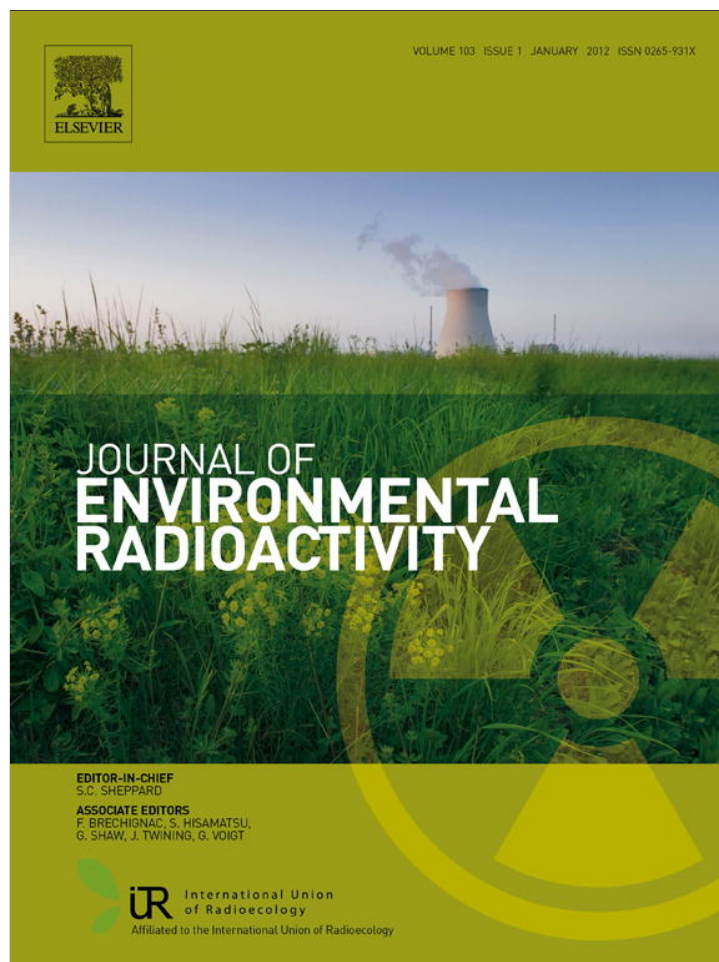


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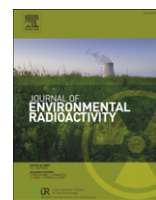
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journal homepage: www.elsevier.com/locate/jenvradCarbon isotopic composition ($\delta^{13}\text{C}$ and ^{14}C activity) of plant samples in the vicinity of the Slovene nuclear power plantMartina Šturm^a, Polona Vreča^{a,*}, Ines Krajcar Bronić^b^a Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia^b Rudjer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia

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ABSTRACT

$\delta^{13}\text{C}$ values of various plants (apples, wheat, and maize) collected in the vicinity of the Krško Nuclear Power Plant (Slovenia) during 2008 and 2009 were determined. By measuring dried samples and their carbonized counterparts we showed that no significant isotopic fractionation occurs during the carbonization phase of the sample preparation process in the laboratory. The measured $\delta^{13}\text{C}$ values of the plants were used for $\delta^{13}\text{C}$ correction of their measured ^{14}C activities.

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1. Introduction

Carbon-14 (^{14}C) is a radionuclide which is produced not only naturally by cosmic ray nuclear reactions in the atmosphere, but also by anthropogenic activities, mainly by nuclear weapon testing and by nuclear power plants. Because of the biological importance of carbon and the long half-life of ^{14}C , it is of interest to measure the releases of ^{14}C and its incorporation into living material in the vicinity of the power plants (Stenström et al., 1996).

The main pathway by which ^{14}C together with stable carbon isotopes (^{13}C and ^{12}C) is incorporated into plants is via the leaf, by photosynthesis of carbon isotopes contained within atmospheric CO_2 (Roussel-Debet et al., 2006). In studies that include plants it is necessary to consider natural isotopic fractionation that occurs during photosynthesis. While the three C isotopes are chemically indistinguishable, lighter ^{12}C atoms are preferentially taken up before the ^{13}C atoms in biological pathways. Similarly, ^{13}C atoms are taken up before ^{14}C . The fractionation of ^{14}C relative to ^{12}C is twice that of ^{13}C , reflecting the difference in mass (Craig, 1954). Consequently, the $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ ratios are lower in plant tissue than in atmospheric CO_2 , whose stable isotopic composition ($\delta^{13}\text{C}$) is

