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# A Study of $^{14}\text{C}$ Concentration in Different Environmental Matrices Around Western Ghats

**Prajna N D<sup>1</sup>, Karunakara N<sup>2</sup>, D'Silva E D<sup>1</sup>**

1. Department of Physics, Centre for PG Studies & Research  
St Philomena College, Puttur
2. Centre for Advanced Research in Environmental Radioactivity (CARER)  
Mangalore University  
Email: prajnanekraje39@gmail.com

**Abstract:** Carbon-14 ( $^{14}\text{C}$ ) is a radioactive carbon isotope present in infinitesimal quantities in the atmosphere. Carbon-12 and Carbon-13 are the stable carbon isotopes and respectively represent 98.9% and 1.1% of the total Carbon. Carbon-14 only exists in trace quantities. It is an important radioactive isotope to be monitored because of its long half-life, environmental mobility and ease of assimilation into living matter. The present study would provide a reliable database on  $^{14}\text{C}$  concentration in some of the environmental matrices around Western Ghats region.

**Key Words:** Pyrolyser, Liquid Scintillation Counter, Carbon-14, Western Ghats.

## 1. Introduction

Carbon-14 ( $^{14}\text{C}$ ) is a radioactive carbon isotope present in infinitesimal quantities in the atmosphere. Carbon-12 and Carbon-13 are the stable carbon isotopes and respectively represent 98.9% and 1.1% of the total Carbon. Carbon-14 only exists in trace quantities. The chemical forms of  $^{14}\text{C}$  vary according to the method of production. In the environment,  $^{14}\text{C}$  exists in two main forms:

- As  $^{14}\text{CO}_2$ , it acts as stable carbon dioxide, which means it can remain in gas form in the air, becoming bicarbonate and carbonate in water (Killough G.G., Rowher P.S., 1978)
- During photosynthesis,  $^{14}\text{CO}_2$  is incorporated in the organic material, forming its carbon skeleton. Equilibrium between the specific activity of the atmospheric carbon and the organic material is then finally reached and maintained by carbon recycling (Cain W. F., Suess H. E., 1976).  
Carbon has 15 isotopes with masses of 8 to 22. Only isotopes 12 and 13 are stable. Carbon 14 is a  $\beta$  emitter, gives rise to stable  $^{14}\text{N}$  with 100% yield.

## **Origins**

### **Natural origins**

Natural <sup>14</sup>C results from cosmic neutrons acting on nitrogen atoms in the stratosphere and in the upper troposphere ( $^{14}\text{N} + n \rightarrow ^{14}\text{C} + ^1\text{p}$ ). The annual production level is around  $1.40 \times 10^{15}$  Bq and the atmospheric stock of carbon-14 at equilibrium is around  $140 \times 10^{15}$  Bq (Libby W.F., 1946)

### **Artificial Origins**

#### *Fallout from atmospheric nuclear explosions*

During nuclear explosions, the emitted neutrons interact with atmospheric nitrogen, as cosmic neutrons do, to form carbon-14, according to the same reaction as above:  $^{14}\text{N} + n \rightarrow ^{14}\text{C} + ^1\text{p}$ . (UNSCEAR Report A/AC. 82/G/L. 1381)

### **Nuclear Reactor Releases**

In nuclear reactors, carbon-14 is produced from reactions in the fuel, the core structural materials and the moderator. The production rate depends upon the spectrum and neutron flux, on cross – sections and on the concentration of the following target elements: uranium, polonium, nitrogen and oxygen (Karin A., Bengt H., 2005; Levin I., *et al*, 1988).

#### *Various sources (medical, industrial and research)*

In research, carbon-14 is widely used in carbonate form for isotopic labeling of molecules. The activities used are greater than 1 GBq. For example, carbon - 14 is used to study the metabolic dysfunction related to diabetes and anemia. It can also be used as a marker to track the metabolism of new pharmaceutical molecules (Sheppard S.C., *et al*, 2006).

