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SEASONAL VARIATIONS OF RADIOCARBON CONTENT IN PLANT LEAVES IN A ^{14}C-DEPLETED AREA

Rana Baydoun[1,2] • Omar El Samad[1] • Bilal Nsouli[1] • Ghassan Younes[3]

ABSTRACT. The determination of radiocarbon content in biogenic samples such as tree leaves and short-lived plants is crucial when studying the anthropogenic impact on the ecosystem and for detecting any alteration in stable and radioactive CO_2. A total of 76 samples of evergreen and deciduous tree leaves as well seasonal plants were collected in winter, spring, and summer. Sampling was carried out from rural villages located in Mount Lebanon Province, Lebanon. Based on the data obtained from a previous study carried out in autumn, which showed that the selected sites are characterized by depletion of ^{14}C caused by the releases of pollutants and CO_2 from a cement factory in the region, further investigation was carried out in the present work to determine possible significant seasonal variations in Δ^{14}C values. Reference samples of identical species were collected in the same period from a clean zone. The conventional ^{14}C method was used to determine the carbon isotopic ratio. Δ^{14}C data are compared to those obtained in autumn. ^{14}C concentration in the studied sites was significantly lower than in the clean area in all seasons. ANOVA tests showed that there is a significant seasonal variation for deciduous leaves and seasonal plants, while this difference was not significant in evergreen leaves. In addition, no significant variation was recognized for different species in the same season.

INTRODUCTION

Radiocarbon is a long-lived radionuclide produced in the upper layer of the atmosphere by the reaction of energetic neutron and nitrogen nuclei (Svetlik et al. 2010). However, anthropogenic impacts on the environment are a major cause of significant change in the isotopic composition of carbon in the atmosphere. Over the last decades, various human activities have affected the ^{14}C concentration. The main contribution comes from the nuclear weapons tests that took place in 1950s and 1960s. At present, as these tests are banned, nuclear reactors have become the main anthropogenic sources of ^{14}C. Another important factor is the Suess effect that happened in the early 19th century. Due to the increased population's need for energy, the combustion of fossil fuels such as petroleum, natural gas, and coal released large amounts of CO_2 to the atmosphere. This caused a depletion in ^{14}C concentration and dilution of $^{14}CO_2$ concentration (Tans et al. 1979; Pawełczyk and Pazdur 2004; Rakowski et al. 2013). Currently, this phenomenon is caused also by industrial complexes, the transport sector, and other practices based on fuel combustion. Thus, in urban and industrialized areas, high emission of dead carbon could be predicted due to fossil fuel combustion, which is rich in ^{12}C.

As tree rings, leaves, and short-lived plants assimilate carbon from the air during photosynthesis, any alteration in stable and radioactive CO_2 can influence the carbon activity in plants; thus, knowing the ^{14}C content in biogenic samples is crucial to understand the anthropogenic impact on the ecosystem. Moreover, it provides an idea about the degree of pollution and enables estimating the total emission of fossil-fuel-derived CO_2 (Pataki et al. 2010; Rakowski et al. 2013).

In Lebanon, various sources of pollution affect the ^{14}C concentration in the atmosphere. The main ones are the transport and energy sectors and other industries. Previous studies based on the determination of Δ^{14}C in tree leaves of evergreen and deciduous trees collected in autumn, the end of the vegetation season, located near a cement factory in the Chouf region of Mount Lebanon Province, showed that this area is highly affected by the factory (Baydoun et al. 2015) and its various processes such as mining, quarrying, crushing, grinding, and calcining. All these activities generate large amounts of pollutants, mainly CO_2 (Chabarekh 2010). In the present work, further investigation in this region was carried out, as a continuation of our previous study (Baydoun et al. 2015), which concluded that this area is characterized by depletion in ^{14}C due to the Suess effect. Δ^{14}C was deter-

1. Lebanese Atomic Energy Commission- National council for Scientific Research, Beirut, Lebanon.
2. Corresponding author. Email: rbaydoun@cnrs.edu.lb.
3. Beirut Arab University, Faculty of Sciences, Chemistry Department, Dibbieh, Lebanon.