roughly -8‰ (Roussel-Debet et al., 2006 and references therein). Isotopic discrimination varies among various species and C3, C4 and CAM plants can be distinguished, based on their individual photosynthetic reactions (Hoefs, 1997; Waller and Mewis, 1979). $\delta^{13}\text{C}$ values of C3 plants (most plants of temperate and cold environments) vary between -24‰ and -34‰ , with an average of -27‰ , whereas $\delta^{13}\text{C}$ values of C4 plants (e.g. tropical grasses, maize, sugar cane) vary between -6‰ and -19‰ , with an average of -12‰ . $\delta^{13}\text{C}$ values of CAM plants (Crassulacean acid metabolism, e.g. cacti) are intermediate between those of C3 and C4 plants, since they use both C3 and C4 photosynthesis pathways and vary between -23‰ and -12‰ , with an average of -17‰ . Such variations in carbon isotopic composition are not related to time and radioactive decay and should be taken into account when reporting results of radiocarbon measurements (Stuiver and Polach, 1977).

Measurements of ^{14}C activity are reported according to the following conventions (Stuiver and Polach, 1977):

- 1) NIST Oxalic Acid I or Oxalic Acid II are used as modern radiocarbon standards,
- 2) Correction for sample isotope fractionation by using $\delta^{13}\text{C}$ of a sample should be performed and the results are normalized to a value of $\delta^{13}\text{C} = -25\text{‰}$ VPDB (defined by convention),
- 3) The so-called conventional age is calculated by using the conventional half-life of 5568 years, and

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- 4) Conventional ^{14}C ages are reported in years BP (Before Present) with the use of 1950 AD as a reference year (1950 AD = 0 BP).

Therefore, the normalized (or $\delta^{13}\text{C}$ -corrected) ^{14}C activity is given as:

$$A_{\text{SN}} = A_{\text{S}} \left\{ 1 - \frac{2(\delta^{13}\text{C}_{\text{S}} + 25)}{1000} \right\} \quad (1)$$

where A_{SN} denotes specific ^{14}C activity in the sample normalised to $\delta^{13}\text{C} = -25\text{‰}$ VPDB; A_{S} denotes non-corrected specific activity in the sample recalculated to the reference year; $\delta^{13}\text{C}_{\text{S}}$ denotes $^{13}\text{C}/^{12}\text{C}$ ratio of the sample with reference to international VPDB standard. The value 2 in Eq. (1) represents the fact that ^{14}C to ^{12}C discrimination is approximately twice the ^{13}C to ^{12}C discrimination.

When reporting ^{14}C results, it is therefore also recommended to report $\delta^{13}\text{C}$ values, either measured or estimated (Stuiver and Polach, 1977). If the laboratory cannot provide $\delta^{13}\text{C}$ measurements, $\delta^{13}\text{C}$ values recommended in the literature for different substances (e.g. Stuiver and Polach, 1977) are used for the correction.

In environmental applications the relative specific ^{14}C activity ($a^{14}\text{C}$) is usually expressed as:

$$a^{14}\text{C} = A_{\text{SN}}/A_0 \times 100\% \quad (2)$$

where A_0 denotes the equilibrium atmospheric specific ^{14}C activity before anthropogenic influences ($A_0 = 226 \text{ Bq kg}^{-1} \text{ C}$). The relative specific ^{14}C activity is expressed in unit pMC (percent of modern carbon) and from the definition it follows $100 \text{ pMC} = 226 \text{ Bq kg}^{-1} \text{ C}$. Later in this paper we use the term " ^{14}C activity" for the relative specific activity ($a^{14}\text{C}$).

In addition to natural fractionation, isotopic fractionation can occur also during sample preparation in the laboratory (e.g. during carbonization) due to incomplete reactions. As summarized by Krull et al. (2003), results from experimental studies dealing with the isotopic fractionation during carbonization are contradictory. A slight decrease in $\delta^{13}\text{C}$, usually by no more than 2‰ but occasionally up to 3‰ at 275 °C, was observed by DeNiro and Hastorf (1985), while a 1.6‰ decrease at 600 °C and 1–1.4‰ decrease at 300 °C was reported by Turney et al. (2006) and Bird and Ascough (2012), respectively. No significant isotopic change after equilibration at 180 °C was observed by Schleser et al. (1999) and a 1–2‰ increase at <700 °C is reported by Poole et al. (2002) and Turekian et al. (1998). In addition, some authors report different behavior of various vegetation types (Das et al., 2010; Turekian et al., 1998; Czimczik et al., 2002).

