Chapter 5

Application of $^{14}$C-based methods for fuels, flue gases and bio-based materials – An overview with discussion & outlook
5.1 Introduction

This final chapter aims to give an overview of how its several users apply $^{14}$C-based methods for bio-fossil discrimination, and how these methods might be used in the coming years. First (in section 5.2), the disconnection is described between experimental research and ‘routine’ international standards and the impact this knowledge gap can have on the standard-based biogenic carbon fraction results. In section 5.3 an overview is given of the different aspects in the application of $^{14}$C-based methods that can (negatively) affect the final biogenic carbon fraction results if not taken into account. Section 5.4 focuses on the future applications and users of $^{14}$C-based methods for the biogenic carbon fraction determination. And finally, section 5.5 discusses the future use of $^{14}$C-based methods in research and for new applications.
5.2 Application of $^{14}$C-based methods for fuels, flue gases and bio-based materials

The application of $^{14}$C-based methods for fuels, flue gases and also for other kinds of bio-based materials, aims to determine the biogenic carbon fraction. Compared to other determination methods, the $^{14}$C-based methods are acknowledged for their independence, accuracy and relatively straightforward principle: just measure the $^{14}$C amount in the sample material and divide this number by a $^{14}$C value representing 100% biogenic carbon ($^{14}$C$_{bio}$; eq. 1.3). In the real-life application of the methods however, different factors can be identified that influence the reliability of the final obtained biogenic carbon fraction result. These factors affect the determined $^{14}$C$_{sample}$ values (like carbon contamination, carbon partitioning in the pre-treatment, and isotope fractionation) or concern the $^{14}$C$_{bio}$ value of the sample material (large variability) and should be taken into account if accurate sample results and reliable interpretations are required.

To take these factors into account for each individual sample, the impact on the biogenic carbon value should be quantitatively determined and either corrected for or incorporated in the overall uncertainty range. This requires 1) methodological research and validation of the $^{14}$C method for different kinds of sample materials; 2) knowledge about and understanding of the variables in the $^{14}$C-based methods by those involved in the $^{14}$C-based biogenic carbon fraction determination (chain of knowledge & shared method expertise); 3) the ability (in time, funding and laboratory equipment) to gain sufficient additional information, such as multiple subsample analyses and investigations of sample carbon composition and origin (carbon sources). This situation is not different from other research fields where $^{14}$C is used as indirect tracer. Examples (based on own research in these directions) are dating of bones and investigating fossil fuel derived CO$_2$ emissions in the atmosphere (van der Plicht and Palstra, in press; Palstra et al., 2008).

Hence, the use of $^{14}$C as indirect tracer of biogenic carbon fractions in sample materials is in practice very often not so simple and straightforward as the principle of measurement suggests. Especially for those applications of the method where the accuracy and reliability of the results is very important (such as in fraud investigations or investigations of bio/fossil carbon input and output products in production processes), sample-specific approaches are often needed performed or coordinated by methodological experts.
Industrial companies are currently the main users of the $^{14}$C-based methods to determine or verify the biogenic carbon fraction in products and flue gas CO$_2$ emissions. Contrary to most other $^{14}$C applications where scientific researchers often work in close cooperation with the $^{14}$C laboratory involved in sample pre-treatment and $^{14}$C measurements, these users of $^{14}$C-based methods lack scientific and/or experimental knowledge about these methods, and in fact they are not interested in the method as such. These companies have a commercial interest: to obtain within a defined and short time period and for minimal costs, a reliable biogenic carbon fraction, regardless of the used method. To facilitate such companies in finding appropriate methods for biogenic carbon fraction determination in specific materials, several international standards were developed for different kind of materials over the last 5-10 years or are currently under construction (among others: ASTM 6866-12, CEN/TS 15540, CEN/TS 16640, ISO 13833, ISO/PRF 16620-2). In these standards $^{14}$C-based methods are used as measurement method. Except for the sampling and pre-treatment part, the descriptions of the $^{14}$C measurement techniques and calculations of the biogenic carbon fraction hardly differ between these different standards (and are often copied to new standards).

