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Environmental Monitoring and Assessment

Examination of honeys and flowers as soil element indicators

--Manuscript Draft--

Manuscript Number:	EMAS-D-17-00363R1
Full Title:	Examination of honeys and flowers as soil element indicators
Article Type:	Original Research
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Funding Information:	
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Examination of honeys and flowers as soil element indicators

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Abstract

Detection of soil element deficiencies is time consuming, requiring a major commitment for field work and analysis. Bees concentrate some elements in their honey which could allow soil element concentrations to be predicted without having to take large numbers of soil samples. We measured 14 element concentrations in soil, sunflower, acacia flower and honey samples from two different regions of Hungary. Across sites, the elements with significant correlation coefficients between honey and soil concentrations, in descending order of probability, were Cu > Ba >Sr = Ni > Zn > Mn = Pb >As. Bioconcentration from soil to honey was similar for areas with acacia and sunflower flowers. In the macroelements it was greatest for K, S and P and least for Mg and Na, and in the microelements greatest for B, then Zn, then Cu, then As, Mo and Sr and least for Fe, Ba, Mn and Pb. It is concluded that in acacia and sunflower growing regions, honey can give an accurate estimate of soil element concentrations for Cu and Ba, and provides relevant information for Sr, Ni, Zn, Mn, Pb and As.

Keywords: bioconcentration, honey, element, flower, soil

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1. Introduction

Honey is a natural substance produced by *Apis mellifera* from flower nectar and/or honeydew. Environmental conditions are favourable for honey production in Hungary, with 18500 tons produced in 2013, and approximately 15000 tons per year exported (FAOSTAT 2016). The most important flowers used for honey production in Hungary are acacia, sunflower, linden, silk grass and oilseed rape.

Honey is a complex food and its properties depend on the botanical, environmental and postharvest conditions, including storage and extraction techniques (Pohl, 2009). It has a low mineral content (0.1-0.2% in nectar honeys) that depends on the botanical origin, soil conditions and treatment, rendering it suitable as an environmental indicator (Almeida-Silva et al. 2011). Soil is the main source of both essential and non-essential elements to plants, with uptake depending on soil properties, plant type, and farming method. The soils and flowers have a major influence on the mineral composition of honeys, and the mineral profile of honeys can be used to determine the floral and geographical origin of honeys (Pohl, 2009; Pohl et al., 2012). Anthropogenic activities, e.g. smelting, mining, burning of fossil fuel, use of fertilizers, pesticides, transport, may also affect soil properties, which change trace element behaviour (Kabata-Pendias and Mukherjee 2007). As bees collect pollen from flowers in a large area, about 7 km^2 (Crane 1984), honey potentially gives valuable environmental information from this area. This could obviate the need to take large numbers of soil samples to identify regional element deficiencies or toxicities. Determination of element content of honeys as a bioindicator has been studied by several authors, e.g. Conti and Botrè (2000), Bratu and Georgescu (2005), Rashed et al. (2009), Pohl et al. (2012), Bastias et al. (2013), Al Naggar et al. (2013). In these works the element content of honeys, pollens or waxes were determined, however they did not simultaneously examine the element content of soils and flowers from the honey collecting area. Al Naggar et al. (2014) measured the Cu, Zn Cd, Pb and Fe concentrations in soil and flower samples and determined the transfer rates of these metals from soil to cotton and clover flowers; however there have been no studies in which the bioconcentration factors have been determined from soil to honey.

The aims of this study were (i) to determine the element content of soil, flower and honey samples; (ii) to calculate the bio-concentration factors between the flower and soil, honey and flower, honey and soil; and (iii) to determine relations between the element content of soil, flower and honey.

2. Materials and methods

2.1. Sampling and sample preparation

Five-five soil, flower and honey samples were collected from five different regions of Hungary in 2015 (Table 1). Two flowers that predominate in these regions are acacia (*Robinia pseudoacacia*) and sunflower (*Helianthus annuus*). Samples of acacia flowers, the soils in which they grew and acacia honeys were collected from one area of Békés County (No.1) and two areas of Szabolcs-Szatmár-Bereg County (No. 2 and 3). Samples of soil in sunflower-growing regions, sunflower flowers and sunflower honeys (No. 4 and 5) came from two agricultural areas of Békés County. Soil of Szabolcs-Szatmár-Bereg County (Northern Hungary) is acidic and sandy, and Békés County (East Hungary) has alluvial meadow soil. Every collecting area was free from industrial activity and traffic.

The sampling of soil and flower samples was carried out during the bees' collecting time. In the case of soil samples, five samples were collected from every examined area at five randomly selected locations per hectare and from the top 15 cm of the soil. The size of sampling areas was five hectares, so the number of samples was 25 in each area. Samples were homogenized by areas and 1-1 kg of soil was used for element determination. Before the digestion, soil samples were oven-dried at 105°C for 5 hours (Memmert UF 75 Universal Oven, Memmert GmbH+Co. KG, Schwabach, Germany) and then ground.

The sampling of flowers was carried out at the same locations as those used for the sampling of soils. Flower samples were oven-dried at 60°C for 12 hours before digestion. For honey sampling, at each location five hives were chosen randomly. Honey centrifugation from the hives was conducted separately for each collecting area, so at the end of centrifuging five honey samples were available. The sampling of honey samples (100 g) was carried out immediately after centrifuging from these five plastic barrels. In case of honey samples the element concentrations were determined in the dry matter.

