147 ± 0.213 [b]	0.495 ± 0.381 [a]	0.271 ± 0.377 [ab]
	min–max	0.020–0.730	n.d.-0.681	n.d.-1.150	n.d.-0.583	0.040–1.280	n.d.-0.959
macroelements							
K	mean ± SD	21571 ± 4637 [a]	340.25 ± 95.17 [b]	26430 ± 11526 [a]	1055 ± 257.6 [b]	17014 ± 2608 [a]	803.88 ± 306.83 [b]
	min–max	15084–31528	215.36–508.01	5260–37284	699.13–1476	13515–22158	438.63–1310
Ca	mean ± SD	14465 ± 5536 [a]	55.09 ± 8.22 [c]	9217 ± 3106 [ab]	82.20 ± 26.90 [c]	10059 ± 1186 [a]	105.81 ± 19.68 [bc]
	min–max	9544–25417	41.73–68.56	5799–14919	41.95–123.06	7901–11997	79.79–143.45
Mg	mean ± SD	2900 ± 576 [a]	22.10 ± 4.18 [c]	2344 ± 700 [a]	30.33 ± 9.80 [c]	2124 ± 444 [ab]	36.22 ± 6.22 [bc]
	min–max	2030–3982	16.67–28.59	1051–3252	12.57–50.44	1565–3053	23.91–46.09
microelements							
Mn	mean ± SD	40.27 ± 16.22 [a]	0.53 ± 0.31 [b]	60.60 ± 35.33 [a]	2.56 ± 2.51 [b]	289.24 ± 167.14 [a]	1.21 ± 0.45 [b]
	min–max	21.71–65.15	0.20–1.24	19.92–129.20	0.31–6.66	101.81–564.89	0.55–1.86
Fe	mean ± SD	76.61 ± 25.05 [a]	1.44 ± 2.35 [b]	163.47 ± 71.28 [a]	1.77 ± 2.79 [b]	101.88 ± 42.97 [a]	1.67 ± 2.30 [b]
	min–max	50.02–139.20	n.d.–6.04	90.47–320.48	n.d.–8.04	56.37–217.08	n.d.–6.90
Zn	mean ± SD	35.48 ± 11.19 [a]	0.42 ± 0.29 [b]	40.18 ± 19.02 [a]	0.79 ± 0.38 [b]	54.67 ± 24.96 [a]	1.05 ± 0.70 [b]
	min–max	20.09–53.82	n.d.-0.99	18.81–95.68	0.31–1.48	21.45–97.46	0.34–2.35
Cu	mean ± SD	5.52 ± 1.75 [ab]	0.05 ± 0.06 [c]	10.40 ± 3.81 [a]	0.28 ± 0.25 [bc]	7.13 ± 2.10 [a]	0.15 ± 0.11 [c]
	min–max	3.08–8.75	n.d.–0.21	4.08–17.35	0.05–0.83	3.46–10.67	n.d.–0.37
Se	mean ± SD	0.09 ± 0.18	0.13 ± 0.13	0.11 ± 0.17	0.12 ± 0.17	0.19 ± 0.26	0.21 ± 0.16
	min–max	n.d.–0.61	n.d.–0.36	n.d.–0.53	n.d.–0.48	n.d.–0.77	0.01–0.49

[a, b, c, d]—Means marked with different superscript letters within the line are significantly different (Tukey's honest significant difference test, $p < 0.05$).

Heavy metals influence includes also disturbances in plant mineral nutrition by competition with other nutrients. Typical symptoms of heavy metal toxicity are often similar or even the same, such as symptoms of essential nutrient deficiency [18]. In the case of macroelements, among the tested plants dandelion was distinguished by the highest content of K, while rapeseed had a slightly lower content of K and exceptionally high content of Ca. In the assessment of microelements, goldenrod was characterized by the highest content of Mn and Se, while dandelion of Fe and Cu.

These results are in line with our earlier study [11], where transfer of toxic metals from soil to honey was studied by the same ICP-OES testing method. The study showed migration of heavy metals in the soil–plant–bee–honey food chain, Cd ($p < 0.05$) especially was accelerated by soil acidity. Consistently with the present study, goldenrod and dandelion plants have been discovered to be cadmium accumulators. Back then, we found rapeseed plant was less contaminated. Other authors state that several *Brassica* species are known to be metal accumulators and have been evaluated as potential phytoextraction plants [19–22]. The fact that some plants, which are also food crops, can accumulate relatively high amounts of toxic metals without visible symptoms, leads to potential contamination of the food chain. Despite the fact that in our study, rapeseed showed the lowest content of heavy metals among the tested plants, the research carried out by Niedźwiedzka and Zamorska-Wojdyła [23] on rapeseed pods grown in industrial areas showed Zn and Cu content similar to our own research, within the range of 22.5–42.8 and 5.2–7.4 mg/kg, respectively. This would indicate that values tested for our samples are comparable to samples from contaminated sites. On the other hand, studies conducted by Zhang et al. [24] of blooming rapeseed collected in the middle of flowering season in a clean mountainous area showed similar concentrations for Cd (0.13 mg/kg), Zn (49.31 mg/kg) and Cu (6.12 mg/kg) and significantly higher for Pb (2.03 mg/kg). The quoted data confirmed that while in industrialized areas the level of plant heavy metals depends primarily on anthropogenic soil contamination (mainly agricultural and industrial), in ecological environments, the dominant factor may be the geochemical composition depending on the bedrock and soil pH [25].