## **Environmental Toxicity**

### **Radio Toxicity of the Radioactive Isotope <sup>14</sup>C**

Emitting  $\beta$  radiation with a half-life of 5,730 years, Carbon 14 follows the cycle of the stable element C, one of the components of the living materials, in which it is diluted. Carbon-14 is indeed around  $10^{-12}$  times less abundant than stable carbon. The main source of exposure is due to naturally occurring <sup>14</sup>C (cosmogenic origin).

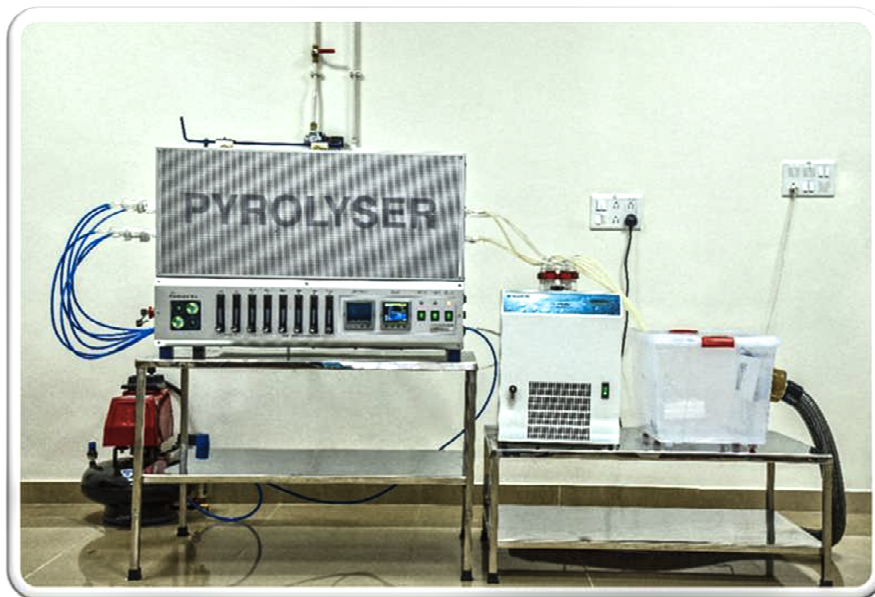
Carbon-14 is a low  $\beta$  emitter, with a low penetrating power which causes radiation stress mainly due to internal irradiation, if the  $^{14}\text{C}$  is incorporated. Carbon-14 is interesting from a radiobiological standpoint because it is integrated in cellular components (proteins, nuclei acids), particularly cellular DNA. The resulting DNA damage involving molecular breaks, may lead to the cell death or induce potentially inheritable mutations (NCRP Report No. 81, USA. 1985).

