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Isotopic study of honey documents widespread plant uptake of old carbon in North America

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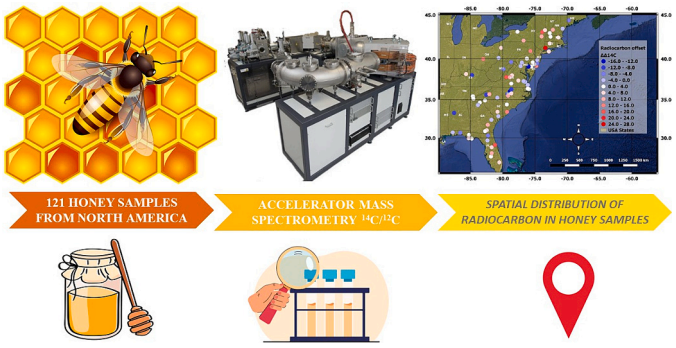
HIGHLIGHTS

- Radiocarbon analysis of honey samples from North America
- Honey shows a mixture of fresh and aged carbon across a large region.
- GIS analysis showed that the ^{14}C offset cannot be attributed to power plants.
- Honey is useful for observing natural plant carbon allocations.
- Radiocarbon ages may be overestimated from soil carbon inputs.

GRAPHICAL ABSTRACT



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ABSTRACT

A comprehensive understanding of carbon cycling pathways in the soil-plant system is needed to develop models that accurately predict global carbon reservoir responses to anthropogenic perturbations. Honey is a carbon-rich natural food produced by wild and managed pollinating insects all over the world; the composition of a single sample is a function of millions of pollinator-plant interactions. We studied the $^{13}C/^{12}C$ and $\Delta^{14}C$ of 121 honey samples sourced from the United States, and found a significant older carbon contribution. The effect is observed

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Radiocarbon
US honey

from 25 to 45° latitude, not correlated with $^{13}C/^{12}C$, and consistent with a previously published study on European honeys. In specific cases, the measured values were up to 20 ‰ ($\Delta^{14}C$) higher than the expected atmospheric $^{14}CO_2$ value for the given year, which shows a significant older carbon contribution. We hypothesize that the older carbon is from plant liquids derived in part from soil carbon or stored nonstructural carbohydrates from plants, which shifts the calibrated age of the sample by 5 years or more. Our work is the first to describe the widespread occurrence of older carbon in honey and shows that radiocarbon measurements can be a powerful tool to trace carbon allocations in terrestrial food webs and detect the atmosphere-soil-plant carbon cycle contributions.

1. Introduction

Plants and soils together hold more than twice the amount of carbon of today's atmosphere, and the amount of carbon cycled between soils and plants annually dwarfs fossil fuel emissions (Friedlingstein et al., 2022). A detailed process-based understanding of soil-plant carbon exchange in terrestrial ecosystems is thus needed to accurately model the global carbon cycle. It's widely known that terrestrial plant acquisition of carbon is largely an above-ground process involving direct atmospheric exchange, but a large body of mostly experimental data shows that plants also draw carbon directly from soils. Irrigation experiments with CO_2 enriched waters demonstrate fixation of inorganic carbon taken through the roots (Enoch and Olesen, 1993; Ford et al., 2007), and isotopic labelling experiments show that phytolith carbon may be fed through the roots (Alexandre et al., 2016). While the mechanisms of soil carbon uptake by plants are known, the significance of soil carbon inputs to the plant's annual carbon budget is not well quantified at the regional scale.

Honey is a naturally produced carbon dense food produced in almost every country of the world by wild and managed bees. A single kilogram of honey is composed of nectar gathered during millions of flower visits typically from an area of <50 km^2 (Grüter and Hayes, 2022; Ribbands, 1951, 1949; Wright et al., 2018). Honey is thus a very powerful environmental sample that integrates information from an incredibly large number of animal pollinator-plant interactions. Several studies have focused on the environmental and biomonitoring potential of honey since its composition does not change over time. Honey preserves the original elemental composition and records environmental information of the harvest period, origin, manufacturing and storage properties (Anklam, 1998; Di Fiore et al., 2023; Kaste et al., 2021; Smith et al., 2020; Taylor, 2019; Zhou et al., 2018). Accordingly, honey captures a fingerprint of biological and chemical conditions from when it was harvested. Due to the specific chemical properties of honey, biological activity does not affect the organic composition of the samples following its collection, so carbonaceous organic compounds can also be investigated as well as the carbon content. Carbon has three natural isotopes, two stable (^{12}C and ^{13}C) and one radioactive - the unstable radiocarbon (^{14}C) isotope with a 5700 $\pm$ 30 years half-life (Kutschera, 2019). Carbon isotope measurements have a long-term tradition in honey research in quality assurance investigations and forensic-related measurements. For example, isotope ratios of $^{13}C/^{12}C$ and $^{14}C/^{12}C$ can be used to investigate honey adulteration and for radiocarbon dating of the carbon-containing materials in honey (Doner and White, 1977; Sajtos et al., 2022; Varga et al., 2020). In contrast, $^{13}C/^{12}C$ isotope ratio is uniquely suited for the investigation of honey dilution of C4-based, low-price sugar syrups, as the sugars produced by C3 and C4 photosynthetic pathways can be separated by their isotopic composition (Doner and White, 1977; Kropf et al., 2010; White and Winters, 1989; Zhou et al., 2018). This method is standardized and can be used as a tool for forensic science studies and also as a quality assurance tool (AOAC, 1995). The radiocarbon and $^{14}C/^{12}C$ ratio measurements are fundamentally known as dating tools for age-determination. Although measurement of the stable carbon isotope composition of honey has a long tradition (Doner and White, 1977; Schellenberg et al., 2010), several studies show that this isotope ratio cannot identify the geographical and botanical origin of the honey samples due to the high global uniformity of values.

To date recent organic materials, the radiocarbon-based "bomb carbon" approach is generally applied (Hua et al., 2022). The elevated atmospheric radiocarbon level, and its constant decline, was caused by atmospheric nuclear weapons testing and continuous exchange of the CO_2 between the atmosphere-ocean and atmosphere-biosphere. The ^{14}C level in atmospheric CO_2 can be used as a natural radiocarbon labelling process, because of the possibility to date biological materials precisely after the peak of this atmospheric radiocarbon level, after 1963 to recent times (Hua et al., 2022). Our previous investigations (Sajtos et al., 2022; Varga et al., 2020), on radiocarbon dating of Hungarian honey samples, showed that radiocarbon ratio had a random offset compared to the expected value, i.e., the known age of the samples. Rape, sunflower and forest or honeydew honeys cannot therefore be accurately dated by ^{14}C analysis, and some samples of black locust honey also showed low offsets. Presumably, some contribution of natural plant-origin fluids, which are collected by the bees (instead of just flower nectar), could shift the $^{14}C/^{12}C$ ratio. These plant fluids have close relationship with soil carbonaceous material and non-structural carbon (NSC) content of the plants (Carbone et al., 2013; Sajtos et al., 2022). The $^{14}C/^{12}C$ ratio of old soil organic matter can be higher or lower than in recent contemporary carbon, depending on whether it was produced before or after the nuclear bomb tests (Becker-Heidmann et al., 2002; Shi et al., 2020; van der Voort et al., 2016; Wang et al., 1996). Depending on the age of the tree or plant, the excreted fluids and their $^{14}C/^{12}C$ ratio can also vary (Carbone et al., 2013; Muhr et al., 2016; Richardson et al., 2015, 2013). For this reason, we have suggested that honey may contain older than recent organic materials, originating from the soil as well as plants (Sajtos et al., 2022; Varga et al., 2020). This phenomenon was not been described previously in terms of quantitative and qualitative parameters, and only our former studies raised the possibility of the old carbon contribution.