In turn, dandelion is considered as a valuable indicator of heavy metal contamination and has been used to assess the bioavailability of As, Br, Cd, Co, Cu, Cr, Hg, Mn, Pb, Sb, Se and Zn [26–29]. Kano et al. [30] used *Taraxacum officinale* to remove Cd and Zn from the soil by phytoremediation, while Hammami et al. [31] showed that dandelion is one of the most effective weed species based on the rate of Cd (II) reduction in contaminated soil. Our findings of Cu, Mn and Zn measured for dandelion flowers are in agreement with results reported by Ligocki et al. [32], who tested dandelion leaves collected from northwestern Poland (Szczecin and its surroundings), found the following intervals: 6.88–15.22, 18.9–68.5 and 24.6–84.1 mg/kg, respectively. However, the Cd and Pb results that we have obtained were significantly higher compared to the author who reported values of 0.016–0.02 and 0.17–0.24 mg/kg, respectively [32]. This observation seems to be mainly the result of increased migration of heavy metals in the acidic soil of Podkarpacie, and in the case of cadmium, of the increased geochemical background [33].

Goldenrod (*Solidago canadensis* L.) is characterized by a high nectar yield, wide range of tolerance to physicochemical conditions, the ability to colonize contaminated soils, high biomass of aboveground parts, an extensive underground root system, as well as the possibility of accumulation of heavy metals and easy uptake from the environment. All of these features increase the usefulness of the plant not only for beekeeping purposes but also in biomonitoring and phytoremediation [34]. On the other hand, this plant is considered an invasive species in Europe. Consequently, even though it can be considered a good bioaccumulator and provider of resources for pollinators, the negative effects should be seriously considered, as it can have negative consequences for flora biodiversity. In beekeeping, goldenrod serves as food for bees during the period when most plants are no longer blooming (September), and they are the last opportunity for honeybees to collect nectar. It is important to assess the quality of this bee forage, because honey produced from this plant nectar serves as food for bees throughout the winter [35]. Bielecka and Królak [34] conducted research on goldenrod inflorescences collected in two locations in Poland: in agricultural and industrialized regions. They found significantly higher Pb content (7.2 and 13.0 mg/kg) than our own research. In the case of Zn, the content of this element in the agricultural region, as tested by the authors, was significantly lower (19.0 mg/kg) than in our research; however, in the industrialized region, it was comparable to our study (45.2 mg/kg). It has to be noted that it is commonly known that the level of bioaccumulation of the same plant species grown in different regions can be influenced by many variables, such as soil type, pH, organic matter, etc. [11,21]. The Subcarpathian environment is characterized by acidic soil that derives from a natural bedrock called the Carpathian flysch, which accelerates migration of heavy metals from soil to plant [11,33].

3.2. Heavy Metals and Mineral Nutrients in Honey

In our previous study, we evidenced that honeybees act as a filter of contaminants originating from the nectar that is later processed into honey, which in turn makes the honey free of these metals and safe for human consumption [10,11]. Similarly, current analyses of the honey samples showed that regardless of the kind of nectar flow, only trace amounts of Cd (<0.015 mg/kg), Pb (<0.043 mg/kg), Al (<1.819 mg/kg), Ni (<0.255 mg/kg) and Tl (<0.271 mg/kg) were found (Table 1). Moreover, with the use of ICP-OES, mercury (Hg) has not been detected in plant inflorescences or in honey, similarly to our previous studies [10,11,36]. As we did not find Hg in soil samples taken from the Subcarpathian region using the ICP-OES either [11], this result was easy to predict.