All samples were stored in sterile glass jars at room temperature before the analysis.

2.2. Determination of the content of elements

All chemicals were analytical grade or better. Ultrapure water (18.2 MΩ·cm) was used to prepare of solutions and dilutions produced by a Milli-Q water purification system (Millipore S.A.S., Molsheim, France). Nitric acid (69% v/v) and hydrogen-peroxide (30% v/v) were from VWR International Ltd. (Radnor, USA). The element standard solutions were prepared from mono-elemental standard solutions (1000 mg L^{-1}; Scharlab S.L., Barcelona, Spain).

The digestion of samples for element analysis was carried out according to the method of Kovács et al. (1996). This method has been validated using animal and plant materials in our accredited laboratory (ISO/IEC 17025:2005). For 3 g plant honey samples and 2 g flower samples 10 ml, and for 3 g soil samples 5 ml, of nitric acid was added, and the samples were allowed to stand overnight. In the pre-digestion phase the samples were heated at 60°C for 30 min (plant and honey samples) or 60 min (soil samples). After the samples had cooled, 3 ml hydrogen-peroxide (plant and honey samples) or 5 ml hydrogen-peroxide (soil samples) was added and the main-digestion was carried out at 120°C for 90 min (plant and honey samples) or 4.5 hours (soil samples). After digestion, ultrapure water was added to make a final volume of 50 ml. Samples were homogenized and filtered using qualitative filter paper (Sartorius Stedim Biotech S.A., Gottingen, Germany). The concentrations of potassium, magnesium, sodium, phosphorus and sulphur were determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Thermo Scientific iCAP 6300, Cambridge, UK). The applied wavelengths (nm) were the following: 769.896 nm for K, 279.806 nm for Mg, 818.326 nm for Na, 213.617 nm for P and 182.563 nm for S. The determination of arsenic, barium, boron, cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, lead, strontium and zinc contents was carried out using Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Thermo Scientific XSeries 2, Bremen, Germany). The measured isotopes (amu) were 75 for As, 11 for B, 137 for Ba, 111 for Cd, 59 for Co, 52 for Cr, 65 for Cu, 55 for Mn, 95 for Mo, 60 for Ni, 206 for Pb, 80 for Se, 88 for Sr and 66 for Zn. Rhodium was used as internal standard (40 µg L^{-1}).

The operating parameters of ICP-OES and ICP-MS are reported in Table 2. For ICP-OES the detection limits (DL) were determined for reagent blank samples (n=10) using the software for ICP-OES (iTEVA) at a confidence level of 99.0%: 0.525 mg kg^{-1} for K, 0.104 mg kg^{-1} for Mg, 0.488 mg kg^{-1} for Na, 0.489 mg kg^{-1} for P and 0.108 mg kg^{-1} for S. For ICP-MS, the DLs were determined by using the following equation: DL= $3*SD_{\text{reagent blank}}$ (n=10) / sensitivity. DLs were as follows: 0.0366 µg kg^{-1} for As, 2.74 µg kg^{-1} for B, 0.185 µg kg^{-1} for Ba, 0.00963 µg kg^{-1} for Cd, 0.008 µg kg^{-1} for Co, 0.0375 µg kg^{-1} for Cr, 0.789 µg kg^{-1} for Cu, 0.09 µg kg^{-1}

for Mn, 0.0187 µg kg^{-1} for Mo, 0.0998 µg kg^{-1} for Ni, 0.643 µg kg^{-1} for Pb, 0.395 µg kg^{-1} for Sr and 2.57 µg kg^{-1} for Zn.

2.3. Statistical analysis

Analytical analysis was carried out in triplicate. Data was described by using general terms (mean, standard deviation, minimum and maximum values), and Independent-Samples T Test, ANOVA. SPSS for Windows Version 13 (SPSS Inc. Chicago, Illinois, USA) was used for the calculations. Bio-concentration factors (BCF) were determined for flower/soil, honey/flower and honey/soil comparisons by using the following equations:

$$BCF\ (flower/soil) = \frac{element\ concentration\ of\ flower\ sample}{element\ concentration\ of\ soil\ sample}$$

$$BCF\ (honey/flower) = \frac{element\ concentration\ of\ honey\ sample}{element\ concentration\ of\ flower\ sample}$$

$$BCF\ (honey/soil) = \frac{element\ concentration\ of\ honey\ sample}{element\ concentration\ of\ soil\ sample}$$

Differences between elements were analysed by one-way analysis of variance with the statistical package Minitab, using Fisher's Pairwise comparisons test to compare means post hoc. Pearson's correlation coefficients and probabilities were calculated for flower/soil, honey/soil and honey/flower mean measurements at each of the five locations, after ascertaining that data was normally distributed by the Anderson Darling test.