Our former studies on EU (Hungarian) samples showed there is a significant non-contemporary carbon contribution in almost all the honey samples. The "old" carbon amount of the contribution appears random and varies honey to honey. In this study, we analysed the contribution of the old carbon in honey samples on a much larger scale than in Sajtos et al. (2022) on another continent, from the eastern part of the USA to verify the previous observations (in the EU) for a contrasting environment and continent. We used modern isotope ratio measurements ($^{13}C/^{12}C$, $^{14}C/^{12}C$) to determine the carbon isotopic composition and radiocarbon age of different US honey samples.

2. Methods

2.1. Samples

121 discrete honey samples were collected from beekeepers between 2010 and 2020 as raw, pure and unfiltered honey by students and researchers of College of William & Mary, Williamsburg, Virginia, USA. There are samples with known botanical origin, but the sample collection contains a significant number of honeys with unknown botanical origin. In the case of geographical origin, only the state and county are known, based on this, the central point of these counties was used in the analysis and maps. The samples were measured for radioactive isotope

^{137}Cs by gamma spectrometry at College of William & Mary within a former study (Kaste et al., 2021). In this international cooperation, the carbon isotopic composition, especially the $^{13}C/^{12}C$ and $^{14}C/^{12}C$ ratios of the bulk honey samples were analysed. The map of the collected samples in the USA is shown in Fig. 1. The detailed list of samples is in the Supplementary material S1 file. The samples were stored and transferred from the USA to Hungary in 15 ml plastic centrifuge tubes packed into a dark box.

2.2. Carbon isotopic composition

Approximately 2–3 mg honey samples were prepared for carbon isotope measurements. The samples were measured into a glass test tube together with ~300 mg MnO_2 powder (Sigma-Aldrich, ≥99 %). Then the test tubes were flame sealed by gas torch under vacuum ($<5*10^{-2}$ mbar). After the sealing, the samples were combusted in a laboratory muffle furnace at 550 °C for 12 h to convert the carbon content of the honey samples to CO_2. Then, the test tubes containing the combusted samples were transferred in a dedicated vacuum line under ($<5*10^{-2}$ mbar) vacuum. The sample gas was purified in this vacuum line using a isopropyl alcohol – dry ice mixture trap (−78 °C) to capture the H_2O from the combusted samples, then the pure CO_2 was collected by a liquid nitrogen (LN) trap (−196 °C). After the purification steps, the volume of the collected CO_2 gas can be determined in a known volume unit using pressure transducer. The sample gas was split, as half of the prepared samples were used for $^{14}C/^{12}C$ ratio measurement, and the other half for $^{13}C/^{12}C$ ratio measurements. The vacuum line used is further described in our former publication Janovics et al. (2018). The samples for

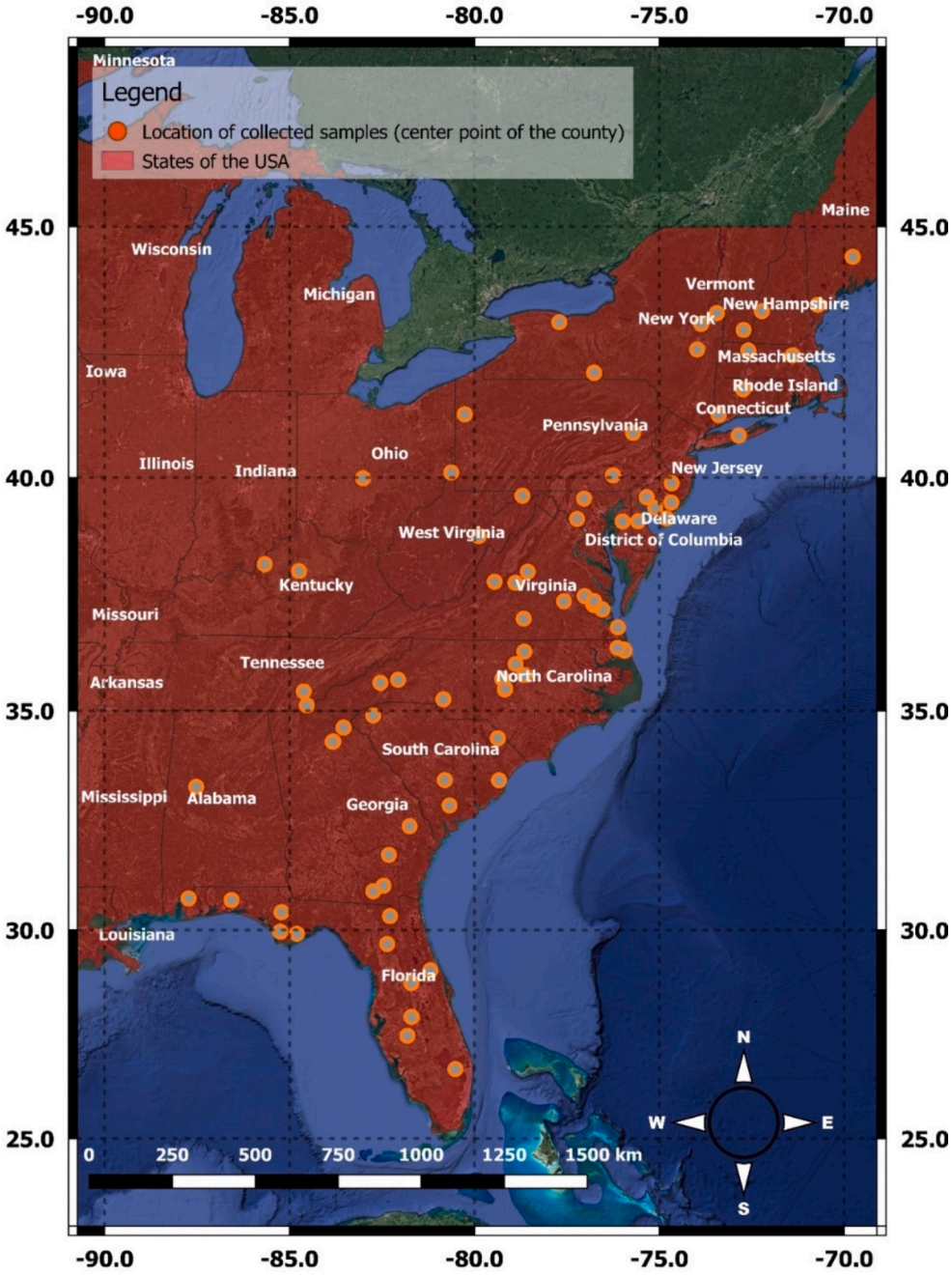

Fig. 1. Map of the collected honey samples in the USA. The coloured symbols show the origin, location of the collected honey samples with county level resolution. The symbols is in the centre point of the county where the honeys where harvested (Kaste et al., 2021).