To estimate the possible influence of the nuclear power plant on environmental ^{14}C activities and the possible contribution to the effective dose of the local population through the food chain, monitoring of ^{14}C activity in atmospheric CO_2 and in biological samples in the close vicinity of the Slovene Nuclear Power Plant at Krško has been performed regularly since 2006 by the Rudjer Bošković Institute (Krajcar Bronić et al., 2009, 2010; Obelić et al., 2010). However, this laboratory cannot perform $\delta^{13}\text{C}$ measurements so $\delta^{13}\text{C}$ correction of ^{14}C activity was performed in the past using literature values (i.e. -25‰ for C3 and -10‰ for C4 plants, respectively).

The aim of our study was therefore to analyse selected C3 and C4 plant samples collected in the vicinity of the Krško Nuclear Power Plant in order to (1) determine their actual $\delta^{13}\text{C}$ values to be used for correction of ^{14}C activity of the samples, (2) investigate potential isotopic fractionation which might occur during the sample carbonization process (pyrolysis), by analysing dried and carbonized counterparts of the plant samples, and (3) correct the ^{14}C activities using actual $\delta^{13}\text{C}$ values.

2. Materials and methods

2.1. Sampling

The Krško Nuclear Power Plant is located in south-eastern Slovenia (45°55'15" N, 15°30'54" E). Biological samples are collected in the vicinity of Krško Nuclear Power Plant twice per year, the first sampling campaign being usually at the beginning of the vegetation period (i.e. end of June or beginning of July) and the second sampling campaign just before harvesting (i.e. in September or early October), depending on the weather conditions (Obelić et al., 2010). For the purpose of this study we selected samples of apples, maize (leaves and grain) and wheat collected in four sampling campaigns, in July and October 2008 and in June and September 2009.

2.2. ^{14}C analysis

In the laboratory, samples were chopped into small pieces and dried at 60 °C. About 50 g of dried sample was used for pyrolysis (600 °C, 15 min) (Krajcar Bronić et al., 2009; Obelić et al., 2010), after which about 14 g of carbonized sample was obtained. Carbonized organic samples were combusted in a stream of pure oxygen. The CO_2 obtained from the sample was absorbed in an absorbing-scintillation cocktail (Carbosorb E and Permafluor E, ratio 1:1, total volume 20 mL). About 2.2 g of CO_2 (0.6 g of carbon) was absorbed in this cocktail. Samples were prepared in duplicate. Measurements were performed in 20 mL low-potassium glass vials on the Ultra-low-level Liquid Scintillation Counter Quantulus 1220 (Walac Oy, PerkinElmer Life Sciences). A counting run of absorbed- CO_2 samples consisted of two standard samples (active and background), both in duplicate and prepared at the same time as the unknown samples, and usually 10 unknown samples prepared in duplicate. Samples were measured in forty intervals of 30-min resulting in a total of 1200 min per sample (Horvatinić et al., 2004; Krajcar Bronić et al., 2009).

^{14}C activities were normalized by using the default $\delta^{13}\text{C}$ values, -25‰ and -10‰ for C3 and C4 plants, respectively (Obelić et al., 2010; Stuiver and Polach, 1977). These values are denoted as $a^{14}\text{C}_{\text{def}}$, while the ^{14}C activities normalized by the measured $\delta^{13}\text{C}$ values are denoted as $a^{14}\text{C}_{\text{new}}$.

2.3. $\delta^{13}\text{C}$ analysis

For this study, both dried and carbonized samples (71 samples in all, Table 1) were used for the determination of stable isotopic composition of carbon ($\delta^{13}\text{C}$). Carbonized samples were ground to fine powder and homogenized using an agate mortar and pestle while the dried samples were ground using various grinding methods depending on the type of samples. Apple samples were ground to fine powder and homogenized using an agate mortar and pestle, since grinding with a micromill is not suitable due to the high sugar content of apples (Stibilj, personal communication). Maize and wheat samples were lyophilized (0.020 mbar, -50 °C) (Lyophilizator CRIST Alpha 1–4, LOC-1, Osterode am Herz, Germany) after being frozen in liquid nitrogen. Afterwards, four lyophilized samples were ground in a Planetary Micro Mill (Fritsch, Pulverisette-7, Idar-Oberstein, Germany), using zirconium oxide grinding bowl and balls (7 min). Since during this process it was not possible to obtain completely homogenized samples, the rest of the maize and wheat samples were grounded and homogenized in an agate mortar. However, complete homogenization of maize leaves could not be achieved with any of the methods applied. After grinding, about 0.7 mg of each carbonized and dried sample was transferred and closed in a tin capsule for stable carbon isotopic analysis ($\delta^{13}\text{C}$).

