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Rape, sunflower and forest honeys for long-term environmental monitoring: Presence of indicator elements and non-photosynthetic carbon in old Hungarian samples

Zsófi Sajtos [a,b], Tamás Varga [c,d,*], Zita Gajdos [a], Petra Burik [a], Máté Csontos [b,e], Zsuzsa Lisztes-Szabó [c], A.J. Timothy Jull [c,f,g], Mihály Molnár [c], Edina Baranyai [a,**]

[a] Atomic Spectroscopy Partner Laboratory, Department of Inorganic and Analytical Chemistry, Faculty of Science and Technology, University of Debrecen, Egyetem Square 1, H-4032 Debrecen, Hungary
[b] University of Debrecen, Doctoral School of Chemistry, Debrecen, Hungary
[c] Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Eötvös Loránd Research Network (ELKH), Debrecen H-4001, P.O Box 51, Hungary
[d] University of Debrecen, Doctoral School of Physics, Debrecen, Hungary
[e] Department of Physical Chemistry, Faculty of Science and Technology, University of Debrecen, Egyetem Square 1, H-4032 Debrecen, Hungary
[f] Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA
[g] University of Arizona, AMS Laboratory, Tucson, AZ 85721, USA

HIGHLIGHTS

- Radiocarbon analysis of Hungarian rape, sunflower and forest honey samples
- Multi-Element analysis of Hungarian honey samples, collected between 1985 and 2018
- Multivariate statistical analysis was carried out on the elemental concentrations of the honeys.
- Radiocarbon analysis suggests non-photosynthetic carbon in the honey samples.

GRAPHICAL ABSTRACT
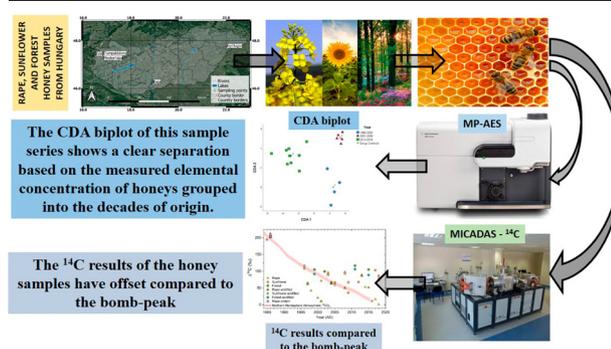
ARTICLE INFO

ABSTRACT

In this paper, we present the time-dependent elemental composition and AMS radiocarbon dating results of 36 rape, sunflower and forest honey samples, collected between 1985 and 2018 in geographically close locations. Based on the elemental information, we conclude that bee products regardless the type provide useful environmental information of the previous decades, such as the decreasing trend of airborne Pb emission can be traced. However, radiocarbon results agree less with the atmospheric bomb peak. Random offsets were observed in the specific radiocarbon activity of the honey samples indicating that rape, sunflower and forest honey samples are not as reliable materials for radiocarbon dating as acacia honeys. The radiocarbon results show that the rape, sunflower and forest honey samples can contain non-photosynthetic carbon, presumably derived from the soil. Thus, the complex application of honey samples for environmental reconstruction requires the species-separated investigation of bee products to reveal their adaptability for assessment approaches.

 * Correspondence to: T. Varga, Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Hungarian Academy of Sciences (Atomki), Debrecen H-4001, P.O Box 51, Hungary.
 ** Corresponding author.
    E-mail addresses: varga.tamas@atomki.hu (T. Varga), baranyai.edina@science.unideb.hu (E. Baranyai).

1. Introduction

Honey is an import-export product of great commercial importance, with numerous health benefits and medicinal importance due to the mineral, enzyme, protein and vitamin content (Fatima et al., 2012; Sajtos et al., 2019; Da Silva et al., 2016). The quality and properties of honeys depend on the nectar-producing sources, that can be investigated by different analytical methods. In recent years, elemental analysis has been applied to support the determination of botanical and geological origin of the apicultural products (Di Bella et al., 2015; Hernández et al., 2005; Louppis et al., 2017) as well as isotope analytical techniques using the stable isotopes of $\delta^{13}C$, $\delta^{15}N$ or $\delta^{34}S$ ratio (Bontempo et al., 2017; Da Silva et al., 2016; Dong et al., 2016; Dunn et al., 2019; Förstel, 2007; Kropf et al., 2010; Padovan et al., 2003; Park et al., 2019; Schellenberg et al., 2010).

Honey serves as a nutrient reservoir for the bee colony to survive adverse weather conditions after the vegetation period is over (Kiliç Altun et al., 2017). An extremely unique feature of this material is the nearly infinite storage time, since in proper storage, no alteration in their quality and quantity occurs. This property provides the opportunity to use apicultural products for long-term environmental assessment and reconstruction. Literature data report the successful application of apiarian products for the investigation of the nectar producing region's environmental status (Anklam, 1998; Majewska et al., 2019; Uršulin-Trstenjak et al., 2017). It is known that the mineral composition of honey samples depends greatly on the geographical and botanical origin (Iuliana and Cecilia, 2005; Rashed et al., 2009; Sajtos et al., 2019), thus honey can be considered as a quality indicator of the pollen producing region (Citak et al., 2012). The agricultural and industrial emission of pollutants influences the composition of the pollen grains, therefore the final bee products thus honeys can be considered as biomarkers in specific environmental assessments (Kaste et al., 2021; Leme et al., 2014; Oroian et al., 2016; Smith et al., 2020; Zhou et al., 2018). In our previous study, we further proved that inorganic environmental factors are preserved in honeys, indicating pollution from both natural and anthropogenic origin of earlier times (Varga et al., 2020b). Beside the geochemical and biological differences, we also highlighted that the collection time from the same location and species result in alteration of the elemental concentration (Varga et al., 2020b). Thus, information regarding the soil properties, climatic conditions as well as human load in environmental factors can be derived on a longer time scale by the analysis of old apicultural products.