radiocarbon measurement were graphitized by the sealed tube graphitization method, detailed in Rinyu et al. (2013).

The $^{14}C/^{12}C$ isotope ratio by Accelerator Mass Spectrometry (AMS) and $^{13}C/^{12}C$ isotope ratio by Isotope Ratio Mass Spectrometer (IRMS) were measured in the Institute for Nuclear Research, Debrecen, Hungary at the International Radiocarbon AMS competence and Training Center using a MICADAS type (ETH Zürich) AMS and a Finnigen DELTA^{PLUS} XP (Thermo Fisher Scientific) type IRMS. For the radiocarbon measurements, solid graphite targets were used for the ~1 h long measurement, to gain high-precision results, and for IRMS measurements gas samples were used in Dual Inlet mode, each results represent 8 measurement run's average. The radiocarbon ($^{14}C/^{12}C$) results are expressed in $\Delta^{14}C$ units, the detailed description of these radiocarbon units can be found in the Stenström et al. (2011) and Stuiver and Polach (1977).

$$\Delta^{14}C = \left(\frac{A_{SN}}{A_{ABS}} - 1\right)1000‰ \quad (1)$$

where A_{SN} is the stable isotope normalized specific radiocarbon activity of the samples, and A_{ABS} is the specific activity of the absolute radiocarbon standard (226 Bq/kg carbon).

Stable carbon isotope ($^{13}C/^{12}C$) results are expressed in conventional delta notation, $\delta^{13}C$ values are relative to VPDB standard. Stable carbon isotope ratio of samples was compared to reference materials to avoid systematic errors. The $\delta^{13}C$ values are calculated using the following equation:

$$\delta^{13}C = 1000\frac{R_{sample} - R_{reference}}{R_{Reference}} \quad (2)$$

where Rsample and Rreference are the measured isotope ratio of the sample and isotope ratio of the reference material, respectively. The $\delta^{13}C$ values are expressed against the Vienna Pee Dee Belemnite (VPDB).

The bulk honey isotopic compositions were measured to investigate botanical and geographical differences (Kropf et al., 2010). The AOAC 978.17–1979 standard method was applied to detect honey adulteration with corn-based sugar. Based on this standard method, the higher than −23.5 ‰ ($\delta^{13}C$ vs. PDB) carbon isotopic ratio means >13 % corn-based sugar contribution in the honeys.

Using the measured and calculated $\Delta^{14}C$ values, the difference between the Northern Hemisphere data and the honey samples in a given year ($\Delta\Delta^{14}C$) were calculated by the following formula:

$$\Delta\Delta^{14}C = \Delta^{14}C_S - \Delta^{14}C_{NH} \quad (3)$$

where $\Delta^{14}C_S$ is the $\Delta^{14}C$ value of the sample, $\Delta^{14}C_{NH}$ is the $\Delta^{14}C$ value of the Northern Hemisphere (Hua et al., 2022) for the given year when the honey sample was collected. Although Hua et al., 2022 distinguish different zones for the Northern Hemisphere, there is no observable difference in the different zones in recent times, so the NHZone2 dataset can be used for the calculation.

A simple model was applied to demonstrate how significant, macroscopic amount of "old" component is needed to shift the expected, recent ^{14}C level to the observed results of the honey samples. We assumed that only one half is made from recent carbon in the honey (from the year of harvest, "r") and the other half is from a somewhat older carbon pool. We have varied the turnover time of the "older" pool such way, that its average carbon $\Delta^{14}C$ level corresponds to an apparent age (^{x}): for example, for 5, 10, 20, 30, 40, 50, 60 years old natural/biogenic carbon. The final, combined ^{14}C value of the modelled honey sample would be calculated as a simple mean $^{h}\Delta^{14}C$ of the recent carbon ($^{r}\Delta^{14}C$) and the carbon from the "x year old pool" ($^{x}\Delta^{14}C$).

$$^{h}\Delta^{14}C = \frac{^{x}\Delta^{14}C + {}^{r}\Delta^{14}C}{2} \quad (4)$$

where "^{h}" means the corresponding apparent age (^{x}) used as old natural/biogenic carbon. This approach of estimating that only half of the honey is made up of recent carbon is only a theoretical approach. In this way we can visualise the time dependence of different aged carbons over time. In nature, different proportions of mixtures can be found. Recognizing the natural variability in carbon sources, we calculated the ±10 % of the weighted average of the "h" fraction contribution. This measure reflects the potential variability and provides a practical means to present the sensitivity of our results. The bomb-peak effect causes a positive offset, but the effect of older carbon than the bomb-peak, such as the soil-related contribution, would cause a negative offset.

2.3. Role of environmental factors

We also studied if the $\delta^{13}C$ and offset values were influenced by environmental factors. Accordingly, we involved the following variables: precipitation (prec), minimum temperature (tmin) and maximum temperature (tmax) of the mean and cumulated values of the period of harvesting and preceding 3 months; elevation (elev) data from the SRTM digital surface model (NASA JPL, 2013); furthermore, the absolute location of honey collection sites (lat/lon) and their distances from the sea/ocean (d_coast) were also determined from Natural Earth data coastline database (Natural Earth Data, 2023). Distances of collection sites from nuclear power plants (NPP) and fossil fuels power plants (FPP) were also determined using the ArcGIS dataset of Power Plants in the U. S, utilizing the data from the Energy Information Administration (EIA, 2023). Forest and rangeland fractions of a 10 and 50 km buffer around the samples had been determined as a ratio of the area (ha) and the area of buffer zones (tree_10, tree 50, rl_10, rl_50), as well as the forest/rangeland ratio within each buffer zone (ratio_10 and ratio_50) (ArcGIS Living Atlas of the World, 2022). Regression modelling was performed with $\delta^{13}C$ stable isotope ratio and $\Delta\Delta^{14}C$ offset values and with the environmental factors as independent variables (year of extraction, d_coast, tmin_mean, tmin_sum, tmax_min, tmax_sum, prec_mean, prec_sum, elev, lat, lon, FPP, NPP, tree_10, tree_50, rl_10, rl_50, ratio_10, ratio_50). We applied a linear (General Linear Model, GLM), and several robust (Support Vector Regression, SVR; Multiple Adaptive Regression Splines, MARS; Random Forest Regression, RFR) models. GLM has assumptions on the normal distribution, linearity, and homoscedasticity, while the robust models' results do not depend on these assumptions. All models were determined with 5-fold cross-validation with 10 repetitions; accordingly, we had 50 model runs and had 50 R^2 and root mean square errors (RMSEs) to evaluate model performance. Variable importance was also determined for the model of the best accuracy. Modelling was conducted with the R 4.3.1 (Team, 2023) with the caret (Kuhn, 2008), rpart (Terry et al., 2023), earth (Milborrow, 2023) and the e1071 (Meyer et al., 2023) packages.