Table 1
 $\delta^{13}\text{C}$ values and ^{14}C activity ($a^{14}\text{C}_{\text{def}}$ and $a^{14}\text{C}_{\text{new}}$) of maize, apple and wheat samples. Letters denote different sample preparation procedures: D – dried, C – carbonized, L – lyophilization, MP – grinding using an agate mortar and pestle, M – grinding using a micromill.

Sample ID	Sample	Sampling period	Sample type	Sample preparation	$\delta^{13}\text{C}$ (‰)	\pm (‰)	$a^{14}\text{C}_{\text{def}}$ (pMC)	\pm (pMC)	$a^{14}\text{C}_{\text{new}}$ (pMC)	Difference $a^{14}\text{C}_{\text{new}} - a^{14}\text{C}_{\text{def}}$
Z-4065	Maize, leaf	1-2008	D	L, MP	-10.9	0.0				
Z-4065	Maize, leaf	1-2008	C	MP	-12.7	0.2	109.69	1.73	110.30	0.61
Z-4201	Maize, grain	2-2008	D	MP	-11.8	0.0				
Z-4201	Maize, grain	2-2008	C	MP	-12.5	0.0	109.84	1.74	110.40	0.56
Z-4205	Apple	2-2008	D	MP	-25.1	0.1				
Z-4205	Apple	2-2008	C	MP	-27.4	0.1	111.34	2.51	111.88	0.54
Z-4207	Apple	2-2008	D	MP	-26.4	0.1				
Z-4207	Apple	2-2008	C	MP	-27.4	0.1	106.48	2.08	106.98	0.50
Z-4208	Apple	2-2008	D	MP	-28.6	0.0				
Z-4208	Apple	2-2008	C	MP	-29.0	0.2	102.95	2.03	103.77	0.82
Z-4210	Apple	2-2008	D	MP	-27.7	0.2				
Z-4210	Apple	2-2008	C	MP	-27.5	0.1	105.36	2.07	105.88	0.52
Z-4309	Maize, leaf	1-2009	D	L, MP	-12.9	/				
Z-4309	Maize, leaf	1-2009	C	MP	-12.2	0.2	106.34	2.05	106.82	0.48
Z-4310	Wheat	1-2009	D	L, M	-27.5	0.1				
Z-4310	Wheat	1-2009	C	MP	-27.8	0.1	104.05	2.05	104.62	0.57
Z-4311	Apple	1-2009	D	MP	-25.0	0.1				
Z-4311	Apple	1-2009	C	MP	-25.7	0.1	111.01	2.19	111.16	0.15
Z-4312	Apple	1-2009	D	MP	-24.8	0.2				
Z-4312	Apple	1-2009	C	MP	-25.5	0.2	135.15	2.44	135.28	0.13
Z-4313	Apple	1-2009	D	MP	-25.7	0.3				
Z-4313	Apple	1-2009	C	MP	-24.9	0.1	108.76	2.10	108.74	-0.02
Z-4315	Maize, leaf	1-2009	D	L, MP	-11.2	0.0				
Z-4315	Maize, leaf	1-2009	C	MP	-11.9	0.1	111.14	3.53	111.58	0.44
Z-4316	Apple	1-2009	D	MP	-27.0	0.1				
Z-4316	Apple	1-2009	C	MP	-27.5	0.1	116.33	2.62	116.90	0.57
Z-4317	Apple	1-2009	D	MP	-27.5	0.1				
Z-4317	Apple	1-2009	C	MP	-27.4	0.1	114.38	2.59	114.93	0.55
Z-4318	Apple	1-2009	D	MP	-28.2	0.0				
Z-4318	Apple	1-2009	C	MP	-27.5	0.0	114.09	2.65	114.65	0.56
Z-4319	Maize, leaf	1-2009	D	L, M	-11.3	0.0	111.98	2.52	112.28	0.30
Z-4320	Apple	1-2009	D	MP	-23.9	0.0				
Z-4320	Apple	1-2009	C	MP	-26.0	0.0	116.72	2.68	116.94	0.22
Z-4321	Maize, leaf	1-2009	D	L, MP	-11.2	0.1	114.28	2.70	114.55	0.27
Z-4322	Apple	1-2009	D	MP	-26.8	0.1				
Z-4322	Apple	1-2009	C	MP	-26.8	0.1	119.53	2.69	119.96	0.43
Z-4323	Apple	1-2009	D	MP	-26.1	0.0				
Z-4323	Apple	1-2009	C	MP	-27.6	0.0	128.15	2.81	128.81	0.66
Z-4324	Apple	1-2009	D	MP	-28.0	0.1				
Z-4324	Apple	1-2009	C	MP	-28.4	0.1	107.95	2.34	108.68	0.73
Z-4325	Maize, leaf	1-2009	D	L, MP	-11.0	0.1	106.55	2.26	106.76	0.21
Z-4326	Wheat	1-2009	D	L, M	-26.8	0.1				
Z-4326	Wheat	1-2009	C	MP	-26.5	0.0	108.62	2.32	108.94	0.32
Z-4327	Wheat	1-2009	D	L, MP	-27.8	0.1				
Z-4327	Wheat	1-2009	C	MP	-27.6	0.1	103.14	2.22	103.67	0.53
Z-4328	Maize, leaf	1-2009	D	L, MP	-10.9	0.1				
Z-4328	Maize, leaf	1-2009	C	MP	-11.7	0.0	101.39	2.17	101.73	0.34
Z-4337	Maize, grain	2-2009	D	L, MP	-12.8	0.0				
Z-4337	Maize, grain	2-2009	C	MP	-12.9	0.0	98.83	2.10	99.41	0.58
Z-4338	Maize, grain	2-2009	D	L, MP	-12.2	0.1				
Z-4338	Maize, grain	2-2009	C	MP	-12.5	0.1	105.22	2.34	105.76	0.54
Z-4339	Apple	2-2009	D	MP	-25.6	0.1				
Z-4339	Apple	2-2009	C	MP	-26.1	0.0	106.85	2.42	106.97	0.12
Z-4340	Apple	2-2009	D	MP	-25.7	0.1				
Z-4340	Apple	2-2009	C	MP	-24.1	0.1	128.96	2.69	128.42	-0.54
Z-4341	Apple	2-2009	D	MP	-24.7	0.1				
Z-4341	Apple	2-2009	C	MP	-24.8	0.2	112.12	2.44	112.06	-0.06
Z-4342	Maize, grain	2-2009	D	L, M	-12.0	0.2				
Z-4342	Maize, grain	2-2009	C	MP	-12.1	0.2	100.06	2.29	100.48	0.42
Z-4343	Apple	2-2009	D	MP	-25.4	0.0				
Z-4343	Apple	2-2009	C	MP	-25.6	0.1	105.50	2.21	105.62	0.12
Z-4344	Apple	2-2009	D	MP	-26.4	0.0				
Z-4344	Apple	2-2009	C	MP	-27.5	0.2	103.57	2.23	104.08	0.51
Z-4345	Apple	2-2009	D	MP	-26.6	0.1				
Z-4345	Apple	2-2009	C	MP	-28.8	0.1	103.87	2.29	104.66	0.79
Z-4347	Apple	2-2009	D	MP	-27.4	0.1				
Z-4347	Apple	2-2009	C	MP	-28.6	0.2	105.25	2.03	106.00	0.75
Z-4348	Apple	2-2009	D	MP	-26.8	0.3				
Z-4348	Apple	2-2009	C	MP	-27.3	0.1	105.42	1.99	105.90	0.48
Z-4349	Apple	2-2009	D	MP	-27.5	0.2				
Z-4349	Apple	2-2009	C	MP	-28.4	0.1	117.47	2.14	118.26	0.79