## **2 Methodology**

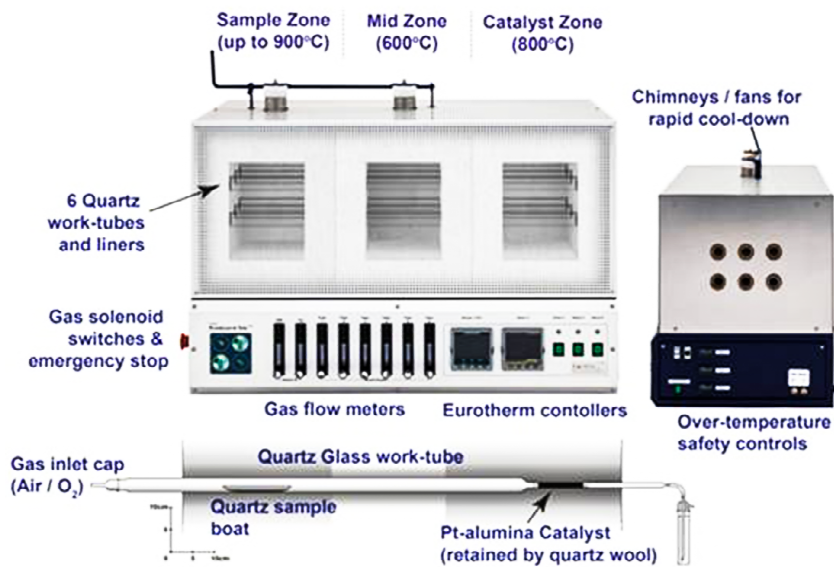
### **2.1 RADDEC Pyrolyser**

**Fig 1(a): RADDEC Pyrolyser Trio TM at CARER, Mangalore University.**

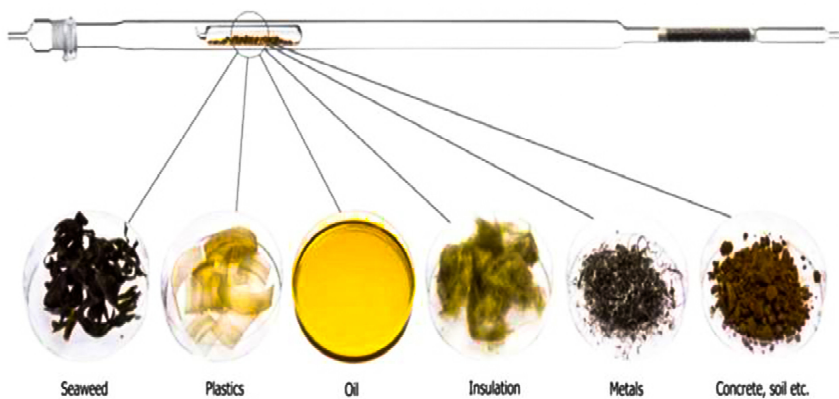
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**Fig 1(b): A View of RADDEC Pyrolyser Trio™ System**



**Fig 1(c): A View of Pyrolyser Work Tube and Samples to be Taken for Analysis**



Environmental samples of interest are combusted by thermal oxidation method using a Pyrolyser Trio system for separation of carbon from the sample (RADDEC, UK, Fig. 1). Pyrolyser is a fully integrated triple-zone furnace system that incorporates six work-tubes (silica) for simultaneous extraction of  $^{14}\text{C}$  and  $^3\text{H}$  from six different samples. Samples of environmental matrix were oven dried at  $80\text{ }^\circ\text{C}$  till complete moisture from the samples was removed. They were then powdered using a sample crusher and evenly spread in a silica sample boat. The silica boat is then placed within the silica glass work tube in sample zone of the furnace and heated under controlled condition. There are eight predefined programs stored in the memory of Pyrolyser system. In addition to this the user can develop/define a program depending upon the specific requirements. Each predefined program differs with the heating temperature; ramp and hold time and is meant for combustion of different types of samples. Normally, for samples such as leaves, fruit and vegetables, the ORGANIC program is selected and for samples such as sediment, soil and sand, NORMAL program is selected.

During the initial heating period, air at a flow rate of  $0.1\text{ l pm}$  is passed through the heating tube using an air compressor. Once the temperature of the sample zone reaches to  $500^\circ\text{C}$ , oxygen is introduced to accelerate oxidation of the remaining sample. The heating cycles are programmed to ensure controlled and complete oxidation of organic-rich samples at low temperatures and prevent sudden pressure excursions within the work tube. The liberated gases pass through a catalyst zone which is filled with  $10\text{g}$  of Platinum-Alumina catalyst pellets to oxidize any organic combustion products to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (HTO). Any water vapour, including HTO, is trapped in a bubbler which is placed in the cryo-cooler (temperature maintained is  $-110^\circ\text{C}$ ) and  $\text{CO}_2$  gets trapped in the bubbler containing  $20\text{ ml}$  of Carbon Trap, which is an amine with trapping efficiency of  $\sim 96\%$ . After the complete combustion of the sample, an aliquot of  $10\text{ ml}$  carbon trap from the bubbler is mixed with  $10\text{ ml}$  of scintillation cocktail (Carbon Count). After mixing, the samples were stored in dark for overnight so that chemi-luminescence is removed. The samples are then analyzed for  $^{14}\text{C}$  activity in Quantulus 1220 Liquid Scintillation Spectrometer (Perkin Elmer, USA).