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mined in the same species collected from the same polluted zones, during three consecutive seasons (winter, spring, and summer), in order to detect any possible seasonal variations.

Benzene synthesis was carried out, followed by measurement using a Tri-Carb 3180 TR/SL liquid scintillation counter. ^{14}C levels were determined in tree-leaf samples, as well as in grass samples collected in winter, spring, and summer from rural areas distributed along 10 locations. Analysis of variance (ANOVA) statistical tests were applied to determine any possible significant difference between species as well as any significant seasonal variation.

MATERIALS AND METHODS

Samples

For the seasonal variation study, sampling was carried during three consecutive seasons. A total of 22 samples from deciduous trees (fig, *Ficus*) were gathered in spring and summer. Eleven leaf samples from evergreen trees (loquat, *Eriobotrya japonica*) were collected seasonally, during winter, spring, and summer, giving a total of 33 samples. At the same time, 22 samples of *Inula* were collected during three seasons depending on the availability in each selected site. As a reference, leaves of the same studied species were collected from a clean zone in the same sampling periods.

Meteorological Data

Lebanon's climate is defined by its geography and location on the Mediterranean Sea. Moderate southwestern winds are dominant most of the year. Winter is the rainy season; however, rainfall levels vary from one year to another. During winter, cold winds from Europe often affect the northern regions of the country, giving rise to a cooler and wetter northern coast. Meanwhile, a drier and warmer climate typifies the southern coastal areas. A hot wind, called the *khamasin*, may provide a warming trend during the fall, but more often occurs during the spring. The coastal regions are characterized by a Mediterranean climate with hot, humid summers and moderate, rainy winters. In the mountains, the temperature during summer days is comparable to levels recorded at coastal areas, but the nighttime temperatures are much lower in the mountains. With increasing altitude, colder winters with more precipitation and snow are expected.

Sampling Sites

Samples were collected from rural areas, far from the main roads, in villages affected by a cement factory that causes depletion in ^{14}C content in the studied region. Sampling was carried out from 10 locations at various distances from the factory and with increasing altitude from 55 to 740 m above sea level (Baydoun et al. 2015). Figure 1 is a map of Lebanon showing the location of the studied region and the selected clean areas.

Chemical Treatment and Benzene Synthesis

The following acid-base-acid (ABA) method was applied to pretreat samples (Park et al. 2013). Samples were rinsed with distilled water, then dried overnight at 105°C. Carbonization was applied to convert samples to charcoal by combustion in a closed crucible at 700–800°C. The conventional method was used for benzene synthesis, based on lithium carbide production under vacuum at 750°C, followed by vacuum hydrolysis to decompose lithium carbide and produce acetylene (C_2H_2), which was converted to benzene (C_6H_6) using a vanadium catalyst regenerated previously at 300–400°C. The obtained benzene was purified using sulfuric acid and vacuum sublimation. Butyl-PBD was used as the scintillator (Baydoun et al. 2015).