Table 2
Descriptive statistics of $\delta^{13}\text{C}$ (in ‰) of dried (D) and carbonized (C) maize (leaf and grain), wheat and apple samples.

Sample	Mean (‰)	STD (‰)	Median (‰)	Min (‰)	Max (‰)	N
C3 plants						
D	-26.5	1.2	-26.7	-28.6	-23.9	26
C	-27.0	1.3	-27.4	-29.0	-24.1	26
C4 plants						
D	-11.8	0.8	-11.9	-12.9	-10.9	8
C	-12.3	0.4	-12.3	-12.9	-11.7	8
Maize, leaf						
D	-11.1	0.1	-11.1	-11.3	-10.9	6 ^a
C	-12.1	0.4	-12.0	-12.7	-11.7	4
Maize, grain						
D	-12.2	0.4	-12.1	-12.8	-11.8	4
C	-12.5	0.3	-12.5	-12.9	-12	4
Wheat						
D	-27.4	0.5	-27.5	-27.8	-27.8	3
C	-27.3	0.7	-27.6	-26.8	-26.5	3
Apple						
D	-26.4	1.2	-26.4	-28.6	-23.9	23
C	-26.9	1.4	-27.4	-29	-24	23

^a Outlier excluded from data ($\delta^{13}\text{C} = -12.9\text{‰}$).