3. Results and discussion

3.1. Macro, micro and trace element content of soil, flower and honey samples

The element concentrations of examined soil, flower and honey samples are presented in Table 3. Analysing the macro element concentrations of soil samples, No.1S sample showed the highest K, Na and S contents. The highest Mg and P concentrations were determined in No.4S and No.5S samples. Examining the mean macro element concentrations, K was present in the highest contents followed by Mg, P, S and Na. Examining the micro element contents the lowest element concentrations were measured in No.2S sample, and No.3S sample showed similar low element contents, except for Mo that was at a high concentration compared to other samples. The highest As, B, Fe and Mn contents were determined in No.1S sample, and No.4S sample showed the highest Ba, Cd, Cu, Pb and Sr concentrations. Forthe other micro elements (Co, Cr, Ni and Zn), the highest contents were measured in the other sunflower soil sample (No.5S). All of the soil samples contained Fe at the highest concentration and Mo and Cd were measured at the lowest contents. According to the mean micro element contents, Ba was the second most abundant element, followed by Mn, Zn, Cr, Ni, Cu, Sr and Pb. Concentrations of Co, As and B were less than 10 000 µg/kg.

Examining the mean macro, micro and trace elements concentration of soil samples, the sunflower soil samples showed higher element concentrations than acacia soil samples, except for Na, S and Mo, however statistically verified differences were determined only in the case of Ba, Cd, Cr, Cu, Pb, Sr and Zn contents (Table 4). Comparing the results of two different counties, the determined element concentrations were higher in samples from Békés County than in samples from Szabolcs-Szatmár-Bereg County, except for Mo. Significant differences (P value < 0.05) were found in K, Mg, P, As, Co, Cr, Cu, Fe, Mo, Ni, Pb, Sr and Zn concentrations (P values = 0.01, <0.001, 0.01, 0.02, 0.002, 0.03, 0.05, <0.001, 0.05, 0.01, 0.03, 0.02 and 0.02, respectively). Note we also found that, comparing the soils used for the growing of acacia and sunflowers, there were significant increases in the following elements in the sunflower soils, compared with the acacia soils: Cd (P=0.005), Cr (P=0.04), Cu (P=0.02), Pb (P=0.04), Sr (P=0.04) and Zn (P=0.04).

In table 3 the element concentrations of flower samples are shown. Examining the macro element concentrations No.1F sample showed the highest Na and S contents, and the highest K and P concentrations were determined in No.2F sample. No.5F sample showed the highest Mg content. In every samples K was present in the highest concentration and based on mean element contents P was the second most abundant element followed by S, Mg and Na. The highest As, Fe and Ni contents were measured in No.2F sample and No.3F sample showed the highest Cr, Mn and Mo concentrations. Sunflower flower samples showed the highest Cd, Pb and Sr (No.4F) as well as the highest B, Ba, Co, Cu and Zn (No.5F) contents. Examining the sunflower flower samples more than 90 times Cd concentration was determined in these flower samples compared to acacia flower samples. Based on mean micro element concentrations, the most abundant element was the Fe followed by Zn, B, Mn, Cu, Sr, Ni and Ba. The concentrations of Mo, Cd, Cr, Co, As and Pb were under 1000 µg/kg. Comparing the two sunflower samples the concentrations of Cr, Cu, Mo and Pb were very similar, however No.4F sample showed higher Cd and Sr concentrations than No.5F sample. Comparing acacia flower samples No.1F samples showed higher Ba, Cd, Pb and Sr concentrations than the other two acacia flower samples. Higher B, Ba, Cd, Co, Cu, Pb, Sr and Zn contents were measured in sunflower flowers than acacia flowers (Table 4), however significant differences (P value < 0.005) between the acacia and sunflower flowers existed for B, Ba, Co, Cu, Fe, Mn, Pb, Sr and Zn contents. Examining the flower samples from two different soil types showed significant differences for P, Co, Cr and Mo (P=0.02, 0.04, 0.002 and 0.007, respectively).

Examining the macro element contents of honey samples, K was present in the highest concentrations followed by P and S in all of the honey samples (Table 3). In the case of acacia honey samples, No.1H sample showed higher K, Mg, Na and S contents than the other two acacia honey samples. No.2H and No.3H acacia honey samples showed very similar K, Mg, Na and P concentrations. Examining the sunflower honeys, No.5H sample showed higher macro element concentrations except for Mg, however major differences were not detected between these two samples. Sunflower honey also tended to have lower P content, which together with the high K in all honey samples, and more in sunflower than acacia honey, confirms our previous studies (Czipa et al., 2015). The macro element concentration orders were the following: Mg<Na<S<P<K for acacia honeys and Na<Mg<S<P<K for sunflower honeys. Comparing the two honey types, higher macro element contents were measured in sunflower honeys than acacia honeys; and significant differences were determined in K and Mg concentrations. Acacia honey samples from Italy, Malaysia and Saudi Arabia have been reported with higher K (719±390, 1277±123 and 429-491 mg kg^{-1}, respectively) Mg (70.0±27.0, 14.1±5.8 and 189-196 mg kg^{-1}, respectively) and Na (91.0±29.0, 529±61 and 15.9-19.0 mg kg^{-1}, respectively) concentrations than ours (Di Bella et al. 2015, Chua et al. 2012 and Alquarni et al. 2014, respectively). Fermo et al. (2013) found similar concentrations in Italian honeys to those of our samples, but they were not from acacia or sunflower. Oroian et al. (2015) also measured high K (554 and 849 mg kg^{-1}), Mg (51.2 and 63.8 mg kg^{-1}) and Na (171 and 154 mg kg^{-1}) in Romanian acacia and sunflower honeys. However, Atanassova et al. (2012) determined similar K (126 and 247 mg kg^{-1}), Mg (6.00 and 14.0 mg kg^{-1}), Na (8.11 and 7.58 mg kg^{-1}), P (24.0 and 41.0 mg kg^{-1}) and S (12.0 and 20.0 mg kg^{-1}) concentrations in Bulgarian acacia and sunflower honeys. North Indian sunflower honey showed higher K (176±0 mg kg^{-1}) and Na (690±0 mg kg^{-1}) concentrations than ours (Nanda et al., 2003).