3. Results

All of the measured data ($\delta^{13}C$ and $^{14}C/^{12}C$ results) can be found in the Supplementary S1 file. Using $^{13}C/^{12}C$ ratio analyses and the AOAC 978.17–1979 standard method, we were able to detect 10 adulterated honey from the 121 samples. In those cases, a carbon isotopic ratio higher than −23.5 ‰ ($\delta^{13}C$ vs. PDB) was observed, which means >13 % corn based sugar contribution in the honeys (Fig. 2). The measured $\delta^{13}C$ values ranged from −27.99 ‰ to −23.78 ‰, excluding the adulterated honeys, while the lowest value was detected in a Tupelo (Nyssa sp. L. from 2018) honey sample, while the highest value in the unadulterated samples occurred in honey of an unknown botanical origin from 2012.

The radiocarbon results varied from −10.0 ± 1.8 to 32.1 ± 2.3 ‰ ($\Delta^{14}C$) (Fig. 3 and Supplementary material S1). The lowest $\Delta^{14}C$ value was measured in a Blackberry/holly honey from 2018, and the highest was measured in an unknown botanical origin honey from 2010 from North Carolina and Virginia, respectively.

The results in Fig. 3b shows that the distribution of measured radiocarbon compared to the expected value (offset, $\Delta\Delta^{14}C$) completely differs from the expected normal distribution, the measured distribution

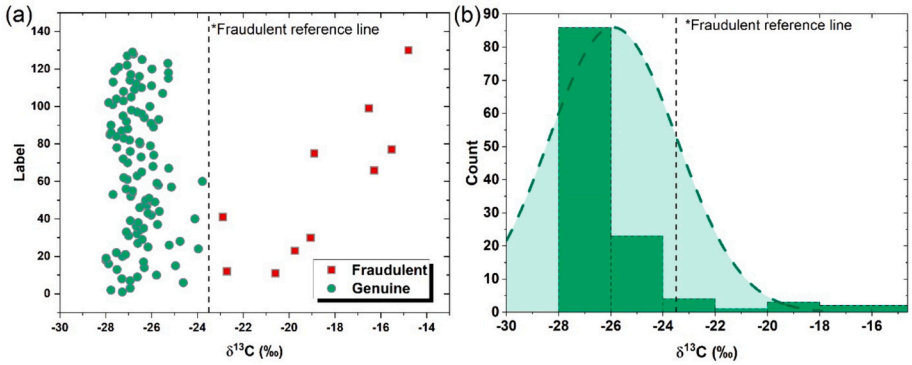

Fig. 2. Stable carbon isotope composition of honey samples in the eastern part of the USA (a) and the distribution of the measured stable carbon isotope data (b) (dashed line: reference value of adulteration with >13 % corn-based sugar; >−23.5 ‰ ($\delta^{13}C$) indicates adulterated honey).

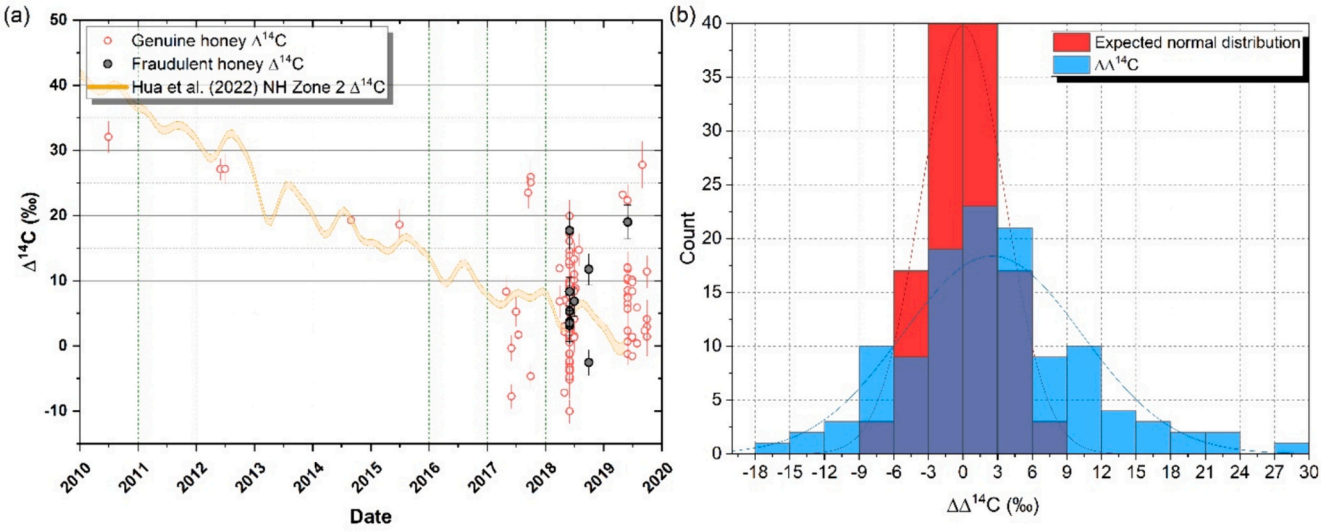

Fig. 3. Raw radiocarbon AMS results of honey samples from the USA (A) and the distribution of radiocarbon offset compared to the expected reference value from Hua et al. (2022) (b). The last available global background $^{14}C/^{12}C$ data is from early 2019, 0.01 ± 0.83 ‰ ($\Delta^{14}C$). The reference value in Hua et al. (2022) is continuously decreasing due to the ocean-atmosphere and biosphere-atmosphere CO_2 exchange and fossil CO_2 emission. The red bars show the expected normal distribution, and the blue bars show the distribution of $\Delta^{14}C$ offset compared to the expected reference value from Hua et al. (2022) (b).

is much flatter, and shows significant offsets, with higher than 3σ measurement error differences. This suggests that in several samples, there is a high older carbon contribution, which affects the measured $^{14}C/^{12}C$ ratio. The distribution of $\Delta\Delta^{14}C$ is flatter than the normal distribution (Fig. 3), indicating generally older, but not older carbon contribution than the ^{14}C bomb-peak effect. The negative part of the distribution can be attributed to older carbon than the ^{14}C bomb-peak effect or fossil contribution. In our previous study (Sajtos et al., 2022) we were also able to detect offset before 2017, but in our current study we do not have a statistically sufficient number of samples to analyse before that year, but a sample from 2010 also has negative offset (−7.3 $\Delta\Delta^{14}C$). To further analyse this time period, we would collect more old honey samples.