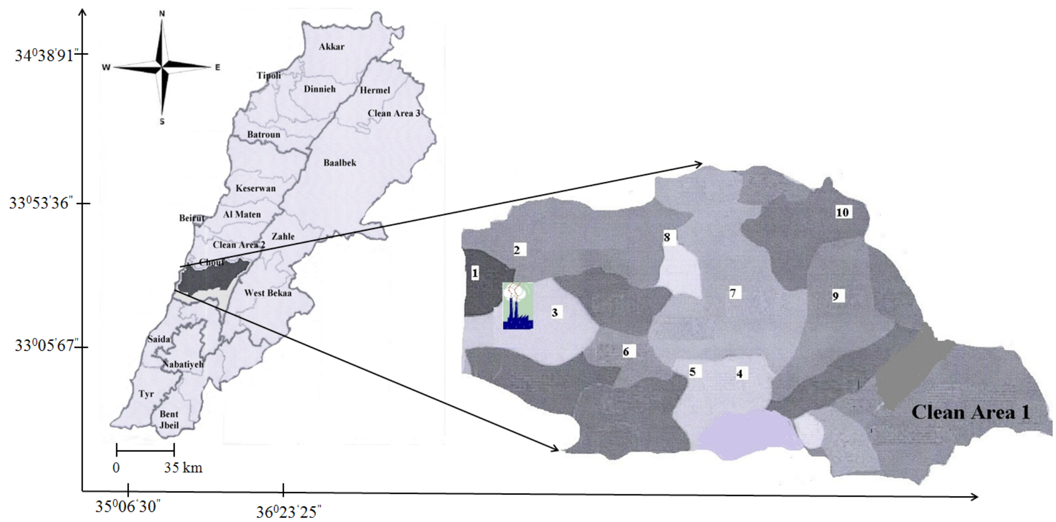

Figure 1 Map of Lebanon showing the studied region and clean areas

Measurement and Calculation

A Tri-Carb 3180 TR/SL low-level liquid scintillation counter was used for sample measurement. Minimization of background interference and discrimination of true beta events were assured through the incorporation of a bismuth germanate ($Bi_4Ge_3O_{12}$) detector as well as a pulse-shape analyzer (PSA). Normalization of the counting system and optimization of the counting region were carried out following Knoll (2010) and Baydoun et al. (2014). Benzene was counted in 20-mL glass vials, with results expressed in terms of $\Delta^{14}C$. Based on the $\delta^{13}C$ values determined previously in the selected species and the fact that they are not significantly different from –25‰ (Baydoun et al. 2015), no correction for isotope fractionation was carried out assuming $\delta^{13}C$ in leaves is –25‰ (Stuiver and Polach 1977; Muraki et al. 2001). To estimate the local decrease in ^{14}C concentration due to the Suess effect during different seasons, the proportion of fossil-fuel-derived CO_2 (F) was calculated as described in the literature (Pazdur et al. 2007, 2013) assuming that $\Delta^{14}C_{foss}$ = –1000‰, as fossil-fuel CO_2 is totally depleted of ^{14}C (Pazdur et al. 2007; Pataki et al. 2010; Baydoun et al. 2015).

RESULTS AND DISCUSSION

$\Delta^{14}C$ values in all samples collected in winter, spring, and summer were below the ^{14}C content in the same species gathered from clean areas in same period. This was expected as the data determined previously in autumn showed that the studied sites are affected by a cement factory that causes depleted $^{14}CO_2$ in the region. Sites were influenced to different degrees depending on their proximity to the factory (Baydoun et al. 2015). Results for *Ficus* and *Inula* plants and loquat leaves are presented in Tables 1, 2, and 3, respectively, and compared with those obtained in autumn.

A remarkable variation was recognized between species within the same season. This may be caused by the difference in leaf size and its maturity (Pataki et al. 2010; Baydoun et al. 2015). However, ANOVA tests showed that this variation is not significant in all seasons as $F < F_{crit}$ and $p > 0.05$. Concerning the difference between seasons for the same species, it was found that $\Delta^{14}C$ values for all samples were lower in winter and summer. This could be attributed to the lifestyle in summer, as well as to the increase in population and road transport, even in rural areas, as some citizens leave their villages in the region during autumn, winter, and spring and return for the summer season. This may cause the depletion in ^{14}C that is well reflected by photosynthesis in plants, whose rate increases during summer. This was recognized even in the clean area, especially in deciduous and seasonal plants; however, values were slightly lower than the estimated background value for atmospheric $\Delta^{14}CO_2$ (Levin et al. 2013). This seasonal variation was not seen in evergreen plants because perennial evergreen leaves may contain carbon fixed from the previous season or even previous years (Baydoun et al. 2015).

Table 1 Seasonal variations of $\Delta^{14}C$ (‰) content in *Ficus* leaves collected from 10 locations and compared with the clean area.