When using these standards, industrial companies sometimes send samples directly to $^{14}$C laboratories with the question to measure the $^{14}$C value of the sample and determine the biogenic carbon fraction according to a specific international standard. In other cases the samples are sent to a commercial laboratory with no $^{14}$C measurement facilities and this laboratory outsources the pre-treatment and $^{14}$C measurement or only the $^{14}$C measurement to a $^{14}$C laboratory (where accredited routine laboratories are sometimes preferred over research laboratories for liability reasons). Several commercial laboratories/research companies as ECN and SGS (see reference list for their websites) have introduced facilitating services for standardized determination of the biogenic carbon fractions in flue gas CO$_2$, based on $^{14}$C measurement results from accredited laboratories only. These services facilitate all steps in the biogenic carbon fraction determination, from sampling to calculation of the fraction.

Accurate determination of the biogenic carbon fraction in a material requires sample-specific approaches, with sample type-specific validated $^{14}$C-based methods, performed by people with specific and sufficient methodological experience and knowledge, and with sufficient means to be able to characterize and minimize systematic and random errors in the obtained biogenic carbon fraction. This is very different to the way in which the $^{14}$C-based methods are currently applied in the standards for industrial purposes. The described standardized $^{14}$C-based methods follow the straightforward approach of a single $^{14}$C measurement of a specific sample material and dividing this measurement value with a fixed ‘standardized’ reference $^{14}$C value for 100% biogenic carbon. By using this simple
approach the standards ignore the different variables within the $^{14}\text{C}$-based methods that should be taken into account if accurate results are required. For example, several standards do not take the large variability in $^{14}\text{C}_{\text{bio}}$ values between different samples into account. Uncertainty ranges in the obtained biogenic carbon fraction are in general not determined for samples individually. Instead, some standards claim a fixed method uncertainty based on average reproducibility results of round-robin assessments (for instance $\pm 3\%$ in ASTM-6866). Isotope fractionation correction for LSC-based $^{14}\text{C}$ results is not a requirement by definition in all the standards, giving erroneous results if the $\delta^{13}\text{C}$ value the biogenic carbon in the sample differs from the normalized value of $-25\%$ (as explained in section 3.4.6).

Biogenic carbon fraction results obtained with standards that apply a simple $^{14}\text{C}$ method approach will only be ‘standardized’ (following a text), but not necessarily accurate nor with minimized uncertainty ranges. Only applying a sample specific method approach can provide that.

Part of the users of the standards might not be interested in very precise and accurate biogenic carbon fraction values ($< \pm 3\%$). For these users, possible deviations in the final result of 10-15% from the true value might not be a problem. This is even likely to be the case if the obtained results are beneficial for the company (which means they are financially more beneficial than a more accurate determination). For those companies the current standards are obviously suitable, as the $^{14}\text{C}$ reference values for 100% biogenic carbon are very often too low compared to the true $^{14}\text{C}_{\text{bio}}$ value, resulting in too high biogenic carbon fractions.

However, companies that want to determine or even verify their product compositions and/or CO$_2$ emissions with smaller systematic errors and higher precision, will likely need more sample-specific methods with additional ($^{14}\text{C}$ and other) measurements and data analysis. The current standards are not suitable for these purposes as they lack sample-specific approaches. Unfortunately, the companies themselves, but also facilitating laboratories and involved (routine) $^{14}\text{C}$ laboratories do not always know this limited applicability of the standards. The mentioned performance characteristics in the standards for a specific group of sample materials might suggest that the standardized method has certain accuracy and is reliable for a whole group of samples. However, this is not necessarily the case. This is misleading for those who are not experienced with the use of $^{14}\text{C}$ as an indirect tracer for the biogenic carbon fraction in different kind of materials.
In the industrial applications of $^{14}$C-based methods, the tendency is to favour the use of standardized methods performed by accredited $^{14}$C laboratories (ISO 17025) only, as this suggests proofed certainty and legal coverage. Currently, only two $^{14}$C laboratories in the world are accredited and perform $^{14}$C analyses for the biogenic carbon fraction determination following ASTM-6866. These are fully commercial laboratories. And only one of these laboratories (Beta Analytics; USA) has long-term experience with $^{14}$C measurements of different fuels, flue gases and bio-based materials. This laboratory was also involved in standardization of the $^{14}$C method for different materials (ASTM and ISO) and is aware of several methodological aspects and shares this with its customers on its website. The other commercial laboratory (Xceleron, USA) has no scientific or methodological expertise with the $^{14}$C method for biogenic carbon fraction determination and only applies the $^{14}$C method according to ASTM-6866. The expertise of this commercial laboratory is in the analysis of (enriched) $^{14}$C samples for pharmaceutical applications.