4. Discussion

The spatial distribution of honey $\delta^{13}C$ results does not show any strong geographical pattern, only a lower $\delta^{13}C$ section is visible in the north, near to the Canadian border: 9 samples were below −27.05 ‰ stable carbon isotope signature (Fig. 4). These lower $\delta^{13}C$ values can be the consequence of geographical origin, as higher latitudes may affect the stable isotope signature (Körner et al., 1991) or may also be caused by the canopy effect in denser forested areas (Bonafini et al., 2013; van der Merwe and Medina, 1991). Similar geographical effects, with lower $\delta^{13}C$ values at higher latitudes, was observed by Schellenberg et al. (2010). Körner et al. (1991) also found that at higher latitudes the lower temperature and less sunshine cause lower $\delta^{13}C$ signature in plant materials. In addition, we did not identify other $\delta^{13}C$ hotspots with higher or lower signatures, the distribution had generally inhomogeneous random spatial pattern or was uniform within a greater range. The spatial distribution of adulteration was not concentrated, and we did not detect any adulterated honey at the northern part of the USA (Fig. 4). In this study, we specifically avoided adulterated honeys by obtaining samples directly through small producers. Although the statistical distribution of $\delta^{13}C$ was slightly elongated to higher values due to the adulterated honeys, most samples varied between −28 and − 26 ‰ and are generally comparable to recent studies, even with European and Asian honey $\delta^{13}C$ values (Cinar et al., 2014; Dong et al., 2016; Schellenberg et al., 2010; Zhou et al., 2018) supporting the observation that the stable isotope composition of honeys is uniform. We did not detect honey with exceptionally diluted $\delta^{13}C$ that would be <−30 ‰.

No correlation was observed between the $\delta^{13}C$ and $\Delta^{14}C$ offset values ($\Delta\Delta^{14}C$). As $\delta^{13}C$ values vary from plant to plant and are influenced by many environmental factors (such as local meteorological and soil conditions), comparison with other parameters such as $\Delta\Delta^{14}C$ values is biased. Furthermore, the older carbonaceous materials may have similar

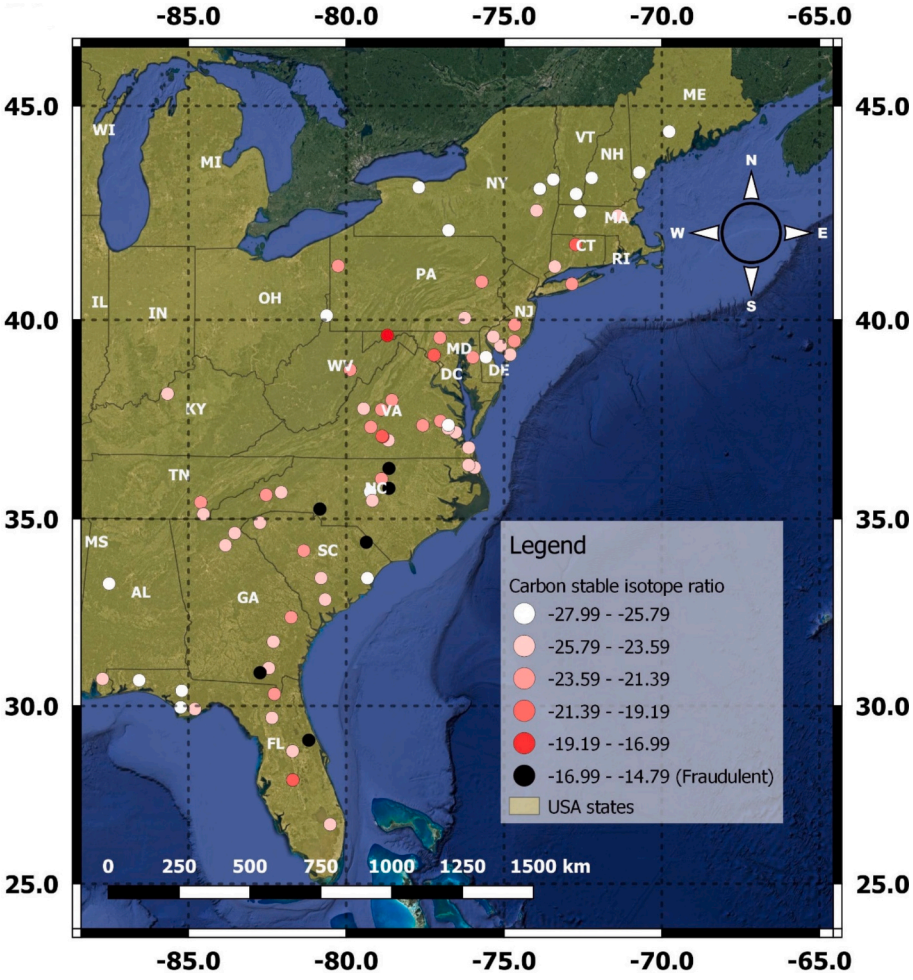

Fig. 4. Spatial distribution of honey $\delta^{13}C$ results. The coloured symbols show the distribution of honey $\delta^{13}C$ values over the Eastern USA region, the black symbols show the location (county) of the adulterated honey samples.

$\delta^{13}C$ values, which does not shift the measured $\delta^{13}C$ values in the honey samples, but shifts the radiocarbon age.