Examining the micro element contents of honey samples, the Cr concentrations were under DL in every honey sample and Cd and Co concentrations were both under DL in acacia honeys (Table 3.). Micro element contents in No.2H and No.3H acacia honey samples were very similar. Acacia honey sample from Békés county (No.1H) showed higher micro element concentrations than the other two acacia honeys from Szabolcs-Szatmár-Bereg county, except for Mo. In the sunflower honey samples (No.4H and No.5H), the concentrations of examined micro elements were similar, however much higher B and Zn contents were measured in No.5H sample.

Overall, honey from sunflowers had higher B, Ba, Cu, Fe, Pb, Sr and Zn contents and lower Ni than honey from acacia flowers, however significant differences (P value < 0.005) were determined only for Ba, Cu, Pb, Sr and Zn contents (Table 4). In relation to micro and trace element content, B, Zn and Fe had the highest values. Mn and As concentrations were similar in both honey types, but Ba, Cu, Sr and Pb were all higher in sunflower than acacia honey samples. However Mo and Ni contents were higher in acacia than sunflower honey samples. The micro element order was as follows: Mo<Pb<As<Ba<Ni<Sr<Cu<Mn<Fe<Zn<B for acacia honey and Mo<Cd<Co<Ni<Pb<As<Ba<Sr<Cu<Mn<Fe<Zn<B for sunflower honey, thus the order from Sr to B was the same.

Oroian et al. (2015) measured higher Ba, Cr, Cu, Fe, Mn, Ni, Pb and Sr but lower As concentrations in acacia (28.0; 51.0; 1820; 19390; 1720; 191; 62.0; 264 and 9.00 µg kg^{-1}, respectively) and sunflower (349; 37.0; 2390; 24010; 1000; 183; 40.0; 351 and 5.00 µg kg^{-1}, respectively) honeys from Romania. Bulgarian acacia and sunflower honeys (Atanassova et al., 2012) had higher Fe (830 and 1930 µg kg^{-1}) and Sr (150 and 210 µg kg^{-1}) but lower Zn (220 and 610 µg kg^{-1}) content than our samples. Micro and trace element contents of Egyptian honeys from sandy soil measured by Rashed et al. (2009) (5.00-430 µg kg^{-1} for Cd, 80-800 µg kg^{-1} for Co, 650-1600 µg kg^{-1} for Cr, 1400-1900 µg kg^{-1} for Cu, 35000-64000 µg kg^{-1} for Fe, 630-1400 µg kg^{-1} for Mn, 200-700 µg kg^{-1} for Ni, 1500-2100 µg kg^{-1} for Pb and 8800-11000 µg kg^{-1} for Zn) were much higher than in our samples and Al Naggar et al. (2013) determined much higher Fe (2800-3730 µg kg^{-1}), and Pb (110-1590 µg kg^{-1}), but lower Zn (1020-1430 µg kg^{-1}), concentrations in their Egyptian honey samples. Conti and Botrè (2000) measured higher Cd (<2.00-63.0 µg kg^{-1}) and Cr (8.40-102 µg kg^{-1},) concentration in Italian honey samples.

Examining the element concentration of sunflower soil and honey samples, the honey collected from soil with higher element contents also had higher element concentrations. In the case of acacia soil and honey samples a similar tendency was observed, except for P, Mo and Ni concentrations.

3.2. Comparing the element contents of soil, flower and honey samples

Combined with the soil, flower and honey samples confirmed that those from soils with high element concentrations showed high element contents for several examined elements. Because the element uptake and transport is influenced by soil properties and plant type, the samples were analysed separately for the different plant types. Examining the acacia samples, the flower and honey samples followed a tendency that was observed in soil samples, namely the flowers and honeys collected from soils with higher Mg, Na, S, Ba, Cu and Pb contents showed higher concentrations of these elements. In the case of K, Fe, Mn and Zn, the element content of flower samples did not follow the element content of soils; however the honeys did showed a similar tendency. Flower samples had similarly high concentrations to soil samples in the case of Mo and Sr, however honey samples did not follow this trend. In the case of P the order of element content of flower and honeys samples was the same but soils showed a different order. In the case of As, B and Ni relations were not able to be determined. Examining the sunflower soils, the order of examined elements of soil, flower and honey samples was the same except for K, Mg, Ba and Fe. In the case of K, Mg and Fe, the element content of soil samples was followed by honey samples; however the flower samples did not show this tendency. In the case of Ba, only the flower and honey samples showed the same trends.