Since the nuclear era, several types of organic materials have been dated using the atmospheric ^{14}C bomb-pulse. Former studies show that not just bone, but other organic related substances, such as hair, skin, wine, paintings or even cocaine can be dated by AMS ^{14}C measurements (Hendriks et al., 2019; Palstra et al., 2008; Povinec et al., 2020; Zoppi et al., 2004). The age determination of relatively young, recent materials may also be effective for forensic studies (Cook et al., 2020; Hendriks et al., 2019; Zoppi et al., 2004). The forensic application of stable isotopes to identify honey adulteration is also widely used, based on the different stable carbon isotope composition of C3 and C4 type plants (White and Winters, 1989). As these earlier studies show, the isotope analytical tools provide powerful opportunity within food investigations including apiarian products. Our previous study with modern, Hungarian acacia honey samples, derived from black locust flowers (false acacia, *Robinia pseudo-acacia*) (Varga et al., 2020b) shows that the acacia honey is an appropriate material for ^{14}C dating without significant radiocarbon offset (Becker-Heidmann et al., 2002; Buró et al., 2019; Graven et al., 2017; Santos et al., 2016; Shi et al., 2020; van der Voort et al., 2016).

In our present study, we continue our novel approach to old honey analysis in an attempt to gain deeper knowledge regarding their applicability as a long-term environmental indicator. MP-AES method coupled with AMS was applied on honeys of different origin with known age and results were compared by previous data collected for the unique, 24 year-long honey sample series originating from the same nectar producing plant and location. Forest, sunflower and rape honeys were analysed during the period of 1985–2018, where atmospheric radiocarbon bomb-peak was used for ^{14}C calibration and elemental analytical results were applied for environmental reconstruction purposes.

2. Materials and methods

2.1. Origin and type of samples

In this study, 36 honey samples were collected between the year of 1985 and 2018 from Hungary, including forest, sunflower and rape honeys. These known-age honeys were collected from the nectar-producing areas of Gór, Tompaládony, Mesterháza, Baja and Nyírlugos, shown in Fig. 1 and Table 1. Gór, Tompaládony and Mesterháza are located at Western Hungary close to each other, while Baja and Nyírlugos are located at the Great Hungarian Plain and the Central and Eastern Hungary region. Honeys
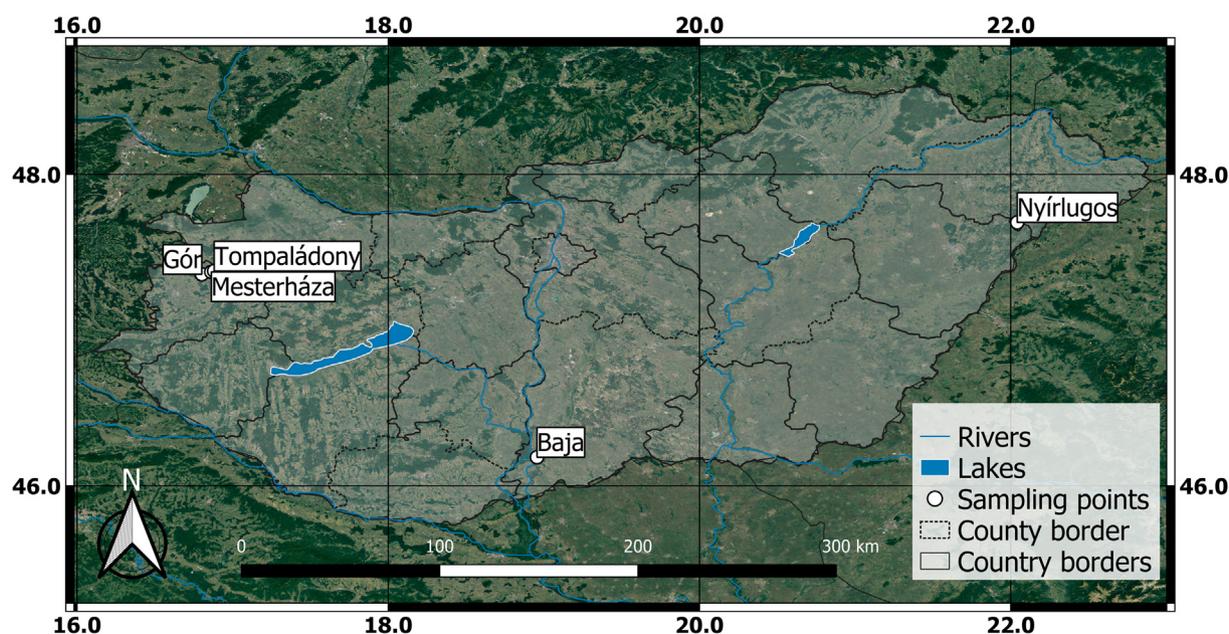

Fig. 1. Location of the sampling sites.