AMS radiocarbon results showed that the $^{14}C/^{12}C$ isotope ratio of numerous samples were different from the expected atmospheric $^{14}CO_2$ values in a much greater region on the eastern part of the USA compared to our previous study (Sajtos et al., 2022), which was specific to a smaller particular area, only a few km^2. The analysis supports our previous findings (in Hungary): contemporary US honey samples also often contain notable quantities of older carbonaceous compounds, characterized by considerably distinct $^{14}C/^{12}C$ ratios. The divergence was not limited to minor proportions but extended to substantial quantities, as a trace-level molecular contribution would be insufficient to result in such a significant shift in the measured ^{14}C value. Both positive and negative offsets can be explained by a soil-originated carbon contribution, as soil organic matter has integrated carbon form the environment before and after the ^{14}C bomb-peak. Other types of possible "unusual" isotope contributions such as nuclear or fossil emission cannot be considered as realistic single/major sources of the observed two-direction (positive and negative) effect, as these emissions would shift the $^{14}C/^{12}C$ results only in one, specific direction (positive if it is a nuclear origin, or negative if it is fossil). Although we found 10 adulterated honey out of the 132 measured samples, the results showed that the corn based sugar addition cannot be the reason for the detected ^{14}C offsets, even for those samples. There was insignificant difference between the calculated $\Delta^{14}C$ offset of genuine and adulterated honeys, but only three adulterated honeys showed more than 3σ difference compared to the expected value. Adulteration with decades-old sugars is theoretically possible but in reality, it is very unlikely as the likelihood of storing sugar for decades is very low. Based on these results, in certain cases the bulk honey contains significant amount of older carbonaceous substances, even more than a few percent, but these are certainly not trace amounts.

The carbon content of certain honeys can be considered to be a 50–50 % mixture of recent and 10 years old carbonaceous substances, although a lower but older contribution is possible, in periods of higher $^{14}C/^{12}C$ ratio due to the atmospheric bomb-peak (Fig. 5). It could be a contribution of carbon with an age of several decades or longer, perhaps over 100 years as well. If this carbon originates from the soil, in the form of aqueous or organic solvent solutions, it can contain various type of materials, molecules, such as hormones, sugars, pesticides etc. Many studies have proven that honey is complex – and while many studies focused on the elemental composition, trace element concentrations and molecular or stable isotope composition, none of them considered the age distribution of carbonaceous materials prior to our previous studies (Bovo et al., 2020; Goretti et al., 2020; Schellenberg et al., 2010; Zhou et al., 2018). Our results showed that recently-harvested honey was not as fresh as we expected: the (radiocarbon) age of freshly extracted honey may be over 1–2 years, even 5 years instead of the time of collection. The samples no. 7, 30, 81 and 123 (from 2019 and 2020) showed more than a 5 years offset based on the calibrated date, using OxCal 4.4 online software (Bronk Ramsey, 2009). These results, along with the studies we reported in Sajtos et al. (2022) and Varga et al. (2020) show that the radiocarbon bomb-calibration does not work for honey samples, as there is a significant offset in the calibrated ages. As this is a bulk age, i.e., a mixed age of different carbonaceous materials which may contain much

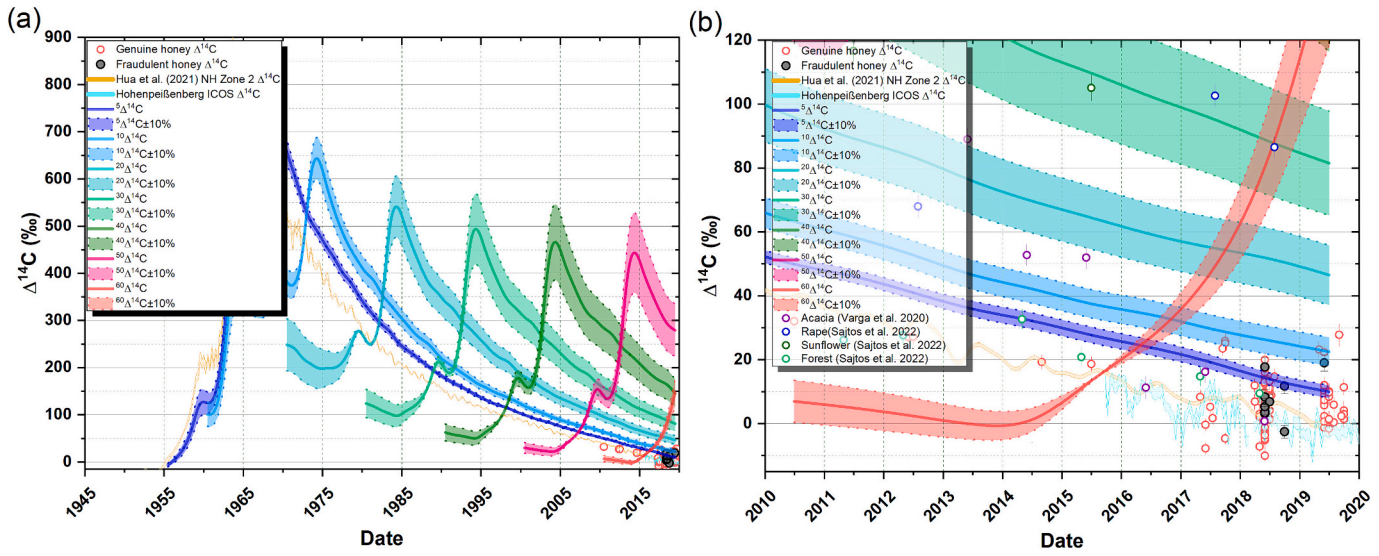

Fig. 5. Measured and modelled Radiocarbon ($^{14}C/^{12}C$) results of American and Hungarian honeys. The yellow and cyan colour bands show the reference curves, monthly expected value from Hua et al. (2022) and Kubistin et al. (2023). The coloured lines show modelled $^{h}\Delta^{14}C$ (x) value curves, when 50 % of the blend is always the $^{14}C/^{12}C$ ratio of fresh, photosynthetic-based carbon (in the given year), and the other 50 % is from 5, 10, 20, 30, 40, 50 and 60 years (x) before. The coloured shaded areas show the ±10 % contribution of the "h" fraction.

older and also recent, fresh materials with zero age in a greater quantity, older components can significantly alter the radiocarbon age. Soil is one of the most complex environmental systems with various composition of carbonaceous materials, older-age components can have a wide range of molecular composition.

The observed generally positive offset in radiocarbon values could be attributed to contributions from honeydew and other plant-derived liquids (Mörtl et al., 2019; Sajtos et al., 2022). Honeydew is a specific type of honey that originates from solutions derived from living parts of plants as well as excretions of aphids and other insects (Ciursă et al., 2021). These plant secretions can contain materials that are several years old, such as non-structural carbohydrates NSC (Carbone et al., 2013; Muhr et al., 2016; Richardson et al., 2015, 2013), which have the potential to alter the radiocarbon ratio present in the honey. For example, bees may collect sap from maple trees which can contain NSC even older than 15 years (Carbone et al., 2013; Jerković et al., 2010; Siddiqui, 1970), resulting in a significantly enriched radiocarbon signature.