From the BCF values of acacia and sunflower samples, it is evident that flower/soil values were greater than 1.00 for K, P, S, B, Cu, Mo, Ni and Zn (acacia) and for K, P, S, B and Mo (sunflower); BCF (honey/flower) values were less than 1.00 in case of all samples; BCF (honey/soil) values were higher than 1.00 for B in both samples (Table 5). In acacia samples considered separately, BCF (flower/soil) values were much lower for samples from Békés County; samples from Szabolcs-Szatmár-Bereg County showed increased BCF (honey/flower) values for Na, S, Ba, Cu, Fe, Mo, Ni and Sr. Examining the honey/soil values for acacia samples, those from Békés County had lower values (except Mn, Mo and Pb) than the other two samples. Sunflower samples showed similar BCF (flower/soil) values for Na, P, Ba, Cd, Co, Cu, Pb, Sr and Zn, however the samples from Sarkad (No.5.) showed higher values for Mg, As, B and Fe. Examining the BCF (honey/flower) values, the sunflower honeys from Sarkad showed higher values for K, Na, S, Co, Mn, Ni and Zn, and sunflower samples from Sarkadkeresztúr had higher values for Mg, P, As, Ba, Cd and Fe. For other elements the values were very similar. Examining the BCF (honey/soil) values, the sunflower samples showed similar values for Mg, As, Ba, Cu, Fe, Mn, Ni and Pb. Samples from Sarkadkeresztúr showed higher values for K, P and Cd.

Considering the samples together (five soils, five flowers and five honeys) the BCF (flower/soil) values were greater for B, K, P, S and Mo than all other elements. The lowest values were determined for As, Co, Cr, Fe and Pb. BCF (honey/flower) values were highest for B and As, then all the other elements, except Ni, which was lower than all of these and

Cd, Co and Cr, which were not determinable. In the case of honey samples, the BCF (honey/soil) values were low (except B), thus the translocation of examined elements from soil to nectar (honey) was low. The BCF (honey/soil) values were highest for B, then K, then all other elements, except Cd, Co and Cr, which were non determinable and P and S which were intermediate between K and the other elements. The BCF orders were very similar for acacia flowers and sunflowers.

Examining the results, there was little movement of Fe through the soil-flower-honey system. Since Fe can be bound to the cell wall of the root rhizodermis of root (Szabó 1998), the translocation of this element from root to other organs (e.g. flower) is limited. Similarly the translocation of two potentially toxic elements, Pb and As, was very low. The translocation of Mo was high between the soil and flower; however this movement was very low to honey. The translocation of Mn and Ba was moderate in this system. In relation to micro elements, the two highest movements were for Zn and B.

Comparing the bio-concentration factors with elements as replicates, these were higher for flower/soil (mean 2.57) than honey/flower and honey/soil (means 0.098 and 0.038, respectively (SED = 0.816, P = 0.005).

Table 6 shows the results of Pearson's correlation between elements of flower and soil, honey and soil or honey and flower system. The elements with significant correlations between honey and soil, in descending order of P value, were Cu> Ba>Pb>Sr=Ni>Zn>Mn>As. The elements with significant correlations between honey and flower, in descending order of P value, were Pb=Sr>Zn>Cu>Ba>Fe>B>Mo. The elements with significant correlations between flower and soil, in descending order of P value, were S>Cd>Ba>Pb>Cu>Co=Mo>Sr>Zn>Cr>Na

4. Conclusions

In this study 19 elements were measured in five-five soil, flower and honey samples (acacia and sunflower) from two Hungarian Counties (Békés and Szabolcs-Szatmár-Bereg County) and BCF values were determined using these samples. Soil samples were collected from unpolluted areas and our results showed low contaminant concentrations, with little bioconcentration in the case of Pb and As, and with Cd undeterminable due to low concentrations. The highest bioconcentration from soil to honey was for B, which was the only element in higher concentrations in honey than soil. K, P, S and Na showed higher bioconcentration than other elements. The strongest correlations between soil and honey were for Cu, Ba and Sr. The results have potential for detecting regional deficiencies in soil, for example as suggested by the correlation coefficients of 0.99 and 0.95 for Cu and Zn, respectively, since bees gather pollen from a region of about 7 km^2, thus avoiding the need to take soil samples over large areas. High Pb and As (CC 0.98 and 0.88, respectively) concentrations in soils may also be successfully determined from their concentrations in honey, but this is yet to be confirmed in contaminated regions. In the literature there are many studies about honey as a bioindicator, however the examination of soils, flowers and honeys element content together is very rare. With this study we are able to verify the relations among the element contents of honeys, flowers and soils.

Acknowledgement

We thank apiarists Gerda Diósi and Péter Heim for the samples and Áron Soós for assistance.

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Table 1. Sample type and floral and geographical origin

Type of sample	Sample number	Sample name	County	Town
Soil	No.1S	Acacia soil	Békés	Sarkadkeresztúr
	No.2S	Acacia soil	Szabolcs-Szatmár-Bereg	Nyírlugos
	No.3S	Acacia soil	Szabolcs-Szatmár-Bereg	Ömböly
	No.4S	Sunflower soil	Békés	Sarkadkeresztúr
	No.5S	Sunflower soil	Békés	Sarkad
Flower	No.1F	Acacia flower	Békés	Sarkadkeresztúr
	No.2F	Acacia flower	Szabolcs-Szatmár-Bereg	Nyírlugos
	No.3F	Acacia flower	Szabolcs-Szatmár-Bereg	Ömböly
	No.4F	Sunflower flower	Békés	Sarkadkeresztúr
	No.5F	Sunflower flower	Békés	Sarkad
Honey	No.1H	Acacia honey	Békés	Sarkadkeresztúr
	No.2H	Acacia honey	Szabolcs-Szatmár-Bereg	Nyírlugos
	No.3H	Acacia honey	Szabolcs-Szatmár-Bereg	Ömböly
	No.4H	Sunflower honey	Békés	Sarkadkeresztúr
	No.5H	Sunflower honey	Békés	Sarkad