In the case of the analyzed macronutrients, the content of K, Ca and Mg was statistically lower ($p < 0.05$) in the honeys compared to the plant samples used as source material to produce these monofloral honeys. A similar trend was found in the analyzed micronutrients, with the exception of selenium (Se), where no significant differences ($p > 0.05$) were found between plant inflorescences and honeys ($p > 0.05$). The concentration of elements in honey samples is variety-dependent. Dark honey types (honeydew and buckwheat honey) contain more essential elements than light honeys [10,11,36–38]. Comparing the mineral composition of the varietal honey used in this research, it can be stated that rapeseed honey is less abundant in essential minerals than dandelion or goldenrod honey. This observation is in line with our previous findings where the level of certain elements was found to be the lowest in rapeseed honey, followed by goldenrod and dandelion honey [36]. In that study, the potassium levels for honey obtained from the same area of Poland were found to be 310.56, 836.06 and 1117.56 mg/kg for rapeseed (n = 10), goldenrod (n = 19) and dandelion (n = 9), respectively. The results obtained for calcium content were even more correspondent. These results clearly confirmed that the mineral composition of honey produced in the same place is strongly dependent on its botanical origin. However, when samples produced in different bee habitats were compared, the mineral composition of the honey was mainly determined by its geographical origin. For example, Uršulin-Trstenjak et al. [39] assessed the content of elements in black locust honey collected from different regions of Croatia and showed statistically significant differences in the levels of Ca, Na, K, Mg, Zn, Fe, Mn and Pb in honey of the same variety from different regions of the country. Similarly, Purcarea et al. [40] found significant difference in mineral composition of the same honey variety that originated from Romania and Poland. Cited studies combined with our findings confirm that mineral composition of honey is directly dependent of both botanical and geographical origin.

3.3. Interactions between Elements

One of the most important factors in heavy metals' influence on plant metabolism are their relationships with other mineral nutrients. Plant responses to combinations of metals in the soil can be divided into three basic groups: additive, antagonistic or synergistic [18]. In order to examine the influence of individual element content on the overall elements concentration, a principal component analysis (PCA) study was carried out. In the PCA analysis, PC1 was mainly related with macroelements and PC2 was positively associated with toxic metals and microelements (Figure 1a). Regarding the influence of the parameters, it can be observed that Cu, Pb and Tl significantly influenced the model, while Ni level had no effect on the overall elements' concentration in plants. On the basis of the model, it is also possible to find a negative relationship between individual macronutrients, i.e., Ca, Mg and K, and harmful elements, i.e., Tl, Cd, Ni, Pb and Al, which indicates their antagonistic effect. The tested plant samples were grouped by species, which indicates a species-dependent accumulation of elements (Figure 1b).

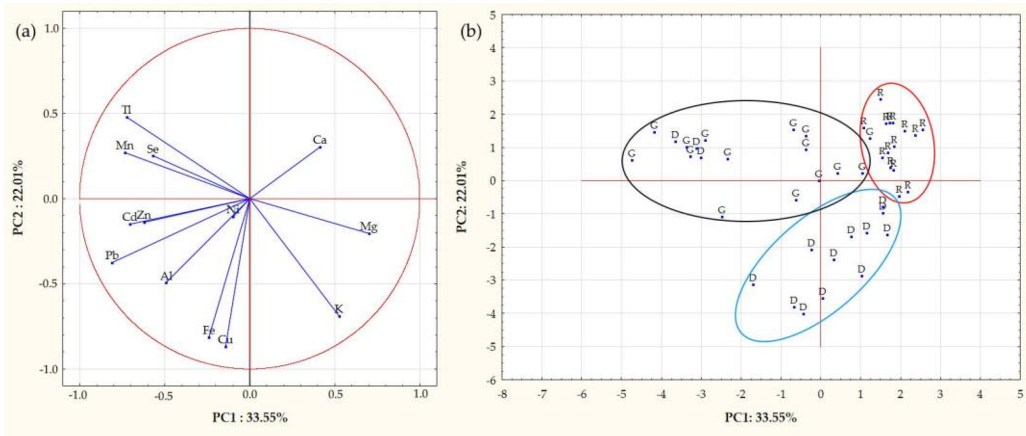

Figure 1. Principal component analysis (PCA) results combining the first two principal components (PC1 and PC2); variable loadings (**a**) and plant individual scores (**b**); R—rapeseed, D—dandelion, G—goldenrod.

The results of the principal component analysis are reflected in Spearman's rank-order correlations, which were calculated between individual elements' concentrations in plants (Table 2). It shows a statistically significant ($p < 0.05$) positive relationship between Pb with Cd and Al (r = 0.512 and 0.652, respectively) as well as Pb and Cd (r = 0.512). Similar observations were made by other authors [26]. On the other hand, statistically significant ($p < 0.05$) negative correlations between Ca with Cd, Pb and Al (r = −0.670, −0.553 and −0.462, respectively), Mg with Pb and Al (r = −0.527 and −0.369, respectively) as well as K and Tl (r = −0.710) were calculated. These observations may indicate a protective effect of macronutrients against selected harmful elements. Literature data support our observations and state that harmful metals interfere with calcium signaling and homeostasis (particularly important in neurons) by interfering with calcium channels [41,42]. Moreover, calculations show a significant positive correlation between Zn and Cd (r = 0.463), which was proved earlier [8]. Such relationships between harmful metals and macronutrients have not been found in the tested honey (Table 3).

Table 2. Spearman's rank-order correlations calculated between individual elements' concentrations in plants.