Given that various tree species capable of exuding similar liquids are common in the USA, this contribution could be more significant in combination with guttation liquid and extrafloral nectar from annual agricultural plants than previously thought. These contributions are not accounted for in pollen counting and analysis since these liquids typically lack pollen due to their non-floral origin. However, they do contribute sugars and other elements to honey affecting its composition. The $\delta^{13}C$ values could also reflect the C3 plant signatures since they may originate from the same plant or plant community. Even if this contribution is related to soil processes, reflecting local plant $\delta^{13}C$ signatures akin to local nectar-producing plants, it would not be detectable by $\delta^{13}C$ analysis. Furthermore, adulteration using maple syrup would not be distinguishable using the IRMS $\delta^{13}C$ method, as this carbon stable isotope signal falls within the range of C3 sugars and plant-based materials (Tremblay and Paquin, 2007). While the syrup can contain much older carbon, as demonstrated by Carbone et al. (2013), the likelihood of adulteration with maple syrup is low due to the comparable prices of honey and maple syrup. In Hungary, as observed in our prior study, maple syrup is not readily available on an industrial scale and is primarily found in the market; nevertheless, a similar $\Delta^{14}C$ offset was detected. Our earlier investigations (Sajtos et al., 2022; Varga et al., 2020) revealed substantial offsets in measurements of rape, sunflower and forest honeys, where in forest honey even ~100 ‰ ($\Delta^{14}C$) offset was detected, corresponding to a turnover time of around 30 years. This turnover time is significantly longer than what we observed here in the honeys from the USA. The US honeys exhibit offset patterns similar to those observed in Hungarian black locust honeys, displaying only moderated differences compared to the expected value and other honeys.

A negative offset can be caused by the local fossil load (Fig. 6.). As Hsueh et al. (2007) observed previously, there is a strong fossil carbon emission at the eastern USA that can be detected in the negative shift of the $^{14}C/^{12}C$ ratio in case of annual plants due to the strong, radiocarbon free, fossil CO_2 emission by traffic and industry. In several samples, we could detect negative offsets which have similar pattern to that observed by Hsueh et al. (2007). However, while Hsueh et al. (2007) found strong fossil contribution at the north-eastern and south-eastern region as well, we experienced strong positive offsets, $^{14}C/^{12}C$ enriched signatures in honey samples from these regions. The spatial distribution of the offsets seems to be random, but a group of samples at the north-eastern region showed a positive offset. The negative offset can clearly be explained by the soil carbon contribution, as soil organic matter can be extremely old compared to the recent atmospheric $^{14}CO_2$ value. Several previous studies have shown that soil carbon can be transferred to nectar through plant fluids, such as extrafloral nectars and guttation fluids.

The USA has extensive nuclear power industry, which is strongly concentrated in the eastern region of the country. The ^{14}C emission from nuclear power plants could affect the plants' $^{14}C/^{12}C$ ratio due to the photosynthesis, if these power plants emit $^{14}CO_2$. Although there are several nuclear power plants around the sample locations, we did not find any reasonable correlation between the detected positive offsets and the distance from the nearest nuclear power plants (Fig. 6a and b). The detected positive offsets are not related to the nuclear emissions. Hsueh et al. (2007) also did not find strong, enriched $^{14}C/^{12}C$ signals at these regions in annual maize plants; however, Stenström et al. (1998) observed a comparable $^{14}C/^{12}C$ increase in tree rings around Swedish nuclear power plants, but quite close, in a ~ 3 km vicinity of these objects. Nevertheless, bees cover a larger area during the nectar collecting period, so the chance to collect all of the honey sources in the prevailing wind direction around a nuclear power plant is quite low.

While anthropogenic nuclear emissions do not account for the observed negative offsets, the significant anthropogenic fossil CO_2