Table 1
Collection years and origin of the studied honey samples.

No.	Year	Botanical origin	Geographical origin
1	1999	Forest	Gór
2	2002	Forest	Gór
3	2006	Forest	Gór
4	2010	Forest	Gór
5	2011	Forest	Gór
6	2015	Forest	Gór
7	2016	Forest	Baja[a]
8	1985	Sunflower	Nyírlugos
9	1996	Sunflower	Mesterháza
10	2003	Sunflower	Mesterháza
11	2005	Sunflower	Mesterháza
12	2009	Sunflower	Mesterháza
13	2012	Sunflower	Mesterháza
14	2018	Sunflower	Mesterháza I.
15	2018	Sunflower	Mesterháza II.
16	2007	Sunflower	Baja[a]
17	2009	Sunflower	Tompaládony
18	2017	Sunflower	Tompaládony
19	1986	Rape	Nyírlugos
20	1997	Rape	Gór
21	1998	Rape	Gór
22	2000	Rape	Gór
23	2001	Rape	Gór
24	2004	Rape	Gór
25	2004	Rape	Mesterháza
26	2007	Rape	Mesterháza
27	2008	Rape	Gór
28	2013	Rape	Gór
29	2014	Rape	Mesterháza
30	2015	Rape	Gór
31	2016	Rape	Mesterháza
32	2016	Rape	Mesterháza
33	2017	Rape	Gór
34	2017	Rape	Mesterháza
35	2018	Rape	Gór
36	2018	Rape	Mesterháza

[a] The exact geographical origin of these honeys is unknown: samples were preserved in a honey museum in Baja without additional information.

from Baja were preserved in a Hungarian honey museum, but the exact geographical origin of these samples are unknown: only the year of the collection is available. Honey samples were kept properly by the professional beekeepers and in the honey museums at temperatures of 8 ± 2 °C in dark and dry places. The same circumstances were used in the laboratory where samples were stored in glass or plastic jars, or centrifuge tubes prior to analysis.

2.2. MP-AES analysis

Continuous stirring was used to homogenise the samples prior to further analysis. Then, 0.5 g of each sample was measured on analytical balance (Precisa 240A) into 50.0 ml volume glass beakers and placed on an electric hot plate to dry until constant weight. Dry mass and moisture content were determined by gravimetric methods. To avoid contamination, the same beaker was further used to wet-digest the samples with a mixture of 4.0 ml 65% (m/m) HNO_3 (reagent grade, Scharlau) and 1.0 ml 30% (m/m) H_2O_2 (reagent grade, Merck). After complete dissolution (4 h at 120 °C), samples were transferred without loss into plastic centrifuge tubes and diluted up to 25.0 ml with ultrapure water (Synergy UV Millipore). All the glassware and laboratory pieces of equipment used was decontaminated by a 1:5 HNO_3:H_2O solution for 24 h and rinsed with deionized water before use. Sample solutions were stored at room temperature prior to the MP-AES analysis.

Based on Sajtos et al. (2019), the elemental determination of honey samples was carried out by microwave plasma atomic emission spectrometry (MP-AES 4200, Agilent Technologies). The concentration of the following 19 elements was quantitatively determined: Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na Ni, Pb, Sr, Zn.

A five-point calibration process was used, where standard solutions were diluted with 0.1 M HNO_3 in ultrapure water. The calibration solutions were prepared from commercially available spectroscopic standards of 1000 mg L^{-1} (Scharlau, ICP IV, Merck). The whole chemical preparation including the MP-AES operating conditions and measurement parameters are the same as applied in our previous study (Varga et al., 2020b) that was validated previously (Sajtos et al., 2019). The residual carbon content was routinely monitored during the elemental analysis to see if there is a significant difference between the digestion efficiency of the samples or if incomplete digestion can be suspected. No carbon signal was detected in either of the measured samples.

2.3. FTIR analysis

Fourier transform infrared spectroscopy (FTIR) was used to acquire infrared (IR) spectra of the honey samples (Cary 660 Agilent Technologies). The instrument is operated by the software MicroLab PC. Measurements were carried out in attenuated total reflection (ATR) mode. Samples were analysed directly as obtained after homogenization, without using purification or addition of any chemical reagents. The crystal was carefully cleaned prior to the analysis and between samples with ethanol (reagent grade, Merck) and ultrapure water. The spectra were measured in a mid-infrared region (4000–400 cm^{-1}) using a nominal recording resolution of 4 cm in five individual replicates. The spectral analysis was carried out using the Unscrambler Xv10.3 software package. For smoothing the FTIR spectra and for derivatization, the Savitzky-Golay method was applied. The Multiplicative Scatter Correction (MSC) was used to compensate for additive and/or multiplicative effects in the spectral data.

2.4. Statistical evaluation of MP-AES and FTIR data

Elemental concentration of the honey samples was compared using a Student's *t*-test and ANOVA. Tukey's multiple response test was used to evaluate significant differences and considered to be statistically different when the *p* value was less than 0.05. A Levene test was applied to verify the homogeneity of variances. Canonical Discriminant Analysis (CDA) was applied for the separation of concentration data considering the years of sample collection. The SPSS software package was used (SPSS Statistic IBM 22) to perform ANOVA and CDA tests. For Principal component analysis (PCA) Unscrambler 11 (Camo Analytics) was used to compare the FTIR measurement results of the honey samples in correlation with the gained radiocarbon data.