Isotopic composition of organic carbon ($\delta^{13}\text{C}$) of 37 dried and 34 carbonized plant samples was determined using a Europa 20–20 isotope ratio mass spectrometer (IRMS) with ANCA-SL preparation module for solid and liquid samples (Europa Scientific Ltd., Crewe, UK). Samples were analysed in duplicate. Results are reported in δ notation in units of per mille (‰) with respect to international standard VPDB, according to the equation:

$$\delta^{13}\text{C}_{\text{sample}}(\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

where R denotes $^{13}\text{C}/^{12}\text{C}$ ratios of the sample and standard, respectively.

The variations of the isotopic measurements were checked with certified reference material IAEA-CH-6 (-10.4‰ , sucrose) and in-house reference materials G-3234 (-28.7‰ , Lucerne) and G-133 (-25.2‰ , beet sugar) and was less than 0.2‰ . The accuracy of $\delta^{13}\text{C}$ measurements in our laboratory has been verified with successful participation in international interlaboratory studies WEPAL International Plant-analytical Exchange Programme, IPE2009.2, IPE2010.2 (Šturm et al., 2009; Šturm and Lojen, 2010).

2.4. Statistical analysis

Data were verified statistically using Statistica 6.0 (StatSoft, Tulsa, OK, USA). Means were compared by the Student's *t*-test and differences were considered to be significant at $p < 0.05$. The Student's *t*-test was not applied to maize and wheat samples due to limited number of samples.

3. Results and discussion

Results of $\delta^{13}\text{C}$ determinations as well as ^{14}C activities obtained using both the default $\delta^{13}\text{C}$ values ($a^{14}\text{C}_{\text{def}}$) and the measured $\delta^{13}\text{C}$ values ($a^{14}\text{C}_{\text{new}}$) of the maize (leaf, grain), apple and wheat samples are presented in Table 1. In addition, the difference between $a^{14}\text{C}_{\text{new}}$ and $a^{14}\text{C}_{\text{def}}$ was calculated (Table 1). Descriptive statistics of dried and carbonized C3 and C4 plants, maize (leaf, grain), wheat and apple samples are presented in Table 2.

Mean $\delta^{13}\text{C}$ values determined for C3 and C4 plants are -27‰ and -12‰ , respectively, and are in accordance with values reported in the literature (Hoefs, 1997; Waller and Mewis, 1979). Comparison of $\delta^{13}\text{C}$ values for dried and carbonized samples of the maize (leaf, grain), apple and wheat is presented in Fig. 1 which shows a difference of only 1‰ (Fig. 1, Table 2) observed between the dried and carbonized maize leaf samples. The greatest variability of $\delta^{13}\text{C}$ values is observed for apple samples and might be attributed to