The other, approximately 140 and mostly academic $^{14}$C measurement facilities in the world that measure $^{14}$C at natural level (not enriched $^{14}$C applications), are not accredited. Only a few of these $^{14}$C laboratories (based on publications roughly < 20) are experienced with the various methodological aspects of the $^{14}$C method for fuels, flue gases and/or bio-based materials and combine academic research and commercial activities for this specific application. These specific laboratories are able to follow standardized $^{14}$C methods, but can also deliver sample-specific biogenic carbon fraction determinations for commercial purposes. The number of not-accredited natural-level $^{14}$C laboratories in the world that are not methodologically experienced, but willing or able to measure $^{14}$C for the biogenic carbon fraction application is difficult to estimate, because part of these facilities is used for a selected group of $^{14}$C applications only and is sometimes not used for commercial applications.

Another reason for companies to choose for one of the two fully commercial $^{14}$C laboratories instead of non- or semi-commercial academic $^{14}$C laboratories, can be the very fast delivery times these commercial companies can offer (1-2 weeks). Because academic research laboratories are usually organised in a different way (combining scientific experimental research with more routine commercial $^{14}$C measurements) and have only partly a commercial interest, their delivery times are usually longer (up to 2 months).

Industrial companies, facilitating companies and a major part of the $^{14}$C laboratories do not have large methodological experience with the $^{14}$C-based methods for biogenic carbon fraction determination. They are therefore in general unaware of the fact that a biogenic carbon fraction based on method descriptions in current standards is not the most accurate value and could be relatively easily improved if an extended sample-
specific $^{14}$C-based method approach would be used. Also, the industrial companies and facilitating companies may not be aware of the fact that not all accredited $^{14}$C laboratories have methodological expertise in the biogenic carbon fraction determination. Especially with $^{14}$C measurements, accreditation of the laboratory itself is not the proof for reliable results if based on words in standards alone. Methodological experience of the $^{14}$C laboratory with both the applied $^{14}$C-based method and with the standardized calculation conventions of the $^{14}$C community, are qualities that might be difficult to ‘prove’ (like accreditation by ISO 17025 gives tools to ‘prove’ quality), but are essential for a reliable determination of the biogenic carbon fraction. One way of testing the quality, reputation and position in the international $^{14}$C network of a $^{14}$C facility, is to check if it has participated in the sequence of large international ring tests for different sample materials (VIRI, Scott et al., 2010).
5.3 Insights in an accurate and reliable application of $^{14}$C-based methods

In this section an overview will be given of different factors that can influence the accuracy and reliability of the $^{14}$C-based biogenic carbon fraction value as determined for any type of material.

Figure 5.1 presents an overview of the general method procedures in $^{14}$C-based methods to measure a certain biogenic carbon fraction in a sample material. In each of the four defined method parts, factors can be identified that affect the final result and its interpretation. These factors determine whether the results are representative for the carbon under investigation and whether the obtained biogenic carbon fraction is in accordance with the real biogenic carbon fraction in the investigated material (accuracy of the method).