2.5. Preparation and AMS ^{14}C measurement

Samples were investigated for AMS ^{14}C at the Hertelendi Laboratory of Environmental Studies (HEKAL), Isotope Climatology and Environmental Research Centre (ICER), Debrecen, Hungary using a MICADAS (Mini Carbon Dating System) type AMS.

Approximately 3 mg honey sample was weighed into pre-heated and cleaned glass test tubes and dried at 80 °C. The dry material was combusted with 300 mg MnO_2 in a vacuum-evacuated ($<10^{-5}$ mbar) sealed glass test tube at 550 °C for 12 h. A dedicated vacuum line was used for the purification of liberated CO_2 gas from the H_2O and other gas phase contaminants. The carbon yield was measured volumetrically in the vacuum line (Janovics et al., 2018). Then, a sealed tube graphitisation method was used to convert the pure CO_2 to graphite (Rinyu et al., 2013). We combusted and measured unprepared standards and unknown materials to confirm the trueness and repeatability of our AMS radiocarbon method. These samples were treated in the same way as the unknown honeys and validation results are shown in the Supplementary material S1. There were three IAEA (International Atomic Energy Agency) standards (C3, C6 and C8) with known pMC values (Fajgelj and Gröning, 2014). All the three repeated (min. $n = 3$ and max $n = 5$) IAEA standard measurements were in a good agreement with the reference values within <0.4 SD. We measured a commercial, fossil plastic sample ($n = 5$) to test the background

of the unprepared samples which gave the result of 0.18 ± 0.09 pMC. A commercial recent sugar sample ($n = 3$) and a commercial honey sample (n = 5) were also used to determine the repeatability of our AMS radiocarbon measurements. The result of the commercial sugar sample was 100.3 ± 0.4 pMC and 100.3 ± 0.04 pMC was gained for the commercial recent honey sample. These results prove a quite good repeatability of the applied AMS method for unknown samples.

For selected samples, pre-acidification was applied to eliminate the inorganic carbon. In this case, 1–2 ml 85% H_3PO_4 solution was added to the honey sample to eliminate the carbon from the inorganic components, then the sample was dried and handled as the above mentioned pure honey samples. Protein content was prepared from two selected sample, to determine the carbon isotopic composition of honey protein. In this case, the standard White and Winters (AOAC 991.41) method was used for the preparation of protein from honey samples (White and Winters, 1989), then the protein was dried and handled as the above-mentioned pure honey samples. During the AMS measurement, the $^{14}C/^{12}C$ and $^{13}C/^{12}C$ isotopic ratio were measured simultaneously for the ^{13}C correction (Molnár et al., 2013b, 2013a; Synal et al., 2007). For ^{14}C data evaluation, "Bats" data reduction software was used (Wacker et al., 2010). For the honey samples, the $\Delta^{14}C$ unit was used, defined as:

$$\Delta^{14}C = 1000\left(Fe^{\lambda_T t} - 1\right) \tag{1}$$

where λ_T is the true decay constant of C-14 isotope, based on the 5700 ± 30-year half-life, and t is the known age of the honey samples. F is the fraction of modern carbon, defined as the $^{14}C/^{12}C$ ratio relative to the 1950 CE (Donahue et al., 1990; Stuiver and Polach, 1977). For the visualization of the bomb-peak in the Northern Hemisphere zone, supplementary data from Graven et al., 2017 were used. The reason for using the curve from Graven et al., 2017 instead of generally-used Calibomb curve is further discussed in the Varga et al. (2020b).

The difference between the Northern Hemisphere data and the honey samples ($\Delta\Delta^{14}C$) were calculated by the following formula:

$$\Delta\Delta^{14}C = \Delta C_S - {}^{14}\Delta^{14}C_{NH} \tag{2}$$

where $\Delta^{14}C_S$ the $\Delta^{14}C$ value of the sample, $\Delta^{14}C_{NH}$ is the $\Delta^{14}C$ value of the Northern Hemisphere for the given year when the honey sample was collected.

3. Results and discussion

3.1. Elemental composition of honey samples

The validation of measurement data is of high importance especially when complex sample matrix is considered for analysis such as honey products (Pohl et al., 2012, 2017). The applied sample preparation and MP-AES method were carefully tested for the elemental determination of honey samples previously and proved to be suitable for the presented task (Sajtos et al., 2019; Varga et al., 2020b). The overall elemental composition of the honeys studied correlates well with our previous experimental results determined for Hungarian apiarian products (Sajtos et al., 2019; Varga et al., 2020b). In the CDA biplot indicated in Fig. 2, the first function accounts for 94.3% of the discriminating ability of the discriminating variables, and 5.7% is the value accounting for the second function. The canonical correlation values are 0.959 and 0.643, as well as the cumulative percentages are 94.3 for CDA1 and 100% for CDA2. The studied honey varieties are clearly grouped according to their botanical origin and forest honeys show the most significant separation from the others. This difference is not due to nectar origin, but honeydew, excreted by phloem-feeding insects (Neerbos et al., 2020) which is known to have higher mineral content (Olga et al., 2012; Pita-Calvo and Vázquez, 2017).