## **2.2 Auantulus 1220 LSC**

The QUANTULUS Liquid Scintillation Spectrometer is a beta counter dedicated to ultra low level counting: the thicker shield eliminates effects of

cosmic radiations and consequently reduces background. This makes the QUANTULUS Liquid Scintillation Spectrometer a good choice for Carbon-14-dating (Lim J.M., *et al*, 2015; Tzu-Han Chuang, *et al*, 2015).

Because of the extremely low natural levels of radiocarbon in the earth's atmosphere (about  $1 \times 10^{-10}$  %), accurate measurement of <sup>14</sup>C is not an easy task. These difficulties are further compounded, by the influence of cosmic and environmental background radiation, other radioisotopes being present, electronic noise and instability, and other factors. These background factors limit the accuracy, precision, and range of the radiocarbon dating method because finite ages can only be calculated where sample activity is at least 3 standard deviations above background activity (Gupta and Polach, 1985). Consequently, each of the components of the LS counting system needs to be totally optimised for low-level counting, so as to maintain high counting efficiency whilst significantly reducing the background. The 'total optimisation concept' (Polach, 1987; p.8) has been applied in the design of the Perkin Elmer 1220 Quantulus.

**Fig 3: Diagram of Quantulus 1220 LSC from CARER**

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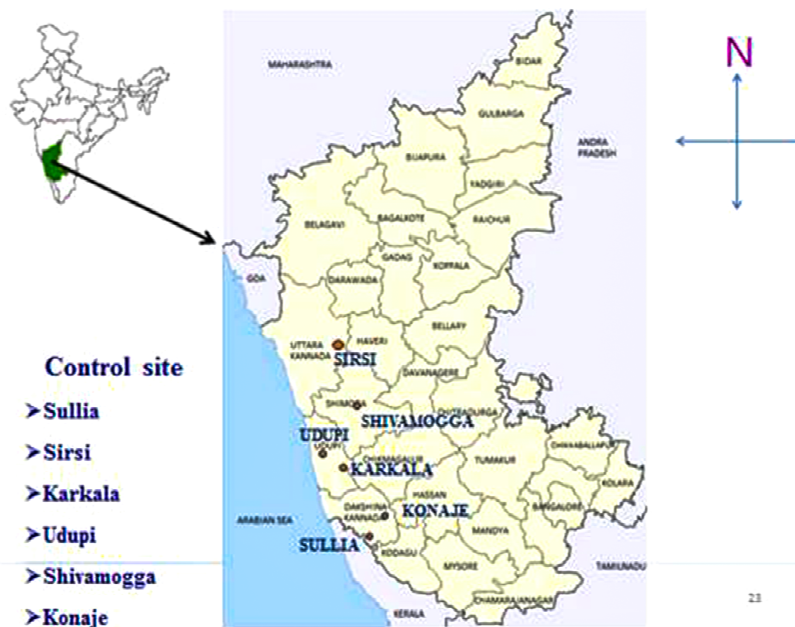
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## Sample Handling

The counting vial is placed into one of three trays located beneath the shield, and counting data (tray position number, 1-60; sample identification number; counting requirements etc) entered into a laboratory computer. The LS vial is housed in a stepped stainless steel sleeve, which forms a light seal when the sample is loaded through the bottom of the shield assembly, by a low activity copper piston. The sample changer and shield areas are refrigerated to reduce the benzene evaporative loss, and also ventilated, to prevent condensation on vials and to eliminate possible radon build-up.

## 2.3 Sample Collection

**Fig 4: Locations from where samples have been collected**



The plant samples such as leaves, vegetables, leafy vegetables and fruits were collected from different locations like Udupi, Mangalore, Sullia, Mala, Shindli and Telagundi.

**Table 1: Location of samples**

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<b>Place</b>	<b>Longitude and Latitude</b>
Udupi	13.3409°N, 74.7421°E
Mangalore	12.9141°N, 74.8560°E
Sullia	12.5581°N, 75.3908°E
Mala	13.2151°N, 74.9961°E
Shindli	14.4905°N 74.9265°E
Telagundi	14.5083°N 74.9150°E

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**Table 2: Biological Name of Collected Samples**

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<b>Samples</b>	<b>Biological Names</b>
Banana Leaves	<i>Musa acuminata</i>
Banana Fruit	<i>Musa acuminata</i>
Guava Fruit	<i>Psidium guajava</i>
Papaya Fruit	<i>Carica papaya</i>

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### **Leaf Samples**

Collected 0.5 kg of fresh tree leaves from the selected location and placed inside a polythene bag, labeled and sealed properly. After bringing the sample to the laboratory, the sample is weighed and stored in the refrigerator till it is taken up for processing.