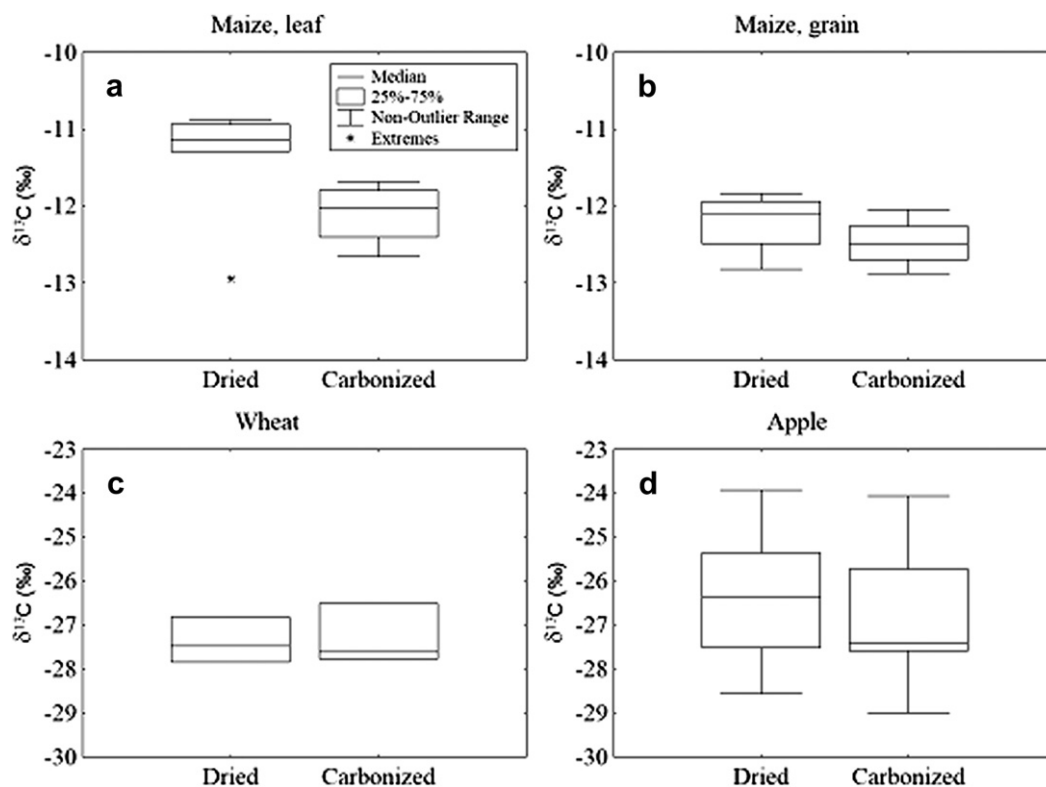


Fig. 1. $\delta^{13}\text{C}$ of dried and carbonized maize leaf (a), maize grain (b), wheat (c) and apple (d) samples.

different varieties of apples. No significant difference was observed either between the dried and carbonized C3 samples ($p = 0.17$; $n = 26$) or within apple samples ($p = 0.15$; $n = 23$), indicating that no significant isotopic fractionation occurred during the sample carbonization process. However, most carbonized samples have slightly (up to 2.2‰) lower $\delta^{13}\text{C}$ values while for 8 samples slightly (up to 1.6‰) higher $\delta^{13}\text{C}$ values were observed (Table 1). Both maxima were observed for apple samples and indicate no systematic change in isotopic composition during carbonization.

^{14}C activities obtained using the default $\delta^{13}\text{C}$ values ($a^{14}\text{C}_{\text{def}}$) and measured $\delta^{13}\text{C}$ values ($a^{14}\text{C}_{\text{new}}$) are compared in Table 1 and basic statistics of the differences between the two values are summarized in Table 3. By applying measured $\delta^{13}\text{C}$ values, the corrected ^{14}C activities become, on average, 0.42 ± 0.28 pMC higher than by using default $\delta^{13}\text{C}$ values. However, the differences obtained are much lower than the measurement uncertainty (usually about ± 2 pMC). If we assume a 2‰ difference between previously used $\delta^{13}\text{C}$ values and mean values from this study and take into account the fractionation of ^{14}C being twice that of ^{13}C , the calculated increase in $a^{14}\text{C}$ (Table 3) is in accordance with the expected.

Distributions of $\delta^{13}\text{C}$ and $a^{14}\text{C}_{\text{new}}$ values of carbonized apple samples during different sampling campaigns (2-2008, 1-2009 and 2-2009) are shown in Fig. 2. No difference was observed between $\delta^{13}\text{C}$ mean values of apple samples collected in June 2009 and September 2009 (Fig. 2a). Therefore, the same $\delta^{13}\text{C}$ value for both, spring–summer and autumn sampling campaigns could be used for $\delta^{13}\text{C}$ correction in future. However, approximately 1‰ higher $\delta^{13}\text{C}$ values were determined for samples collected in 2009 as compared to 2008. To confirm the statistical difference between the years more detailed investigation should be performed over several years.

Variations in $a^{14}\text{C}_{\text{new}}$ of apple samples (Fig. 2b) deserve an explanation, although analysis of spatial and temporal distribution of $a^{14}\text{C}$ is not the main task of the present paper. The 5-year-long monitoring of $a^{14}\text{C}$ in biological samples in the vicinity of the Krško Nuclear Power Plant revealed slightly increased ^{14}C activities in all sampling campaigns in an SW–NE direction which reflects the prevailing winds. The monitoring period encompasses several refuelling outage periods (refuelling is performed at 18-month intervals). As expected, higher activities of ^{14}C were measured in biological material which used CO_2 released to the atmosphere in the refuelling outage periods. In 2009 the power plant was refuelled in spring so the apples, having their vegetation period immediately afterwards, used more $^{14}\text{CO}_2$ for photosynthesis. Therefore, ^{14}C activities measured in June 2009 (campaign 1-2009 in Fig. 2b) were higher than the previous year (campaign 2-2008) and also show larger variability. ^{14}C activities in the autumn sampling period (2-2009) are again lower, but still show slightly higher values and larger variability than in the year when there was no spring refuelling (Obelić et al., 2010).