Since the sampling locations of the studied material are close to each other and Hungary is quite homogeneous considering the geological aspects of honey composition (Czipa et al., 2015; Sajtos et al., 2019), the separation
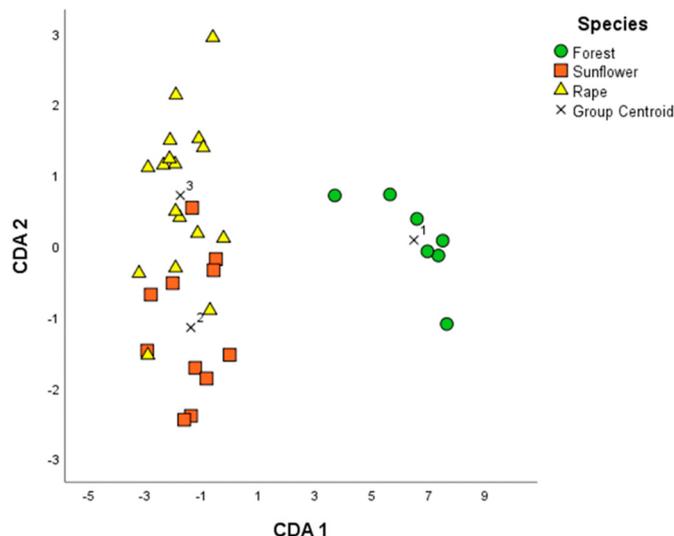

Fig. 2. CDA biplot of the honey samples differentiated by the studied species.

of the elemental concentration solely reflects a species-specific alteration. Potassium and manganese are found by Chudzinska and Baralkiewicz (2011) to be significant predictors in the statistical discrimination of honey types, in a study where chemometric methods were assessed to evaluate ICP-MS elemental analytical data for the verification of honey authenticity (Chudzinska and Baralkiewicz, 2011). Potassium is also an important marker of the geographical origin contributing to one-third of the total mineral content (Pohl, 2009). In the present study, honeys are from nearby sampling locations but originate from different pollen producing plants, thus geochemical alterations can be negligible. No significant difference was found between the K and Mn level of sunflower (K: 452 ± 165 mg kg^{-1}; Mn: 0.251 ± 0.114 mg kg^{-1}) and rape honeys (K: 445 ± 133 mg kg^{-1}; Mn: 0.260 ± 0.116 mg kg^{-1}), while significantly lower concentration of Mn was present in the acacia samples (0.164 ± 0.06 mg kg^{-1}, F = 0.620, $p = 0.438$) with statistically similar K level (402 ± 39 mg kg^{-1}, F = 0.450, $p = 0.508$) collected from the same site, published in our previous study (Varga et al., 2020b). Forest honeys showed a higher concentration of both elements (K: 655 ± 276 mg kg^{-1}, F = 7.134, $p = 0.000$; Mn: 0.365 ± 0.08 mg kg^{-1}, F = 14.135, p = 0.000).

Since in this study, rape samples were available in the highest amount with good year homogeneity, this species was used to evaluate the effect of collection years on the elemental composition. Fig. 3 summarizes the
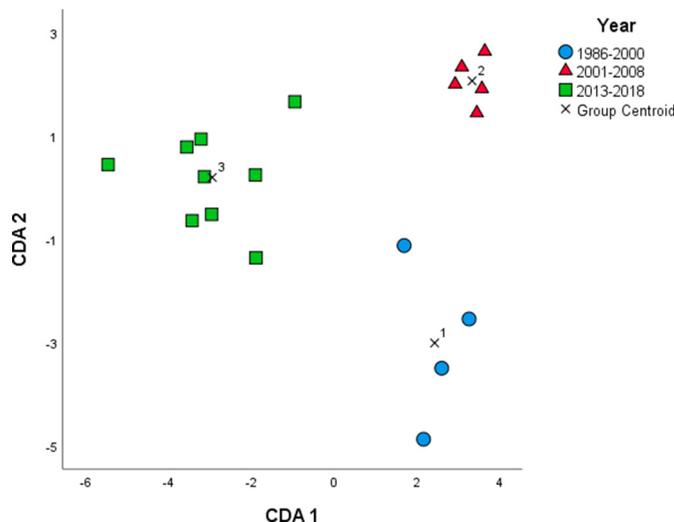

Fig. 3. CDA biplot of the rape honeys grouped according to the decades of origin.

CDA biplot where collected rape honeys are grouped into the decades of origin: 1986–2000; 2001–2008; 2013–2018.

The CDA1 accounts for 73.1% of the discriminating ability of the discriminating variables, while CDA2 accounts for 26.9%. The cumulative percentages are 73.1% and 100%, respectively. The canonical correlation values regarding the first function are 0.955 and 0.891, regarding the second function. A clear separation is observed between the different decades indicating the influence of environmental changes in the past on the studied apiarian products which shows a good agreement with our previous findings (Varga et al., 2020b).

A significant difference was found in the Fe and Pb concentration of the sunflower samples: the levels are decreasing from the older to the present ones showing the most markedly observable trend in the concentration of the measured elements against the years of origin. The phenomenon is indicated in Fig. 4 through the example of sunflower honeys originating from the same sampling site of Mesterháza. In this sample series, the species and geochemical related heterogeneity can be excluded thus the alteration of the elemental concentration is considered to be solely age-specific.