Table 2. Operating parameters of ICP-OES and ICP-MS

Parameters (ICP-OES)		**Paramaters (ICP-MS)**	
Operating power	1350 W	Rf power	1400 W
Plasma gas flow rate	16 l min^{-1}	Plasma gas flow rate	14.0 l min^{-1}
Auxiliary gas flow rate	1.0 l min^{-1}	Auxiliary gas flow rate	1.0 l min^{-1}
Nebuliser gas flow rate	1.0 l min^{-1}	Nebuliser gas flow rate	0.9 l min^{-1}
Rinsing time	30 sec	CCT gas flow rate	6.0 ml min^{-1}
Rinsing pump speed	75 rpm	Sample uptake rate	0.5 ml min^{-1}
Stabilization time	5 sec	CCT gas	7% H_2 in 93% He
Integration time		Dwell time	100 ms
Low WL* range	10 sec	Sweeps	9
High WL* range	10 sec	Main runs	3

*WL: wavelength

Table 3. Results of element contents of examined soil, flower and honey samples. For the county of origin for each sample see table 1.

Elements	**No.1S**	**No.2S**	**No.3S**	**No.4S**	**No.5S**	**Mean±SD**
K (mg kg^{-1})	3451±11	825±12	1009±5	2410±17	3322±29	2203±1243
Mg (mg kg^{-1})	2729±70	653±9	792±9	3039±18	2891±32	2021±1191
Na (mg kg^{-1})	215±4	27.7±1.1	42.4±0.3	89.7±3.3	103±2	94.9±74.0
P (mg kg^{-1})	772±19	225±5	233±14	600±20	834±14	533±290
S (mg kg^{-1})	731±9	161±10	140±4	209±2	229±5	294±247
As (µg kg^{-1})	10869±323	1473±5	1423±76	7014±46	8003±53	5756±4180
B (µg kg^{-1})	3216±23	2359±15	2304±18	2611±6	3152±8	2728±432
Ba (µg kg^{-1})	73142±144	15334±102	17029±180	300105±559	297000±694	140521±146129
Cd (µg kg^{-1})	176±4	63.9±1.0	34.5±2.9	594±12	518±5	277±261
Co (µg kg^{-1})	8608±58	1498±1	1984±32	9479±52	10706±58	6455±4371
Cr (µg kg^{-1})	39269±158	5376±84	6734±84	66163±176	72447±506	37998±31714
Cu (µg kg^{-1})	22444±174	6556±153	4874±102	46070±149	45278±428	25044±20043
Fe (mg kg^{-1})	25426±3	4505±2	5561±6	24343±2	22638±2	16495±10516
Mn (µg kg^{-1})	161472±452	94823±554	137426±614	139722±319	155627±716	137814±26120
Mo (µg kg^{-1})	79.4±1.8	110±1	152±6	45.8±4.3	69.3±4.3	91.2±40.9
Ni (µg kg^{-1})	39170±379	4218±23	5471±16	56797±217	63504±447	33832±27918
Pb (µg kg^{-1})	18201±143	7689±10	5426±63	30834±151	27523±164	17935±11400
Sr (µg kg^{-1})	22071±441	5625±75	4206±90	38416±232	33558±252	20775±15655
Zn (µg kg^{-1})	64310±201	14204±137	15137±114	105993±2123	109102±833	61749±46475
Elements	**No.1F**	**No.2F**	**No.3F**	**No.4F**	**No.5F**	**Mean±SD**
K (mg kg^{-1})	17036±157	18636±242	16344±354	17458±122	16447±21	17184±929
Mg (mg kg^{-1})	941±23	838±13	907±22	1320±11	1663±18	1134±350
Na (mg kg^{-1})	65.8±1.8	33.3±1.5	35.4±0.9	31.8±1.1	34.4±0.8	40.1±14.4
P (mg kg^{-1})	2292±52	3796±182	3726±104	2150±54	2918±98	2976±773
S (mg kg^{-1})	2849±107	1735±26	1647±23	1751±25	1809±1	1958±501
As (µg kg^{-1})	119.5±0.6	135±4	104±3	61.4±1.3	89.2±2.3	102±28
B (µg kg^{-1})	11670±192	13990±132	14711±681	51793±411	78061±48	34045±29703
Ba (µg kg^{-1})	4218±45	2011±14	3175±12	7094±45	7456±14	4791±2402
Cd (µg kg^{-1})	6.28±0.01	3.18±0.09	2.22±0.06	393±11	328±2	147±197
Co (µg kg^{-1})	120±1	59.5±1.2	61.3±0.1	161±1	191±2	119±59
Cr (µg kg^{-1})	86.6±1.7	251±19	300±1	89.8±4	86.2±0.1	163±104
Cu (µg kg^{-1})	9888±13	9537±58	6679±62	16084±15	16203±101	11678±4262
Fe (mg kg^{-1})	108±1	128±1	93.8±0.6	49.6±0.0	67.9±0.0	89.4±31.2
Mn (µg kg^{-1})	25885±184	25608±245	29970±389	11771±26	17394±57	23326±5521
Mo (µg kg^{-1})	261±24	413±2.24	481±21	207±1	211±1	315±125
Ni (µg kg^{-1})	5933±84	10518±60	6079±84	3671±5	3749±86	5990±2780
Pb (µg kg^{-1})	65.2±1.9	45.7±2.6	41.0±8.2	138±4	127±0.13	83.3±45.9
Sr (µg kg^{-1})	4360±17	2575±13	2159±21	17504±41	16132±64	8546±7612
Zn (µg kg^{-1})	33023±111	32151±182	30631±249	41366±58	44059±109	36246±6040
Elements	**No.1H**	**No.2H**	**No.3H**	**No.4H**	**No.5H**	**Mean±SD**
K (mg kg^{-1})	285±2	209±1	228±1	431±9	492±4	329±126
Mg (mg kg^{-1})	2.82±0.15	1.22±0.01	1.37±0.22	15.1±0.1	13.8±0.0	6.88±6.99
Na (mg kg^{-1})	2.75±0.11	2.31±0.42	2.36±0.49	3.61±0.0	4.97±0.12	3.20±1.12
P (mg kg^{-1})	28.9±1.5	31.2±0.8	30.7±1.2	52.9±0.8	61.8±1.6	41.1±15.2
S (mg kg^{-1})	18.7±1.5	17.3±0.6	12.7±2.4	20.3±0.1	23.6±0.3	18.5±4.0
As (µg kg^{-1})	15.4±0.1	11.2±0.1	11.7±0.2	15.6±0.1	16.9±0.1	14.1±2.5
B (µg kg^{-1})	2971±44	2797±60	2851±90	3244±90	4775±18	3328±827
Ba (µg kg^{-1})	18.9±0.2	10.7±0.5	15.1±1.8	39.9±1.6	34.6±1.2	23.8±12.7
Cd (µg kg^{-1})	<DL	<DL	<DL	1.18±0.19	0.750±0.012	0,967±0.306
Co (µg kg^{-1})	<DL	<DL	<DL	0.871±0.050	1.71±0.15	1.29±0.60
Cr (µg kg^{-1})	<DL	<DL	<DL	<DL	<DL	<DL
Cu (µg kg^{-1})	76.3±3.0	57.5±1.2	51.9±2.0	129±3	131±4	89.3±38.6
Fe (mg kg^{-1})	0.437±0.026	0.287±0.004	0.421±0.008	0.612±0.011	0.553±0.009	0.462±0.126
Mn (µg kg^{-1})	191±4	123±3	140±3	146±2	172±4	154±27
Mo (µg kg^{-1})	0.514±0.560	0.871±0.026	0.831±0.048	<DL	0.326±0.02	0.636±0.261
Ni (µg kg^{-1})	14.8±0.9	20.9±1.9	25.9±0.3	3.90±0.19	6.38±1.26	14.3±9.3
Pb (µg kg^{-1})	2.45±0.0	0.516±0.014	0.451±0.041	7.46±0.30	6.77±0.12	3.53±3.38
Sr (µg kg^{-1})	44.5±2.9	28.4±0.3	31.9±1.9	98.2±0.6	93.2±2.6	59.2±33.9
Zn (µg kg^{-1})	967±46	420±4	575±5	2866±130	3233±21	1612±1333