Location	Autumn (Baydoun et al. 2015)	Spring (current work)	Summer (current work)
1	44.99 ± 2.78	32.41 ± 0.35	20.56 ± 0.67
2	28.48 ± 0.49	28.88 ± 0.40	20.22 ± 0.50
3	10.51 ± 0.11	12.96 ± 0.23	–20.18 ± 0.60
4	11.79 ± 0.29	13.14 ± 0.55	4.50 ± 0.22
5	8.39 ± 0.23	4.41 ± 0.10	–45.67 ± 1.84
6	17.44 ± 0.58	13.75 ± 0.33	–15.76 ± 0.22
7	13.25 ± 0.35	13.60 ± 0.25	–23.38 ± 0.40
8	43.13 ± 0.11	30.22 ± 0.88	–38.53 ± 0.20
9	43.15 ± 0.60	30.42 ± 0.51	–10.55 ± 0.40
10	42.50 ± 0.58	32.31 ± 0.64	20.00 ± 0.57
Clean area	52.24 ± 2.40	35.97 ± 0.65	22.50 ± 0.67

Table 2 Seasonal variations of $\Delta^{14}C$ (‰) content in *Inula* leaves collected from 10 locations and compared with the clean area.

Location	Autumn (Baydoun et al. 2015)	Winter (current work)	Spring (current work)	Summer (current work)
1	—	—	9.89 ± 0.15	–48.70 ± 2.1
2	—	—	23.68 ± 1.33	—
3	–7.55 ± 0.14	16.86 ± 0.40	19.62 ± 1.09	–11.44 ± 0.58
4	28.67 ± 0.35	—	25.03 ± 1.22	—
5	28.16 ± 0.55	—	3.78 ± 0.10	–4.50 ± 0.48
6	—	—	13.84 ± 0.55	—
7	15.75 ± 0.24	27.76 ± 0.78	–4.49 ± 0.14	–17.40 ± 1.11
8	27.67 ± 0.92	—	11.21 ± 0.53	5.54 ± 0.50
9	42.31 ± 0.46	24.45 ± 0.40	24.47 ± 1.10	11.57 ± 0.63
10	—	—	23.70 ± 1.01	—
Clean area	53.48 ± 1.25	39.50 ± 1.10	42.40 ± 2.10	23.40 ± 0.56

The decrease in ^{14}C content during winter may be caused by the extensive Suess effect due to heating of buildings and atmospheric inversion that could happen during this season (Molnár et al. 2007). As shown by the ANOVA test, this seasonal variation was significant for *Ficus* and *Inula* as $F > F_{crit}$ and $p < 0.05$. While for the loquat, ANOVA results in $F < F_{crit}$ and $p > 0.05$, showing that this variation was not significant.

Fossil-fuel fraction values for the selected species collected in different seasons are listed in Tables 4, 5, and 6 for each study location. Values confirm that the studied sites were affected by the anthropogenic CO_2 released by the cement factory.

Table 3 Seasonal variations of $\Delta^{14}C$ (‰) content in loquat leaves collected from 10 locations and compared with the clean area.

Location	Autumn (Baydoun et al. 2015)	Winter (current work)	Spring (current work)	Summer (current work)
1	31.25 ± 0.60	33.50 ± 0.81	31.25 ± 0.60	27.67 ± 0.78
2	–47.09 ± 0.94	32.36 ± 0.50	30.79 ± 0.61	–47.81 ± 1.20
3	17.77 ± 0.29	30.82 ± 0.34	24.43 ± 0.50	24.22 ± 0.58
4	33.74 ± 0.61	27.41 ± 0.35	14.10 ± 0.33	7.60 ± 0.22
5	27.06 ± 0.35	37.25 ± 0.54	36.31 ± 0.80	–18.13 ± 0.62
6	22.50 ± 0.31	15.15 ± 0.86	7.14 ± 0.32	6.25 ± 0.10
7	33.25 ± 0.58	19.00 ± 0.18	22.38 ± 0.60	–23.38 ± 0.40
8	30.45 ± 1.11	20.45 ± 0.20	30.45 ± 1.11	15.90 ± 0.50
9	27.77 ± 0.26	11.15 ± 0.50	30.28 ± 0.65	17.90 ± 0.34
10	32.28 ± 0.59	–0.69 ± 0.01	30.28 ± 0.60	13.04 ± 0.31
Clean area	54.34 ± 1.25	45.77 ± 0.77	51.10 ± 1.22	48.97 ± 0.60

Table 4 Fossil fuel fractions (F %) derived from ^{14}C content in *Ficus* leaves.