Iron is an essential micronutrient, so if bee products contain it in a certain concentration range (Pasupuleti et al., 2017) this is beneficial for human health. The concentration of Fe was found to be between 2.98 and 16.2 mg kg^{-1} in honeys from Sindh, Pakistan (Lanjwani and Channa, 2019), 3.51–1279 mg kg^{-1} in Turkish samples (Altunatmaz et al., 2019), 0.52 mg kg^{-1}–7.59 mg kg^{-1} in Brazilian samples from the Lower Amazonian Region, and an average of 1.19 mg kg^{-1} (acacia) and 3.28 mg kg^{-1} (honeydew) was measured in Serbian apicultural products (Spirić et al., 2019), where the latter value is similar to the findings of Pisani et al. (2008) for honeys collected in Siena county, Italy (Pisani et al., 2008). In the Hungarian samples measured in our previous studies the average iron content of the different honey types ranged between 0.594 and 14.65 mg kg^{-1} (Sajtos et al., 2019; Varga et al., 2020b). Decreasing Fe level in sunflower samples originating from the same region over the years can be explained by changes in soil properties, thus might be the result of agricultural depletion of soil nutrients. Iron is essential for proper plant growth and its availability is affected by several physical, chemical and biological properties (Colombo et al., 2014). Some interesting research results suggest the overall nutrient depletion of edible plants due to the atmospheric CO_2 increase. A significant decrease of the Fe level in grasses and legumes was reported with elevated CO_2 concentration (Myers et al., 2014) and more recent research highlights similar findings (Beach et al., 2019; Ujiie et al., 2019). Even pollinator food sources can be affected with reduced protein concentration due to higher atmospheric CO_2 levels (Ziska et al., 2016). However, there is still a lack of data available explaining the biochemical mechanism of this phenomenon in which higher CO_2 emission reduce the nutrient concentration of crops. The increased carbohydrate production called carbohydrate dilution is one reason suggested, yet the mechanism is indicated to be potentially more complex (Mcgrath and Lobell, 2013). One possibility to explain decreasing Fe level in honey samples over time could be the higher atmospheric CO_2 concentration (Dlugokencky et al., 2021; Myers et al., 2014), however, this is only an assumption and much more investigation is required either to confirm or to confront the theory. Nevertheless, old honey samples are strongly suggested to be considered for further analysing this phenomenon as they preserve inorganic materials of older times thus provide a possibility to assess the nutrient status against time.

Bee products available commercially and originating from small holdings must both be free of toxic substances such as metals with known adverse health effects. The Agency for Toxic Substances and Disease Registry (The Agency for Toxic Substances and Disease Registry, 2015) lists Pb among the most unfavourable, as well as the The Joint FAD/WHD Expert Committee on Food Additives (JECFA), which suggested no accepted threshold limit value was tolerable by the human body (World Health Organization, 2011; Altunatmaz et al., 2019). Similarly to our previous study conducted with acacia samples (Varga et al., 2020b). Pb concentration shows a decreasing trend from the older to more recent honeys and sunflower samples collected before the complete prohibition of lead-containing fuel in 1999 shows the highest Pb level. Regardless of the honey type, major pollutants such as the mainly airborne Pb strongly connected to industrial, accidental and vehicular exhaust can be detected and even the expected trend showing reduced emission is preserved in the samples (Smith et al., 2020).

3.2. Radiocarbon analysis of honey samples

In our previous work, we showed the usefulness of radiocarbon dating for acacia honeys using the atmospheric bomb-peak (Varga et al., 2020b). However, in the present study a significant offset was observed in the AMS results of the rape, sunflower and forest honey samples compared to the atmospheric bomb-peak (Figs. 5 and 6). The acidification of pure honey samples, and separate measurement of the protein content of selected samples did not eliminate the offset compared to the atmospheric $^{14}CO_2$ in the given year.

The offset in the radiocarbon data is not consistent and change year by year. There can be many reasons that may have affected the final ^{14}C results:

I. A possible fossil contribution may be the reason of the negative offset, detected in rape honey samples. Most of the samples were collected close to the Mihályi-Répcelak natural CO_2 reservoir system, where industrial CO_2 extraction can be a great fossil CO_2 emitter. However, this cannot explain the positive offset, that was also detected in rape honey samples. Furthermore, a greater than −40‰ shift compared to the background level was detected only close to busy crossroads and highly industrialized areas in Hungary (Varga et al., 2019, 2020c).
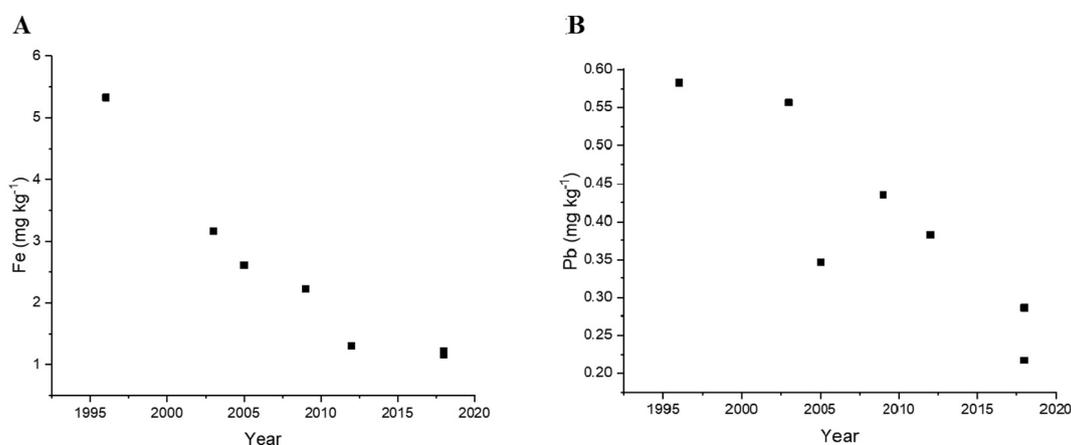
Fig. 4. The Fe (A) and Pb (B) concentration of honeys plotted against the year of origin through the example of sunflower samples from the sampling location of Mesterháza.
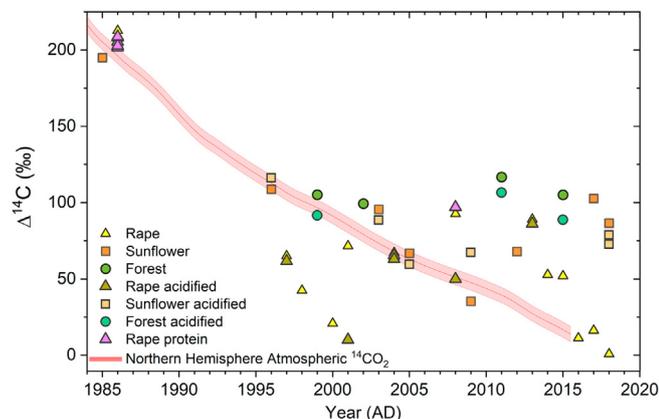
Fig. 5. $\Delta^{14}C$ values of different type honeys.

The observed $-80‰$ offset possibly cannot be explained by the emission from the CO_2 mining industry located more than 10 km from the honey collection area.

II. Volcanic activity also can be a great fossil CO_2 contributor (Cook et al., 2001; Shore et al., 1995), but there is no volcanic activity in the sampling area.

III. Generally, the positive $\Delta^{14}C$ signals can be explained by radioactive carbon emission from nuclear power plants or nuclear facilities. The sampling area is located far from (170 km) the Paks Nuclear Power Plant, Hungary (Molnár et al., 2007; Varga et al., 2020a; Veres, 1995), and also far from the Slovak Nuclear Power Plants and facilities. Based on the sampling location, radiocarbon contribution from nuclear facilities can be assumed to be negligible. C-14 excess in biota, near the Paks Nuclear Power Plant is less than 20 ‰, in a 2 km distance (Janovics et al., 2013).

IV. Biomass burning of bomb-peak labelled trees or materials can emit CO_2 elevated in radiocarbon. However, the more than 80‰ positive offset in the $\Delta^{14}C$ results presumably cannot be explained by wildfires, and the household and heating related biomass burning are also negligible during the spring and summer, when the nectar collection is active.

V. A significant amount of contamination can greatly shift the $\Delta^{14}C$ value of the samples, but the carbon yield after the combustion does not show significant differences between the samples showing offset and no offset (Fig. S1) compared to the expected radiocarbon values. The contamination of the samples and cross-contamination by the preparation line
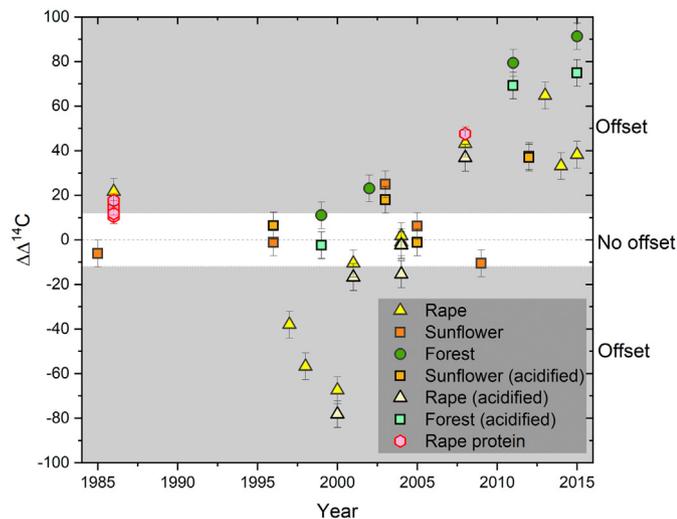

Fig. 6. Deviation from the Northern Hemisphere $\Delta^{14}C$ values. $\Delta\Delta^{14}C$ value expressed by the equation formula (2). No offset interval (light grey) means 2σ error of the ^{14}C AMS measurement.

is also expected to be negligible since it is generally used for archaeological materials and the reference blank material (IAEA-C9) showed a good agreement with the nominal values.