![Diagram of 14C-based method procedures](image)

*Figure 5.1. An overview is given of the general $^{14}$C-based methods steps that influence the reliability and accuracy of the measured biogenic carbon fraction.*

5.3.1 Cases in which $^{14}$C-based methods cannot be applied

Prior to the selection of sample material from any type, it should always be examined first whether a $^{14}$C-based method can be used at all to determine the biogenic carbon fraction in the material. Obviously, if a sample material contains no carbon $^{14}$C-based methods cannot be used.

If sample materials contain carbon that is neither from recent biomass (< 200 years), nor from ‘fossil’ ($^{14}$C value 0%; > 50 ka) carbon materials, for instance peat or other
organic soil materials, then a $^{14}\text{C}$ method can only be used if the definition of ‘biogenic’ carbon would be changed. Also, biomass materials from plants that have grown in greenhouses with added fossil CO$_2$ have $^{14}\text{C}_{\text{bio}}$ values that are lower than atmospheric values and are therefore not 100% biogenic by definition (as applied in the $^{14}\text{C}$-based methods), which can be in conflict with other definitions for biomass.

5.3.2 Selection of representative carbon

A very important issue in the determination of the biogenic carbon fraction is whether the carbon used for the $^{14}\text{C}$ analysis is representative for the carbon in the material for which the biogenic carbon fraction has to be determined. The carbon of interest should be specified before sampling and be the only selected and measured carbon source, with no changes in biogenic carbon fraction during the application of the analysis method (incl. sampling and pre-treatment). The molecular carbon composition of the material of interest and the rate of homogeneity in the distribution of biogenic and fossil carbon atoms over the molecules and particles (in case of solid and liquid materials) should therefore be taken into account in the selection of carbon in the different stages of the applied method.

Particles of mixed biogenic and fossil solid materials can contain either biogenic or fossil carbon and the sizes of these particles combined with the amount of subsample that is pre-treated, influences the representativeness of the biogenic carbon fraction that is measured in the selected subsample. To obtain a representative biogenic/fossil carbon mixture, the particles should be as small as possible and homogeneously mixed, and the selected material (subsample) should be as large as possible (feasible within the laboratory logistics/combustion system set ups) to make it representative for the batch under investigation.

For solid fuel composition investigations at large industrial plants (like waste incinerator plans) the most accurate way to determine the biogenic carbon fraction of the input material is by investigation of the flue gas CO$_2$, as was demonstrated in chapter 2.

In $^{14}\text{C}$-based methods the sample materials are always pre-treated such that the carbon of interest in the sample material is obtained as pure CO$_2$. If the carbon in the sample is not CO$_2$ yet, the carbon components of interest are transformed to CO$_2$ in an extraction process (if CO$_2$ is ‘trapped’ as CO$_3^{2-}$ in an alkaline solution) or in a combustion process. If the sample material contains a mixture of different carbon components with different chemical and physical properties and each component has a different biogenic carbon fraction, bio-fossil carbon partitioning (chapter 4) can occur if not all carbon in the sample is transformed into CO$_2$. This can be the case prior to the combustion for liquids with partly volatile carbon components. After sealed storage of the sample material, the
composition of the liquid that is combusted to CO₂ can change during the time period between weighting of the material and the combustion of this subsample, if the volatile components can escape from the subsample. Bio-fossil carbon partitioning can also occur during combustion of mixtures of carbon components, if part of these components are not combusted well at the used combustion temperature and remaining carbon ends up in the ash-fraction.

As volatility and optimized combustion temperatures depend on the chemical composition of the sample materials, additional information about this composition is essential in investigating whether bio-fossil partitioning is likely to occur in the applied pre-treatment method. Pre-treatment methods should be adjusted such that undesired bio-fossil carbon partitioning is limited for the sample under investigation.

Chapters 2, 3 and 4 of this thesis give examples of applications of ¹⁴C-based methods in which specifically defined carbon was investigated. In chapter 2 the fuel-derived biogenic carbon fraction was determined in flue gas CO₂ of a power plant. As the interest was in the fuel-derived carbon only, the measured ¹⁴C results in this study had to be corrected for the ¹⁴C contributions of two other carbon sources: CO₂ from combustion air and CO₂ contamination of the alkaline sampling solution.