Table 3

Descriptive statistics of the differences between $a^{14}\text{C}_{\text{def}}$ and $a^{14}\text{C}_{\text{new}}$ (in pMC) of carbonized maize (leaf and grain), wheat and apple samples. The expected difference between the default values and measured values estimated from $\delta^{13}\text{C}$ values is calculated as $2(\delta^{13}\text{C}_{\text{default}} - \delta^{13}\text{C}_{\text{measured}})/10$ and expressed in pMC.

Sample	Mean	STD	Median	Min	Max	N	Expected difference
All samples	0.41	0.28	0.5	-0.54	0.82	37	
C3 plants	0.41	0.32	0.51	-0.54	0.82	26	0.40
C4 plants	0.39	0.18	0.42	0.04	0.61	11	0.46
Maize, leaf	0.38	0.14	0.34	0.21	0.61	7	0.42
Maize, grain	0.53	0.07	0.55	0.42	0.58	4	0.50
Wheat	0.47	0.13	0.53	0.32	0.57	3	0.46
Apple	0.41	0.34	0.51	-0.54	0.82	23	0.38

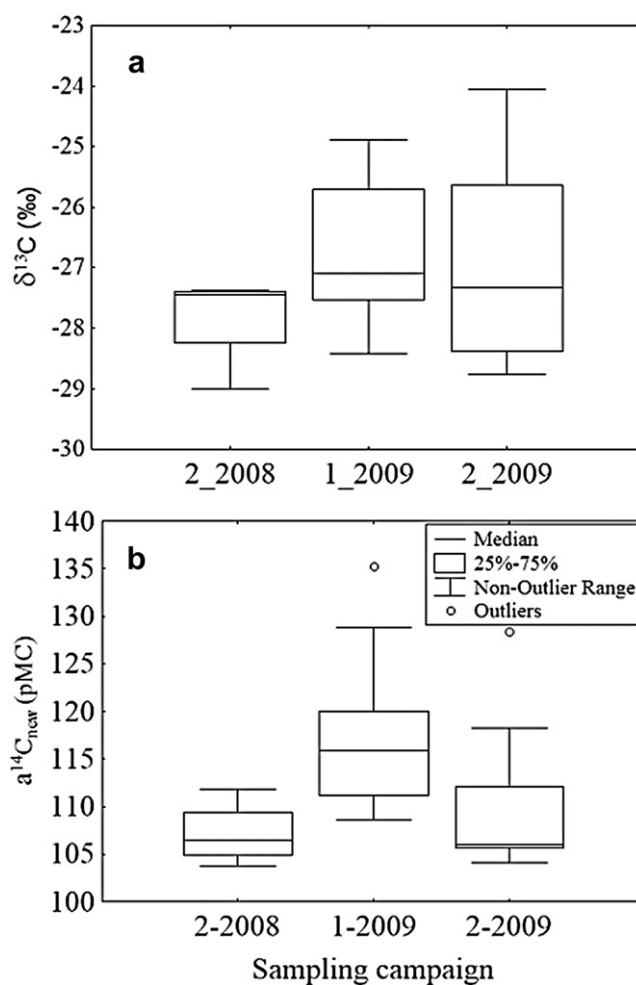


Fig. 2. $\delta^{13}\text{C}$ of carbonized apple samples (a) and $a^{14}\text{C}_{\text{new}}$ values of carbonized apple samples (b) collected during different sampling campaigns (2-2008, 1-2009 and 2-2009).

4. Conclusion

By measuring a total of 71 plant samples collected in the vicinity of the Krško Nuclear Power Plant in Slovenia we determined the actual $\delta^{13}\text{C}$ values of plants to be used for correction of ^{14}C activities. By measuring dried samples and their carbonized counterparts we showed that no significant isotopic fractionation occurred during the carbonization phase of the sample preparation process in the laboratory. The measured $\delta^{13}\text{C}$ values will be used for correction of previously reported ^{14}C activities (Obelić et al., 2010). Furthermore, mean $\delta^{13}\text{C}$ values determined for C3 and C4 plants in this study will be applied in future determinations of ^{14}C activity in plant samples.

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