VI. Carbon-containing soil organic and inorganic materials can have quite variable ^{14}C concentration (Becker-Heidmann et al., 2002; Shi et al., 2020; van der Voort et al., 2016; Wang et al., 1996). If the nectar contained soil related materials, that could shift the measured $^{14}C/^{12}C$ ratio as well. However, honeys of different botanical origin and other bee products may utilize different carbon sources such as honeydew that has a wide range of carbon origin with possibly older carbon pools (Pita-Calvo and Vázquez, 2017). The organic material of soil or decomposing organic material can have different ^{14}C content compared to the recent atmospheric $^{14}CO_2$ level, thus inputs from similar, soil related material may affect the radiocarbon content of the recent honeys. Many plants take up carbonaceous compounds from the soil through their roots (Corbineau et al., 2013; Reyerson et al., 2016). Due to the bomb pulse, the shift can be positive or negative by the old soil material as well (Becker-Heidmann et al., 2002; Buró et al., 2019; Graven et al., 2017; Harkness et al., 2016; Novák et al., 2018; Rethemeyer et al., 2005; Santos et al., 2016; Shi et al., 2020; Tóth et al., 2018; van der Voort et al., 2016; Wang et al., 1996). These old components enter the plant xylem with the soil solution, and from here, an apoplastic passive pathway is available toward the nectar glands through the cell walls and the intercellulars. Reed et al. (1971) describe that the active sugar accumulation in floral nectaries is accompanied by a passive water flow, diluting the nectar. Botías et al. (2015) also reported that honey might contain pesticide residues of soil origin as well. At the same time, at a certain part of the day, bees choose to collect the sap of extrafloral nectaries or liquid of hydathodes (Free, 1964; Nicolson, 2009). The connection of extrafloral nectaries and hydathodes to the soil solution transported by the xylem is evident due to the anatomical structure (Nepi, 2007; Roy et al., 2017). Further evidence for this connection is that significant concentrations of neonicotinoid substances have been found in the guttation liquid of plants whose seeds have been coated with these insecticide agents (Girolami et al., 2009; Mörtl et al., 2019; Tapparo et al., 2011).

The qualitative and quantitative composition of soil is also reflected in the chemical features of honey. Baroni et al. (2015) concluded, that elemental and isotopic honey contents are related to soil and water characteristics of the nectar producing region. Thus, we investigated whether those samples where a radiocarbon offset was observed showed alteration in their chemical composition which may reflect soil variability. As indicated in Fig. S2, the concentration of the measured macro- (A) and micro (B) elements is rather invariant which is further shown by statistical analysis: no significant difference was found between the elemental composition of honey samples showing no offset and offset compared to the expected ^{14}C data (Al: $p = 0.124$; B: $p = 0.621$; Ca: $p = 0.458$; Cu: $p = 0.298$; Fe: $p = 0.097$; K: $p = 0.051$; Mg: $p = 0.361$; Mn: $p = 0.865$; Na: $p = 0.301$; Pb: $p = 0.532$; Zn: $p = 0.758$). This phenomenon suggests that AMS ^{14}C data variance is not reflected in the inorganic constituents of honey samples.

FTIR-ATR analysis was used to gain a deeper knowledge regarding the organic material composition of the honey samples. Principle Component Analysis (PCA) was performed on the FTIR spectra. The result can be found in Fig. S3. Each point corresponds to a spectrum, the points were coloured with respect to the AMS offsets. No spontaneous group formation of the points was observed, which means there is no significant spectral differences between the samples with and without AMS offset. Our results indicate that neither the inorganic composition nor the organic constituents show corresponding pattern to the AMS deviation (Fig. S3).

4. Conclusion

Our present study further proves the applicability of old apiarian products as an indicator of long-term changes in environmental factors and

apicultural technologies. The inorganic composition of the investigated rape, sunflower and forest products show a differentiation in correlation with the collecting years providing age-specific information, similarly to the acacia honeys (Varga et al., 2020b). However, a remarkable random off-set was observed in the ^{14}C dating values compared to the radiocarbon bomb-peak, which was unexpected based on the AMS data of the old acacia samples (Varga et al., 2020b), where the atmospheric bomb-peak was well reconstructed from the sample series. This interesting phenomena cannot be related to fossil or nuclear atmospheric emission and contribution due to the distance from these sources of the nectar producing area, but we assume these are the result of soil-related effects. We suggest that bomb-peak ^{14}C labelled soil components can access the nectar via biochemical processes occurring in the nectar producing plants. Our results indicate that substances with non-photosynthetic origin are present in the nectar of the studied annual crops that shift AMS ^{14}C results. Also, as forest honeys are honeydews, they might have a more complex carbon source composition affecting the ^{14}C/^{12}C ratio. Further studies are necessary to gain a deeper understanding of the species-specific relationship between the honey types and AMS dating adaptability of old apiarian products which is a new finding in this work.

CRediT authorship contribution statement

Zsófi Sajtos: Conceptualization, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Tamás Varga**: Conceptualization, Investigation, Data curation, Visualization, Writing – original draft, Writing – review & editing. **Zita Gajdos**: Investigation. **Petra Burik**: Investigation. **Máté Csontos**: Investigation, data curation, methodology. **Zsuzsa Lisztes-Szabó**: Writing – review & editing, conceptualization, investigation. **A.J. Timothy Jull**: Supervision, Writing – review & editing. **Mihály Molnár**: Methodology, Resources, Supervision, Writing review & editing. **Edina Baranyai**: Conceptualization, Resources, Methodology, Visualization, Writing – original draft, Writing – review & editing, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.152044.

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