In chapter 3 the ¹⁴C values of the two major carbon fractions in the raw biogas samples, CH₄ and CO₂, were measured separately, to investigate differences in carbon origin and isotope fractionation. If a gas sample is sent to a laboratory for biogenic carbon fraction determination and the sample contains different carbon molecules, it should be (made) clear on forehand, which carbon molecules are of interest. If the interest is only in the CH₄ fraction, this fraction has to be separated from the other carbon molecules first, before ¹⁴C measurement. This separation is needed, because the ¹⁴C value of CH₄ can be different from the other carbon fractions.

In chapter 4 the biogenic carbon fractions of raw SNG and process flue gas were investigated. Differences in the biogenic carbon fraction between the solid input material, the flue gas, and the raw SNG, due to carbon partitioning in the SNG production process, made clear that individual carbon in- and output flows are not necessarily representative in biogenic carbon fraction for other carbon flows in the same production process. They should therefore be investigated individually.

Norton (2008) describes an example of regulations (by the United States Department of Agriculture, USDA) in which the bio-based fraction should only be determined in the total organic carbon fraction of the sample. This means that the fraction of inorganic carbon in the (solid) sample material should be excluded somewhere in the method (which can be rather complicated), especially if this fraction has a very different ¹⁴C value compared to the organic carbon fraction and the inorganic fraction in the total carbon is
relatively large. According to Norton: “(...), because of the potential magnitude of the analytical errors involved with analysing carbonate-bearing products, the analyst must always be cognizant of the carbonate issue and must be full aware of its implications”. Specification of the type of carbon to be investigated is in these cases essential, as it determines which (chemical) pre-treatment of the sample material should be used before combustion to CO₂.

The selection of representative carbon requires attention for different features of the carbon selection process by all people involved in this process. The purpose of the investigation and the $^{14}$C measurements should be clear, the carbon of interest should be described, and sampling and laboratory pre-treatment methods should be adjusted and optimized to obtain this specific carbon fraction. If the carbon of interest is only a fraction of the total carbon in the sample, and if this fraction cannot be separated from the total carbon fraction during sampling or pre-treatment, additional information and measurements are required to estimate the carbon contribution that is not of interest and to correct the measured $^{14}$C value of the sample for this contribution.

5.3.3 Reliable determination of $^{14}$C$_{\text{sample}}$

After pre-treatment of the sample material, the obtained carbon fraction is measured in a $^{14}$C laboratory with either AMS, measuring $^{14}$C/$^{12}$C (or sometimes $^{14}$C/$^{13}$C) ion count ratios, or with proportional gas counters (Beta ionization) or LSC instruments, measuring beta counts from $^{14}$C decay.

The reliability of a $^{14}$C$_{\text{sample}}$ value in the biogenic carbon fraction determination is high if 1) this value is calibrated well; 2) it only represents the $^{14}$C amount of biogenic carbon from the carbon of interest; 3) is reproducible (high precision); and 4) equals the true value of the carbon of interest (high accuracy). $^{14}$C laboratories handling enriched $^{14}$C samples are in principle not suitable for the bio-fossil carbon application, due to the high risk of $^{14}$C contamination (affects item 2 and possibly also item 1).

As already explained in section 1.3.2, equation 5.1 (1.4 in section 1.3.2) is used to obtain the same $^{14}$C$_{\text{sample, measured}}$ values for samples with the same biogenic carbon fraction, regardless the origin (in time and formation process) of the carbon materials, the applied $^{14}$C measurement technique and used reference materials (for calibration).

$$^{14}C_{\text{sample, measured}} = 14 a_N = \frac{14 A_N}{14 A_N} = \frac{14 A_{\text{sample}}}{14 A_N} \cdot \left[ \frac{1 + 13 \delta^{13} C_N}{1 + \delta^{13} C_{\text{sample}}} \right]^2 \cdot e^{-\lambda(1950-t_S)} \quad (5.1)$$
This calculation is the internationally agreed, but often confusing, standardized calculation for atmospheric CO₂ samples and atmospheric CO₂-derived sample materials of 1950 and later. It should be used in all \(^{14}\text{C}\) applications in which the biogenic carbon fraction is to be determined. As mentioned in 1.3.2, the decay correction can be left out, if the decay corrections applied in the calculations of \(^{14}\text{C}_{\text{sample}}\) and \(^{14}\text{C}_{\text{bio}}\) are equal.