Element	Al	Cd	Ni	Pb	Tl	Ca	Cu	Fe	K	Mg	Mn	Se	Zn
Al	-	0.349	0.179	0.692	−0.117	−0.462	0.516	0.790	0.186	−0.369	0.116	0.138	0.134
Cd	0.349	-	0.123	0.512	0.378	−0.670	0.349	0.213	−0.228	−0.123	0.571	0.213	0.463
Ni	0.179	0.123	-	0.164	0.191	−0.290	0.110	0.001	−0.089	0.065	0.060	0.044	0.127
Pb	0.692	0.512	0.164	-	0.132	−0.553	0.412	0.505	−0.179	−0.527	0.424	0.281	0.275
Tl	−0.117	0.378	0.191	0.132	-	0.067	−0.362	−0.253	−0.710	−0.344	0.654	0.340	0.370
Ca	−0.462	−0.670	−0.290	−0.553	0.067	-	−0.248	−0.222	0.082	0.269	−0.064	−0.129	−0.012
Cu	0.516	0.349	0.110	0.412	−0.362	−0.248	-	0.582	0.580	0.233	−0.010	−0.086	0.421
Fe	0.790	0.213	0.001	0.505	−0.253	−0.222	0.582	-	0.420	−0.165	−0.058	0.039	0.267
K	0.186	−0.228	−0.089	−0.179	−0.710	0.082	0.580	0.420	-	0.493	−0.562	−0.387	−0.072
Mg	−0.369	−0.123	0.065	−0.527	−0.344	0.269	0.233	−0.165	0.493	-	−0.419	−0.292	0.000
Mn	0.116	0.571	0.060	0.424	0.654	−0.064	−0.010	−0.058	−0.562	−0.419	-	0.183	0.459
Se	0.138	0.213	0.044	0.281	0.340	−0.129	−0.086	0.039	−0.387	−0.292	0.183	-	0.228
Zn	0.134	0.463	0.127	0.275	0.370	−0.012	0.421	0.267	−0.072	0.000	0.459	0.228	-

Results in red are statistically significant ($p < 0.05$).

Table 3. Spearman's rank-order correlations calculated between individual elements' concentrations in honey.

Element	Al	Cd	Ni	Pb	Tl	Ca	Cu	Fe	K	Mg	Mn	Se	Zn
Al	-	0.197	−0.090	0.240	0.166	0.211	0.354	0.218	0.371	0.260	0.209	−0.135	0.291
Cd	0.197	-	0.060	−0.096	0.017	0.161	0.047	0.353	0.077	0.070	0.200	0.209	−0.062
Ni	−0.090	0.060	-	−0.077	0.142	0.056	0.207	0.082	−0.051	0.064	0.093	0.302	−0.013
Pb	0.240	−0.096	−0.077	-	0.339	0.179	0.343	0.055	0.329	0.332	0.386	0.048	0.434
Tl	0.166	0.017	0.142	0.339	-	0.112	0.061	−0.081	0.149	0.183	0.215	0.299	0.400
Ca	0.211	0.161	0.056	0.179	0.112	-	0.432	0.070	0.557	0.756	0.471	0.243	0.548
Cu	0.354	0.047	0.207	0.343	0.061	0.432	-	0.301	0.644	0.543	0.481	−0.011	0.533
Fe	0.218	0.353	0.082	0.055	−0.081	0.070	0.301	-	0.147	0.096	0.204	−0.068	−0.003
K	0.371	0.077	−0.051	0.329	0.149	0.557	0.644	0.147	-	0.482	0.598	0.133	0.584
Mg	0.260	0.070	0.064	0.332	0.183	0.756	0.543	0.096	0.482	-	0.685	0.086	0.478
Mn	0.209	0.200	0.093	0.386	0.215	0.471	0.481	0.204	0.598	0.685	-	0.184	0.432
Se	−0.135	0.209	0.302	0.048	0.299	0.243	−0.011	−0.068	0.133	0.086	0.184	-	0.267
Zn	0.291	−0.062	−0.013	0.434	0.400	0.548	0.533	−0.003	0.584	0.478	0.432	0.267	-

Results in red are statistically significant ($p < 0.05$).

Among the tested elements, thallium (Tl) showed the highest translocation factor from plants to honey (from 0.66 to 0.84). This may indicate that in the case of this element, unlike other toxic metals, the bee does not have the ability to accumulate it and thus it does not constitute a barrier limiting honey contamination. Regarding the plant species, the highest translocation factors of Cd, Pb and Tl were calculated for rapeseed (Table 4). However, this does not reflect entirely the content of harmful metals in rapeseed honey, because the level of these elements in rapeseed plants was the lowest among the tested plant species. The translocation factor calculated for macroelements (K, Ca, Mg) was very low and did not exceed 0.06. This means that despite the relatively high content of these elements in honeys [11,39,40], only trace amounts of those elements are being transferred from plants to honey. Among the beneficial microelements, a specific tendency was observed for Se, where the translocation coefficient exceeded the value of 1 for rapeseed and goldenrod. Thus far, few studies have examined the effects of forage plant tissues containing soilborne Se on pollinators' health. Se as a micronutrient is essential for survival, but higher concentrations can be toxic for an insect. Higher accumulation of heavy metals seems to increase the concentration of selenium in the plant, which results in the enrichment of honey in this element. However, this element is known as a valuable antioxidant; therefore, this tendency positively affects the antioxidant properties of honey [43].