Table 4. Element concentrations of samples of soil, flowers and honeys in acacia and sunflower-growing regions

Element	**_Soil, acacia mean±SD*_**	**_Soil, sunflower mean±SD_**	**_SED**_**	**_P value_**	**_Flower, acacia mean±SD*_**	**_Flower, sunflower mean±SD*_**	**_SED**_**	**_P value_**	**_Honey, acacia mean±SD*_**	**_Honey, sunflower mean±SD*_**	**_SED**_**	**_P value_**
K (mg kg^{-1})	1762±1466	2866±645	1144	0.406	17339±1176	16953±715	954	0.713	241±40	462±43	37.2	0.010
Mg (mg kg^{-1})	1391±1161	2965±105	867	0.167	895±52	1492±243	174	0.169	1.80±0.88	14.5±0.9	0.818	0.001
Na (mg kg^{-1})	95.0±104	94.9±11.5	77.9	0.998	44.9±18.2	33.1±1.8	13.6	0.450	2.47±0.24	4.29±0.96	0.694	0.216
P (mg kg^{-1})	410±314	717±165	249	0.306	3271±849	2534±543	694	0.366	30.3±1.2	57.4±6.36	4.55	0.098
S (mg kg^{-1})	344±335	219±14	250	0.651	2077±670	1780±41	500	0.594	16.2±3.1	22.0±2.3	2.64	0.119
As (µg kg^{-1})	4588±5439	7509±699	4071	0.525	120±16	75.4±19.7	15.5	0.065	12.8±2.3	16.3±0.9	1.48	0.145
B (µg kg^{-1})	2626±511	2882±383	431	0.596	13457±1598	64927±18574	9861	0.014	2873±89	4010±1083	767	0.376
Ba (µg kg^{-1})	35168±32897	298553±2196	24546	0.002	3135±1104	7275±256	834	0.016	14.9±4.1	37.3±3.7	3.64	0.009
Cd (µg kg^{-1})	91.5±74.7	556±54	62.4	0.005	3.89±2.12	361±46	32.5	0.058	<DL***	0.965±0.304	-	-
Co (µg kg^{-1})	4030±3972	10093±868	2996	0.136	80.3±34.4	176±21	28.0	0.042	<DL	1.29±0.59	-	-
Cr (µg kg^{-1})	17126±19188	69305±4443	14492	0.037	213±112	88.1±2.6	83.3	0.232	<DL	<DL	-	-
Cu (µg kg^{-1})	11291±9695	45674±560	7232	0.018	8701±1760	16143±84	1313	0.011	61.9±12.8	130±1	9.56	0.006
Fe (mg kg^{-1})	11830±11786	23490±1206	8807	0.277	110±17.2	58.8±12.9	14.5	0.039	0.382±0.082	0.583±0.042	0.065	0.054
Mn (µg kg^{-1})	131240±33752	147675±11247	25846	0.570	27154±2442	17583±267	1826	0.014	151±35	159±18.4	28.1	0.803
Mo (µg kg^{-1})	114±36	57.6±16.6	28.5	0.143	385±113	209±3	84.0	0.127	0.739±0.196	<DL	-	-
Ni (µg kg^{-1})	16286±19828	60150±4743	14999	0.061	7510±2606	3710±54	1943	0.145	20.5±5.6	5.12±1.78	3.45	0.036
Pb (µg kg^{-1})	10438±6816	29179±2341	5228	0.037	50.6±12.8	133±8	10.4	0.004	1.14±1.14	7.12±0.49	0.885	0.007
Sr (µg kg^{-1})	10634±9930	35987±3435	7620	0.045	3031±1169	16818±971	1010	0.001	34.9±8.47	95.7±3.54	6.58	0.003
Zn (µg kg^{-1})	31217±28663	107548±2198	21396	0.038	31935±1211	42713±1904	1350	0.004	654±282	3050±260	251	0.002