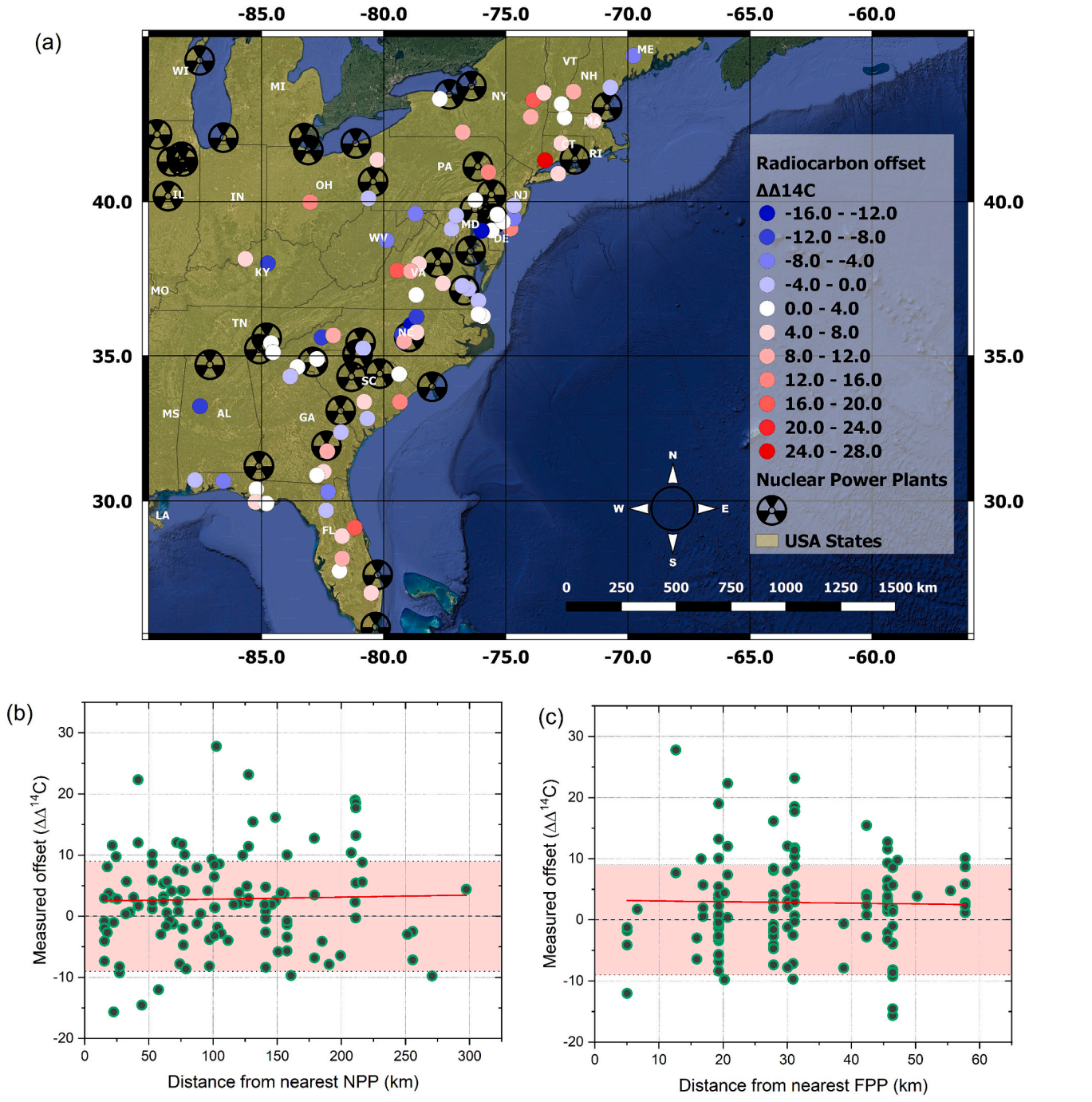

Fig. 6. Observed radiocarbon offset ($\Delta\Delta^{14}C$). Spatial distribution of honey radiocarbon ($^{14}C/^{12}C$) offset compared to the expected value ($\Delta\Delta^{14}C$) at Eastern USA (a). The symbols show the difference compared to the expected value based on the honey collecting season and associated atmospheric radiocarbon data from Hua et al. (2022). Measured radiocarbon offset versus distance from the nearest Nuclear Power Plant (NPP) (b). Measured radiocarbon offset versus distance from the nearest Fossil-based (coal, petroleum and natural gas) power plant (NPP) (c).

emission prevalent in the region can indeed induce negative offset: Hsueh et al. (2007) even reported a more pronounced fossil contribution than our findings. While we did not establish a strong correlation between the nearest fossil-fuel power plants and the measured negative radiocarbon offsets, it is worth noting that these power plants are not the sole sources of emission. Vehicular traffic, which also emits considerable amount of fossil CO_2 may impact of other sources, such as natural emissions of old carbon from plants and soil, through the dilution effect of fossil, radiocarbon-free CO_2.

Modelling with the environmental factors showed that the involved variables did not have large influence on the offset or $\delta^{13}C$ values measured in the honey, with median R^2s of 0.19 (RFR algorithm) and 0.17 (SVR algorithm), respectively, determined from the 50 models calculated (Fig. S1). We then ran models keeping only the variables having at least 50 % contribution (Fig. S2, lat, lon, year of extraction, d_coast, prec_mean, prec_sum, ratio_10) to the RFR, as the best algorithm

of the offset was repeated and provided 5 % better result with 0.23 lower RMSE (i.e., 0.24 and 6.83) related to the median. Furthermore, for $\delta^{13}C$, the new model (with lon and tmax_mean) did not perform better, the R^2 was 0.16, and the RMSE was slightly higher (2.23 related the previous 2.21). Although the models provided 19–20 % of the explained variance, these results did not reflect that the environmental variables were well-correlated with either the offset or $\delta^{13}C$ or the offset, signifying that the explanations should be found with other predictors.

Our findings here together with Sajtos et al., 2022 demonstrate that the uptake of soil carbon by plants is widespread in nature and reveals the global significance of soil-to-plant carbon transfers. The allocation, consumption and/or oxidation of plant-produced nectar is a previously unquantified pathway for aged soil carbon loss (Hensgens et al., 2021). Moreover, this process may impact ^{14}C-dating of plant fragments or materials and could explain discordant results (Soter, 2011). The introduction of soil derived elements into honey may impact the honey's broader composition, including its mineral and organic content, while potentially elevating the risk of contamination. As demonstrated in multiple studies, guttation liquids and specific types of plant fluids might harbour pesticides that are detrimental to honey bees and other insect communities (Calvo-Agudo et al., 2022; Mörtl et al., 2019; Saleem et al., 2020). The outcomes presented herein represent the first results with broad spatial coverage, highlighting the presence of significant aged carbon allocation and contributions beyond the smaller and spatially more specific Hungarian observations reported previously (Sajtos et al., 2022; Varga et al., 2020). The presence of carbon contributions from decades ago regardless of their origin, raises noteworthy considerations for the global food supply given that the inclusion of aged materials in fresh food items could potentially raise concerns about food safety. Conversely, the introduction of old carbon stemming from soil or plant fluids might be influenced by anthropogenic activities that stress ecosystems. Although the introduction of this aged carbon increases the radiocarbon concentration of honey, it does not give rise to health concerns. The increase is only discernible through mass spectrometry methods, with no significant impact from a radiological health point of view on the specific radiocarbon activity concentration of honey (in Bq/kg).

5. Conclusions

The study demonstrates the applicability of honey samples as environmental indicators and highlights the role of nectar and honey materials in the biogeochemical cycle. The presented honey radiocarbon dataset, based on over 100 samples from the US, shows a significant contribution of old carbon. This phenomenon is not limited to an isolated European site, as previously presented in our former studies, but is widespread across two continents. The study demonstrates the diversity of the carbon pool in honey, with some samples containing up to 50 % carbon that is over 5 years older. This indicates that plants allocate both fresh and old carbon to produce nectar. The results provide valuable insight into the production of nectar and the carbon allocation process. A jar of honey represents the work of millions of flowers and bees across a wide region. The carbon contribution observed in the honeys, which is more than a few years old and was revealed by accelerator mass spectrometry-based $^{14}C/^{12}C$ analysis, can be attributed to stored non-structural carbon from trees or extrafloral nectars and guttation liquids in annual plants. Our GIS and statistical analysis showed that the positive or negative offset cannot be attributed to emissions from nuclear or fossil-based power plants. The presented results demonstrate the diverse role of plant liquids, particularly honey as a bee product, in the complex biogeochemical cycle. They also highlight how easily soil-based organic materials or aged plant liquids can enter the food chain unnoticed.

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CRediT authorship contribution statement

Tamás Varga: Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Zsófi Sajtos:** Writing – original draft, Investigation, Formal analysis. **Edina Baranyai:** Writing – original draft, Formal analysis. **Zsuzsa Lisztes-Szabó:** Investigation, Formal analysis. **Ágota Ragyák:** Writing – original draft, Investigation, Formal analysis. **Mihály Molnár:** Writing – original draft, Supervision, Methodology, Investigation, Funding acquisition, Conceptualization. **A.J. Timothy Jull:** Writing – original draft, Supervision. **Szilárd Szabó:** Writing – original draft, Investigation, Formal analysis, Conceptualization. **Krisztina Hajduné Kosdi:** Methodology, Investigation. **István Futó:** Methodology, Investigation. **James M. Kaste:** Writing – original draft, Supervision, Formal analysis, Data curation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Zsuzsa Lisztes-Szabó reports financial support was provided by Ministry for Culture and Innovation, Hungary. Edina Baranyai reports financial support was provided by Ministry for Culture and Innovation, Hungary. Ágota Ragyak reports financial support was provided by Ministry for Culture and Innovation, Hungary. Zsófi Sajtos reports financial support was provided by Ministry for Culture and Innovation, Hungary. Mihály Molnár reports financial support was provided by National Research, Development and Innovation Fund of Hungary. Szilárd Szabó reports financial support was provided by Széchenyi Plan Plus program. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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