While the negative effects of plant contamination on honey mineral composition were found to be insignificant, the consequences for pollinators were not evaluated in this research. The impact of heavy metals on the condition of bees was not studied, however, as they have frequent and direct contact with melliferous plants, filter heavy metals present in nectar, and accumulate toxic elements in their bodies. According to the Agency for Toxic Substances and Disease Registry, arsenic (As), lead (Pb), cadmium (Cd) and mercury (Hg) are some of the common heavy metal pollutants with serious health impact on the honeybee *Apis* spp. [44]. Nisbet et al. [45] studied the effect of metallic cocktails on bee physiology and showed that honeybees exposed to Pb, Cd and Cu not only accumulated significant levels of these metals in their bodies, but also had lower concentrations of dopamine in the brain compared to control honeybees. Additionally, according to Di et al. [46] Cd and Cu had a weak synergistic effect on honeybee survival. Research by Monchanin et al. [42] showed that low doses of Pb and Se also impair the behavior and cognition of honeybees, suggesting their widespread negative effects on pollinators. We think that this is a very interesting observation, which should be verified in laboratory studies in the future, as a continuation of this work.

Table 4. Translocation factors calculated for honey samples.

Element	Rapeseed	Dandelion	Goldenrod
Cd	0.08 ± 0.11 [a]	0.04 ± 0.05	0.02 ± 0.02 [b]
Pb	0.32 ± 0.06 [a]	0.08 ± 0.07 [b]	0.06 ± 0.11 [b]
Al	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
Ni	0.39 ± 0.03 [a]	0.06 ± 0.06 [b]	0.01 ± 0.07 [b]
Tl	0.84 ± 1.05	0.66 ± 1.24	0.67 ± 1.42
K	0.01 ± 0.01 [a]	0.06 ± 0.07 [b]	0.05 ± 0.02 [b]
Ca	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.01
Mg	0.01 ± 0.01	0.00 ± 0.00	0.01 ± 0.01
Mn	0.01 ± 0.01 [b]	0.05 ± 0.05 [a]	0.01 ± 0.00 [b]
Fe	0.03 ± 0.04	0.01 ± 0.02	0.02 ± 0.03
Zn	0.01 ± 0.01	0.02 ± 0.01	0.03 ± 0.03
Cu	0.01 ± 0.01	0.04 ± 0.04	0.02 ± 0.02
Se	1.32 ± 0.80	0.67 ± 0.96	1.96 ± 2.69

[a, b] Different superscript letters within the line are significantly different (Tukey's honest significant difference test, $p < 0.05$).

Our results indicate that accumulation of heavy metals in plants lowers the level of K, Ca and Mg; however, this is not reflected in the composition of honey. It means that bees not only retain heavy metals but also ensure a constant level of macroelements in the honey. This observation indicates that the probable mechanism of heavy metal accumulation in bee bodies may involve antagonistic interelement interactions, e.g., Cd-Ca, Cd-Mg, as described in the literature. Moreover, the content of macro- and microelements in the examined honeys does not seem to be dependent on contamination with heavy metals. In dandelion and goldenrod honeys, higher contents of Ca and Mg were observed, with lower contamination with Cd and Pb. Our previous research indicated that there were no significant correlations between the concentrations of tested elements in honey and in bee bodies ($p > 0.05$) [10]. Interestingly, a weak inverse correlation between Cd and Pb and antagonistic elements in the bee body and honey was observed, but was nonsignificant, except Pb-Zn. Other studies have shown that properly supplying the body with selected nutritional elements might help counteract the effects of cadmium and lead accumulation [47]. However, the mechanisms of heavy metal–other nutrient interactions are very complex and may involve changes in subcellular distribution of nutrients, water balance, functioning of enzymes or even hormone levels of plants [18]. It has to be noted that simple observations of the mineral content of plants and honeys do not provide an extensive explanation for these mechanisms. Due to a large number of variables, their clarification is not possible based only on environmental samples. This would rather require a controlled experiment introducing a single factor to the soil. Similarly, controlled experiments are also required to prove that sufficient supply of beneficial elements to bee organisms can effectively prevent honey contamination. Only the use of molecular methods to assess the mineral balance in bees could explain the nature of metal–metal interactions, which can boost or limit transfer of elements from the plant to honey. It may suggest that a sufficient supply of bee organisms with beneficial elements could effectively prevent honey contamination.