### **Fruits**

Collected 0.5 kg of fruits straight from the garden and wiped the fruits clean and placed them inside a polythene bag, labeled and sealed properly. After bringing the sample to the laboratory, stored the sample in the refrigerator till it is taken up for processing.

## **2.4 Sample Preparation**

### **Leaf Samples**

The tree leaf samples were taken out of the refrigerator and noted the wet weight. The sample was dried at 80°C, in an oven till complete moisture

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from the sample is removed. The dry weight is noted. The oven dried samples are finely powdered using sample crusher and powdered samples are stored in an air tight polythene container.

### **Fruits**

Stored fruit samples were taken out of the refrigerator. Removed the non-edible portions like seed, skin etc., from the sample and noted the wet weight. The sample was dried at 80°C in an oven till complete moisture from the sample is removed and the dry weight was noted. Next the oven dried samples were finely powdered using sample crusher.

**Fig 5: Fresh Banana Fruit Sample**



**Fig 6: Powdered Banana Fruit Sample**



**Fig 7: Dried Samples Ready for Combustion**



## **2.5 Sample Processing**

At Center for Advanced Research in Environmental Radioactivity (CARER), the environmental samples are combusted by thermal oxidation method (using a Pyrolyser Trio system from RADDEC, UK) for separation of carbon from the sample.

Different leaf and fruit samples from various locations were collected. These were then powdered using a sample crusher and placed in the silica glass work tube within the sample zone of the Pyrolyser and combusted using ORGANIC program in the pyrolyser. The liberated gases during the combustion process are passed through a catalyst zone which is filled with 10 g of Pt-Alumina catalyst pellets to oxidize any organic combustion products to CO<sub>2</sub> and H<sub>2</sub>O (HTO). Any water vapour, including HTO, is trapped in a bubbler which is placed in the cryo cooler (temperature maintained is -110°C) and CO<sub>2</sub> gets trapped in the bubbler containing 20 ml of carbon trap, which is an amine. After the complete combustion of the sample, an aliquot of 10 ml carbon trap from the bubbler is mixed with 10 ml of scintillator and counted in LSC.

### **LSC Calibration**

The sample and standard should have same window settings. Since quenching will affect the spectrum, standard should be prepared in the similar matrix with respect to physical and chemical properties. Also standard should have the same sample to cocktail ratio. Using proper standards calibrate the analyser and estimate the efficiency of C-14.

### **Counting Time**

Counting time for background, sample and standard is 500 min, 300 min and 20 min respectively.

## **3 Results and Discussion**

As mentioned above the plant samples in the form of leaves and fruits were collected and combusted in the RADDEC Pyrolyser to determine the <sup>14</sup>C concentration in the particular samples. The values obtained are given as follows:

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## Leaf Samples

**Table 3: Activity of Leaf Samples**

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Sample name	Place	Activity $\pm$ SDBq kg <sup>-1</sup> C
Banana Leaves	Udupi	250 $\pm$ 24
Banana Leaves	Mala	245 $\pm$ 29
Banana Leaves	Shindli	252 $\pm$ 24
Banana Leaves	Telagundi	230 $\pm$ 23
Banana Leaves	Mangalore	242 $\pm$ 23
Banana Leaves	Sullia	255 $\pm$ 21