*SD: Standard Deviation; **SED: Standard Error Difference, ***under detection limit

Table 5. Bioconcentration factors for the flower/soil, honey/flower and honey/soil transitions

	Flower/Soil			**Honey/Flower**			**Honey/Soil**		
	Acacia	Sun-flower	Overall	Acacia	Sun-flower	Overall	Acacia	Sun-flower	Overall
K	14.6	6.10	11.2	0.014	0.027	0.019*	0.188	0.164	0.178
Mg	0.924	0.505	0.757	0.002	0.010	0.005	0.002	0.005	0.003*
Na	0.781	0.351	0.609	0.059	0.129	0.087*	0.051	0.045	0.048
P	11.9	3.54	8.58	0.010	0.023	0.015	0.103	0.081	0.094
S	8.80	8.15	8.54	0.008	0.012	0.010	0.074	0.100	0.085
As	0.059	0.010	0.039	0.108	0.222	0.153*	0.006	0.002	0.004
B	5.32	22.2	12.1	0.216	0.062	0.154*	1.12	1.38	1.22
Ba	0.125	0.024	0.085	0.005	0.005	0.005	0.0006	0.0001	0.0004
Cd	0.050	0.647	0.289*	-	0.003	-	-	0.002	-
Co	0.028	0.017	0.024	-	0.007	-	-	0.0001	-
Cr	0.031	0.001	0.019	-	-	-	-	-	-
Cu	1.09	0.353	0.795	0.007	0.008	0.008	0.008	0.003	0.004
Fe	0.017	0.003	0.011	0.004	0.010	0.006	0.00005	0.00002	0.00004
Mn	0.216	0.119	0.177	0.006	0.009	0.007	0.001	0.001	0.001
Mo	3.41	3.79	3.56	0.002	-	-	0.007	-	-
Ni	1.25	0.062	0.776	0.003	0.001	0.002	0.003	0.0001	0.002
Pb	0.006	0.005	0.005	0.020	0.054	0.033	0.0001	0.0002	0.0002*
Sr	0.390	0.468	0.421	0.012	0.006	0.009*	0.005	0.003	0.004
Zn	1.60	0.397	1.12	0.020	0.071	0.041*	0.028	0.028	0.028

* Correlation is significant at the 0.05 probability level

428 Table 6. Pearson's correlation coefficients for flowers and soils, honeys and soils, and honeys and flowers

	Flowers and soils		**Honeys and flowers**		**Honeys and soils**	
	Corr.	P value	Corr.	P value	Corr.	P value
K	-0.422	0.479	-0.374	0.535	0.694	0.194
Mg	0.717	0.173	0.911	0.031	0.784	0.117
Na	0.895*	0.040	-0.235	0.703	0.184	0.767
P	-0.796	0.107	-0.394	0.512	0.583	0.302
S	0.998*	<0.001	0.139	0.824	0.166	0.790
As	-0.290	0.636	-0.600	0.285	0.884*	0.046
B	0.414	0.488	0.916*	0.029	0.592	0.293
Ba	0.976*	0.004	0.975*	0.005	0.982*	0.003
Cd	0.981*	0.003	-	-	-	-
Co	0.962*	0.009	-	-	-	-
Cr	-0.903*	0.036	-	-	-	-
Cu	0.964*	0.008	0.981*	0.003	0.993*	0.001
Fe	-0.601	0.284	-0.972*	0.006	0.765	0.132
Mn	-0.271	0.659	-0.220	0.722	0.893*	0.041
Mo	0.963*	0.009	0.951*	0.049	0.843	0.157
Ni	-0.827	0.084	0.700	0.188	-0.954*	0.012
Pb	0.972*	0.006	0.995*	<.001	0.979*	0.004
Sr	0.935*	0.020	0.996*	<.001	0.954*	0.012
Zn	0.930*	0.022	0.989*	0.001	0.950*	0.013

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