4. Conclusions

The highest pollution with heavy metals was found for goldenrod and dandelion inflorescence, whereas rapeseed was less polluted. The pollution of plants decreases the level of essential metals in their flowers, which was observed for goldenrod and dandelion compared to rapeseed. However, these tendencies were not reflected in honey mineral composition. Regardless of the forage plant species, only traces of harmful metals were found in honey, what makes it safe for consumers. Moreover, the negative consequences of contamination of melliferous plants with heavy metals did not affect the mineral composition of honey. A high translocation factor from plants to honey was found only for thallium and selenium. On the other hand, our findings suggest that in contaminated environments, toxic metals could negatively affect pollinators, as they keep impurities in their bodies that in turn disturb their mineral balance. Such a tendency was found especially in the case of goldenrod and dandelion, which are known plant accumulators of toxic metals. Due to the research being carried out in a rural, clean bee habitat, the obtained results require confirmation for samples of plants and honeys collected from industrial, more polluted environments. In the next study, the control of soil mineral profile should be necessarily included, as it is a great limitation of this study. We suggested that soil composition and acidity play a key role in the studied components' migration within the trophic chain; however, this should be confirmed with soil tests. Despite the presented study not being complete, the observations obtained give some new data that may be important for beekeepers, both in choosing the location of the apiary and in choosing a honey flow base for bees, as these are key factors for the high quality of honey.

Author Contributions: Conceptualization: M.D. and M.T.; methodology: M.T. and G.Z; software: M.T.; validation: G.Z. and M.T.; formal analysis: M.T. and C.P.; investigation: M.T., G.Z. and M.K.; resources: C.P.; data curation: M.T.; writing—original draft preparation: M.T.; writing—review and editing: M.D.; visualization: M.T.; supervision: M.D.; project administration: M.D.; funding acquisition: M.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the University of Rzeszów research project PB/KCHTZ/2022.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Bărbulescu, A.; Barbeș, L.; Dumitriu, C.Ș. Impact of Soil Pollution on Melliferous Plants. *Toxics* **2022**, *10*, 239. [CrossRef]
2. Al-Ghamdi, A.A.; Al-Khulaidi, A.; Al-Sagheer, N.A.; Nuru, A.; Tadesse, Y. Identification, characterization and mapping of honey bee flora of Al-Baha region of Saudi Arabia. *J. Environ. Biol.* **2020**, *41*, 613–622. [CrossRef]
3. Bhalchandra, W.; Baviskar, R.K.; Nikam, T.B. Diversity of nectariferous and polleniferous bee flora at Anjaneri and Dugarwadi hills of Western Ghats of Nasik district (M.S.) India. *J. Entomol. Zool. Stud.* **2014**, *2*, 244–249.
4. Ollerton, J. Pollinator Diversity: Distribution, Ecological Function, and Conservation. *Annu. Rev. Ecol. Evol. Syst.* **2017**, *48*, 353–376. [CrossRef]
5. Ollerton, J.; Winfree, R.; Tarrant, S. How many flowering plants are pollinated by animals? *Oikos* **2011**, *120*, 321–326. [CrossRef]
6. Hung, K.-L.J.; Kingston, J.M.; Albrecht, M.; Holway, D.A.; Kohn, J.R. The worldwide importance of honey bees as pollinators in natural habitats. *Proc. R. Soc. B Biol. Sci.* **2018**, *285*, 20172140. [CrossRef]
7. Jabłoński, B.; Kołtowski, Z. Nectar secretion and honey potential of honey-plants growing under Poland's conditions—Part XV. *J. Apic. Sci.* **2005**, *49*, 59–63.
8. Bogdanov, S. Contaminants of bee products. *Apidologie* **2006**, *37*, 1–18. [CrossRef]
9. Bargańska, Ż.; Ślebioda, M.; Namieśnik, J. Honey bees and their products: Bioindicators of environmental contamination. *Crit. Rev. Environ. Sci. Technol.* **2016**, *46*, 235–248. [CrossRef]
10. Dżugan, M.; Wesołowska, M.; Zaguła, G.; Kaczmarski, M.; Czernicka, M.; Puchalski, C. Honeybees (*Apis mellifera*) as a biological barrier for contamination of honey by environmental toxic metals. *Environ. Monit. Assess.* **2018**, *190*, 101. [CrossRef]
11. Tomczyk, M.; Zaguła., G.; Puchalski, C.; Dżugan, M. Transfer of some toxic metals from soil to honey depending on bee habitat conditions. *Acta Univ. Cibiniensis Ser. E Food Tech.* **2020**, *24*, 49–59. [CrossRef]
12. Edo, C.; Fernández-Alba, A.R.; Vejsnæs, F.; van der Steen, J.J.M.; Fernández-Piñas, F.; Rosal, R. Honeybees as active samplers for microplastics. *Sci. Total Environ.* **2021**, *767*, 144481. [CrossRef] [PubMed]
13. Martinello, M.; Manzinello, C.; Dainese, N.; Giuliato, I.; Gallina, A.; Mutinelli, F. The Honey Bee: An Active Biosampler of Environmental Pollution and a Possible Warning Biomarker for Human Health. *Appl. Sci.* **2021**, *11*, 6481. [CrossRef]