Location	Autumn (Baydoun et al. 2015)	Spring (current work)	Summer (current work)
1	0.69 ± 0.36	0.34 ± 0.07	0.19 ± 0.09
2	2.26 ± 0.26	0.68 ± 0.07	0.22 ± 0.08
3	3.97 ± 0.29	2.22 ± 0.08	4.17 ± 0.15
4	3.84 ± 0.29	2.20 ± 0.10	1.76 ± 0.09
5	4.17 ± 0.30	3.05 ± 0.10	6.67 ± 0.28
6	3.31 ± 0.28	2.14 ± 0.08	3.74 ± 0.13
7	3.71 ± 0.29	2.16 ± 0.08	4.49 ± 0.15
8	0.87 ± 0.23	0.56 ± 0.11	5.97 ± 0.19
9	0.86 ± 0.24	0.54 ± 0.08	3.23 ± 0.12
10	0.93 ± 0.23	0.35 ± 0.08	0.24 ± 0.09

Table 5 Fossil fuel fractions (F %) derived from ^{14}C content in *Inula* plants.

Location	Autumn (Baydoun et al. 2015)	Winter (current work)	Spring (current work)	Summer (current work)
1	—	—	3.12 ± 0.25	7.05 ± 0.27
2	—	—	1.80 ± 0.25	—
3	5.79 ± 0.18	2.18 ± 0.13	2.19 ± 0.25	3.40 ± 0.11
4	2.36 ± 0.14	—	1.67 ± 0.26	—
5	2.40 ± 0.14	—	3.70 ± 0.27	2.73 ± 0.10
6	—	—	2.74 ± 0.29	—
7	3.58 ± 0.15	1.13 ± 0.13	4.50 ± 0.36	3.99 ± 0.15
8	2.45 ± 0.16	—	2.99 ± 0.26	1.75 ± 0.08
9	1.06 ± 0.13	1.45 ± 0.12	1.72 ± 0.22	1.16 ± 0.09
10	—	—	1.79 ± 0.24	—

Table 6 Fossil fuel fractions (F %) derived from ^{14}C content in loquat leaves.

Location	Autumn (Baydoun et al. 2015)	Winter (current work)	Spring (current work)	Summer (current work)
1	2.19 ± 0.11	1.17 ± 0.28	1.89 ± 0.14	2.03 ± 0.10
2	9.62 ± 0.20	1.28 ± 0.16	1.93 ± 0.14	9.23 ± 0.17
3	3.47 ± 0.10	1.43 ± 0.06	2.54 ± 0.14	2.36 ± 0.08
4	1.95 ± 0.11	1.76 ± 0.09	3.52 ± 0.15	3.94 ± 0.08
5	2.59 ± 0.10	0.81 ± 0.03	1.41 ± 0.14	6.40 ± 0.11
6	3.02 ± 0.10	2.93 ± 0.13	4.18 ± 0.16	4.07 ± 0.09
7	2.10 ± 0.11	2.56 ± 0.11	2.73 ± 0.14	6.90 ± 0.12
8	2.27 ± 0.14	2.42 ± 0.50	1.96 ± 0.16	3.15 ± 0.09
9	2.52 ± 0.10	3.31 ± 0.56	1.98 ± 0.14	2.96 ± 0.08
10	2.09 ± 0.11	4.44 ± 1.17	1.98 ± 0.14	3.43 ± 0.10

CONCLUSIONS

^{14}C content in plants and tree leaves was used to assess the anthropogenic impact on the ecosystem. The study was done in a zone characterized by depletion in ^{14}C. A significant seasonal variation was detected in deciduous leaves and seasonal plants, but was not significant in evergreen leaves. No significant variation was found between species in the same season. Further studies and measurements will be carried out in the Chouf region to determine a possible Suess effect in other neighboring villages, and to observe any change in the ^{14}C content and pollution degree from year to year.

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