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## Fruit Samples

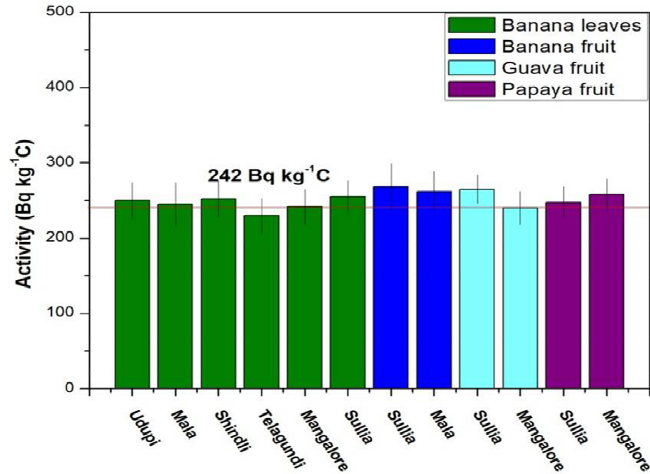
**Table 4: Activity of Fruit Samples**

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Sample name	Place	Activity $\pm$ SDBq kg <sup>-1</sup> C
Banana	Sullia	268 $\pm$ 31
Banana	Mala	262 $\pm$ 26
Guava	Sullia	265 $\pm$ 19
Guava	Mangalore	240 $\pm$ 22
Papaya	Sullia	247 $\pm$ 21
Papaya	Mangalore	258 $\pm$ 21

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**Fig 11: <sup>14</sup>C Concentration in Different Leaf and Fruit Samples from Various Locations**



The calculated <sup>14</sup>C concentration in different leaf and fruit samples from region covering 4 districts show that the values match well with the worldwide <sup>14</sup>C Concentration. Minute increase in the <sup>14</sup>C concentration may be due to the various processes involved in the processing. The standard deviation will take care of the increase in the calculated value of <sup>14</sup>C concentration.

### Estimation of Activity

Following equation must be used to estimate the activity in the sample.

$$A = \frac{(C_s - C_b)}{60 \times E \times Y \times W \times C}$$

Where A is the activity in the sample (Bq kg<sup>-1</sup>C), C<sub>s</sub> is the sample count rate obtained in the sample (Counts/m), C<sub>b</sub> is the background count rate (Counts/m), Y is recovery factor, E is fractional counting efficiency derived from SQP(E) of the sample (derived from the quench curve), W is the weight (kg) of the sample taken for analysis, C is the fractional carbon percent of the sample.

**Estimation of MDA:** Minimum detectable activity of particular radionuclide of a particular system. MDA is calculated using below equation.

$$\text{MDA} = \frac{4.56 \times \sqrt{C_b}}{60 \times E \times W \times C \times T \times Y}$$

Where  $C_b$  is the background count rate (Counts /m), E is fractional counting efficiency derived from SQP(E) of the sample (derived from the quench curve), W is the weight (kg) of the sample taken for analysis, C is the fractional carbon percent of the sample, T is the counting time in minutes, Y is recovery factor.

For 1 g of a sample, counted in LSC for 300 min. with 52% counting efficiency, MDA achieved for  $^{14}\text{C}$  using Pyrolyser – LSC method is 11 Bq  $\text{kg}^{-1}\text{C}$ . Worldwide  $^{14}\text{C}$  background concentration is ~ 242 Bq  $\text{kg}^{-1}\text{C}$ . Pyrolyser-LSC method is capable of measuring  $^{14}\text{C}$  concentration ~20 lower than the background concentration.

#### 4 Conclusion

The carbon-14 concentration in different fruit and leaf samples from various locations of Dakshina Kannada, Uttara Kannada, Udupi region were measured using Pyrolyser - LSC method at Centre for Advanced Research in Environmental Radioactivity (CARER), Mangalore University. The mean values of carbon-14 concentration in Banana leaves is found to be  $246 \pm 9$  Bq  $\text{kg}^{-1}\text{C}$ ; similarly for Banana fruit,  $^{14}\text{C}$  concentration is found to be  $265 \pm 4$  Bq  $\text{kg}^{-1}\text{C}$ .  $^{14}\text{C}$  concentration for Guava and Papaya fruit is found to be  $253 \pm 18$  Bq  $\text{kg}^{-1}\text{C}$  and  $252 \pm 8$  Bq  $\text{kg}^{-1}\text{C}$  respectively.

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