14. Papa, G.; Maier, R.; Durazzo, A.; Lucarini, M.; Karabagias, I.K.; Plutino, M.; Bianchetto, E.; Aromolo, R.; Pignatti, G.; Ambrogio, A.; et al. The Honey Bee *Apis mellifera*: An Insect at the Interface between Human and Ecosystem Health. *Biology* **2022**, *11*, 233. [CrossRef]
15. Yakovleva, S.N.; Fatkullin, R.R. Accumulation of heavy metals in melliferous plants in the territory of Nagaybaksky district of Chelyabinsk region. *IOP Conf. Ser. Earth Environ. Sci.* **2019**, *341*, 012004. [CrossRef]
16. Fatkullin, R.R. Heavy metals in a trophic chain "soil-plant-bee body-beekeeping products" in the conditions of a forest-steppe zone of the Southern Urals. *Bull. Orenbg. State Agrar. Univ.* **2017**, *4*, 271–273.
17. Romeh, A.A. Potential risks from the accumulation of heavy metals in canola plants. *Environ. Sci. Pollut. Res.* **2021**, *28*, 52529–52546. [CrossRef]
18. Siedlecka, A. Some aspects of interactions between heavy metals and plant mineral nutrients. *Acta Soc. Bot. Pol.* **1995**, *64*, 265–272. [CrossRef]
19. Van Ginneken, L.; Meers, E.; Guisson, R.; Ruttens, A.; Elst, K.; Tack, F.M.G.; Vangronsveld, J.; Diels, L.; Dejonghe, W. Phytoremediation for heavy metal-contaminated soils combined with bioenergy production. *J. Environ. Eng. Landsc. Manag.* **2007**, *15*, 227–236. [CrossRef]
20. Gall, J.E.; Rajakaruna, N. The physiology, functional genomics, and applied ecology of heavy metal-tolerant brassicaceae. In *Brassicaceae: Characterization, Functional Genomics and Health Benefits*; Lang, M., Ed.; Nova Science Publishers: Hauppauge, NY, USA, 2013; pp. 121–148.
21. Mourato, M.P.; Moreira, I.N.; Leitão, I.; Pinto, F.R.; Sales, J.R.; Martins, L.L. Effect of Heavy Metals in Plants of the Genus *Brassica*. *Int. J. Mol. Sci.* **2015**, *16*, 17975–17998. [CrossRef]
22. Zeremski, T.; Randelovic, D.; Jakovljevic, K.; Marjanovic; Jeromela, A.; Milic, S. *Brassica* Species in Phytoextractions: Real Potentials and Challenges. *Plants* **2021**, *10*, 2340. [CrossRef] [PubMed]
23. Niedźwiecka, A.; Zamorska-Wojdyła, D. The bioaccumulation of heavy metals in *Brassica napus* L. in the area around Turów Power Station, Poland. *E3S Web Conf.* **2017**, *17*, 00065. [CrossRef]
24. Zhang, Z.; Wu, W.; Tu, C.; Huang, H.; Zhang, J.C.; Fang, H.; Huo, H.; Lin, C. Relationships between soil properties and the accumulation of heavy metals in different *Brassica campestris* L. growth stages in a Karst mountainous area. *Ecotoxicol. Environ. Saf.* **2020**, *206*, 111150. [CrossRef] [PubMed]
25. Handzel, A.; Królczyk, J.B.; Latawiec, A.E.; Pluta, K.; Malina, D.; Sobczak-Kupiec, A. Determination of element contents and physicochemical properties of selected soils. *Infrastruct. Ecol. Rural Areas* **2017**, *2*, 419–432. (In Polish) [CrossRef]
26. Czarnowska, K.; Milewska, A. The content of heavy metals in an indicator plant (*Taraxacum officinale*) in Warsaw. *Pol. J. Environ. Stud.* **2000**, *9*, 125–128.
27. Petrova, S.; Yurukova, L.; Velcheva, I. *Taraxacum ofcinale* as a biomonitor of metals and toxic elements (Plovdiv, Bulgaria). *Bulg. J. Agric. Sci.* **2013**, *19*, 241–247.
28. Degórska, A. An assessment of urban habitat contamination with selected heavy metals within the city of Katowice using the common dandelion (*Taraxacum officinale* Web.) as a bioindicator. *Environ. Socio-Econ. Stud.* **2013**, *1*, 29–40. [CrossRef]
29. Adamczyk-Szabela, D.; Lisowska, K.; Wolf, W.M. Hysteresis of heavy metals uptake induced in *Taraxacum officinale* by thiuram. *Sci. Rep.* **2021**, *11*, 20151. [CrossRef] [PubMed]
30. Kano, N.; Hori, T.; Zhang, H.; Miyamoto, N.; Anak, D.E.V.; Mishima, K. Study on the Behavior and Removal of Cadmium and Zinc Using *Taraxacum officinale* and Gazania under the Application of Biodegradable Chelating Agents. *Appl. Sci.* **2021**, *11*, 1557. [CrossRef]
31. Hammami, H.; Parsa, M.; Mohassel, M.H.R.; Rahimi, S.; Mijani, S. Weeds ability to phytoremediate cadmium-contaminated soil. *Int. J. Phytoremediation* **2016**, *18*, 48–53. [CrossRef]
32. Ligocki, M.; Tarasewicz, Z.; Zygmunt, A.; Aniśko, M. The common dandelion (*Taraxacum officinale*) as an indicator of anthropogenic toxic metal pollution of environment. *Acta Sci. Pol. Zootech.* **2011**, *10*, 73–82.
33. Reszel, R.; Reszel, H.; Pęcak, J.; Hadam, B. The content of sulfur and heavy metals in soils of agricultural land and plants of protected areas of the Podkarpackie Voivodship. In *Progress in Environmental Engineering*; Tomaszek, J.A., Ed.; Rzeszów University of Technology Publishing House: Rzeszów, Poland, 2003; pp. 435–445. (In Polish)
34. Bielecka, A.; Królak, E. Selected Features of Canadian Goldenrod That Predispose the Plant to Phytoremediation. *J Ecol. Eng.* **2019**, *20*, 88–93. [CrossRef]
35. Amtmann, M. The chemical relationship between the scent features of goldenrod (*Solidago canadensis* L.) flower and its unifloral honey. *J. Food Compos. Anal.* **2009**, *23*, 122–129. [CrossRef]
36. Dżugan, M.; Zaguła, G.; Wesołowska, M.; Sowa, P.; Puchalski, C. Levels of toxic and essential metals in varietal honeys from Podkarpacie. *J. Elem.* **2017**, *22*, 1039–1048. [CrossRef]
37. Oroian, M.; Prisacaru, A.; Hretcanu, E.C.; Stroe, S.G.; Leahu, A.; Buculei, A. Heavy metals profile in honey as a potential indicator of botanical and geographical origin. *Int. J. Food Prop.* **2016**, *19*, 1825–1836. [CrossRef]
38. Ligor, M.; Kowalkowski, T.; Buszewski, B. Comparative Study of the Potentially Toxic Elements and Essential Microelements in Honey Depending on the Geographic Origin. *Molecules* **2022**, *27*, 5474. [CrossRef] [PubMed]
39. Uršulin-Trstenjak, N.; Levanić, D.; Primorac, L.; Bošnir, J.; Vahčić, N.; Šarić, G. Mineral Profile of Croatian Honey and Differences Due to its Geographical Origin. *Czech J. Food Sci.* **2015**, *33*, 156–164. [CrossRef]

40. Purcarea, C.; Dzugan, M.; Wesolowska, M.; Chis, A.M.; Zagula, G.; Teusdea, A.C.; Puchalski, C. A Comparative Study of Metal Content in Selected Polish and Romanian Honey Samples. *Rev. Chim.* **2017**, *68*, 1163–1169. [CrossRef]
41. Bridges, C.C.; Zalups, R.K. Molecular and ionic mimicry and the transport of toxic metals. *Toxicol. Appl. Pharm.* **2005**, *204*, 274–308. [CrossRef] [PubMed]
42. Monchanin, C.; Drujont, E.; Devaud, J.M.; Lihoreau, M.; Barron, A.B. Metal pollutants have additive negative effects on honey bee cognition. *J. Exp. Biol.* **2021**, *224*, jeb241869. [CrossRef]
43. Hladun, K.R.; Smith, B.H.; Mustard, J.A.; Morton, R.R.; Trumble, J.T. Selenium Toxicity to Honey Bee (*Apis mellifera* L.) Pollinators: Effects on Behaviors and Survival. *PLoS ONE* **2012**, *7*, e34137. [CrossRef] [PubMed]
44. Dubey, V.K.; Sahoo, S.K.; Sujatha, B.; Das, A. Impact of Heavy Metals on Honey Bees. *Vigyan Varta* **2022**, *3*, 101–103.
45. Nisbet, C.; Guler, A.; OrmancÄ±, N.; Cenesiz, S. Preventive action of zinc against heavy metals toxicity in honeybee. *Afr. J. Biochem. Res.* **2018**, *12*, 1–6. [CrossRef]
46. Di, N.; Zhang, Z.; Hladun, K.R.; Rust, M.; Chen, Y.F.; Zhu, Z.Y.; Liu, T.X.; Trumble, J.T. Joint effects of cadmium and copper on *Apis mellifera* forgers and larvae. *Comp. Biochem. Physiol. Part C Toxicol. Pharmacol.* **2020**, *237*, 108839. [CrossRef] [PubMed]
47. De Castro, C.S.; Arruda, A.F.; Da Cunha, L.R.; SouzaDe, J.R.; Braga, J.W.; Dórea, J.G. Toxic metals (Pb and Cd) and their respective antagonists (Ca and Zn) in infant formulas and milk marketed in Brasilia, Brazil. *Int. J. Environ. Res. Public Health* **2010**, *7*, 4062–4077. [CrossRef] [PubMed]