In many published papers with \(^{14}\text{C}\)-based biogenic carbon fraction determinations, it is often not clear how the reported \(^{14}\text{C}\) values were calculated exactly. Used reference material and applied corrections (isotope fractionation, decay) are not always mentioned. Instead, authors often refer to the paper of Stuiver and Polach (1977). But, as different \(^{14}\text{C}\) applications have different corrections (see also Mook and van der Plicht, 1999), the applied calculation method will not be clear from this paper. The standard way of expressing the \(^{14}\text{C}_{\text{sample}}\) value is usually in %. This \(^{14}\text{C}_{\text{sample}}\) value is sometimes called ‘fraction Modern’ and is expressed as fraction or %. This percentage is often (in research papers and in the standards) called ‘percent Modern Carbon’, abbreviated to pMC and this ‘unit’ then replaces ‘%’ in reported results. Because of the different reference materials, corrections and used symbols and units, the best way to avoid confusion about what the reported \(^{14}\text{C}\) value exactly represents, is to explain in each paper exactly which reference material has been used, whether corrections for isotope fractionation and decay have been applied, how the \(^{14}\text{C}\) values are symbolized and in which unit they are expressed.

To check the validity of the determined \(^{14}\text{C}_{\text{sample, measured}}\) values as obtained under certain measurement conditions and calculated according to equation 5.1, additional measurements under the same measurement conditions of reference materials with known \(^{14}\text{C}_{\text{sample}}\) values need to be performed as well (as part of quality control/quality assurance procedures: QC/QA). At the CIO laboratory the calibration of the \(^{14}\text{C}\) values is checked with certain reference materials and repeated analyses of different types of bio-based materials give indications of the reproducibility of the applied measurement method. Systematic deviations from the true \(^{14}\text{C}\) value, due to the sample pre-treatment step to CO₂, are monitored in inter-comparison tests for different sample materials (THIRI, FIRI and VIRI tests; see Scott et al., 2010 for information about VIRI). So far, these tests did not include the kind of sample materials that are investigated for biogenic carbon fraction determination. CIO participated in different round-robin tests that were organized for validation purposes of standards: for solid recovered fuel (SRF) samples, flue gas CO₂ samples, bio-based materials and rubber, as part of validation tests of international standards (CEN/TS 15440, ISO 13833, CEN/TS 16640 and ISO 19984-2). The results of these tests give an indication of the performance of the CIO analyses compared to other laboratories in the world. To verify whether the obtained \(^{14}\text{C}\) value is a ‘true value’, reference materials are needed which represent the type of sample material with its
specific behaviour during sampling and pre-treatment to CO₂, and for which the ¹⁴C value is exactly known. These reference materials, with different ¹⁴C values that cover the zero to atmospheric ¹⁴C value range, might be for some sample materials difficult to find or produce (in case of mixtures).

In chapter 3, examples were given for the systematic errors in determined biogenic carbon fractions if the isotope fractionation correction (3.4.6; absolute errors up to -10%) and/or the decay correction (3.4.4; absolute errors up to -1%) are not applied at all, or were applied with assumptions that are not exactly valid: neglecting the fossil carbon contribution in the isotope fractionation correction or accept differences in decay correction between the ¹⁴C_sample and the ¹⁴C_bio values.

In addition to figure 3.2, figure 5.2 gives an overview of relative errors in the determined biogenic carbon fractions, if the isotope fractionation correction (based on δ¹³C_bio values) is not applied at all.

Figure 5.2. Relative difference in calculated biogenic carbon fraction with the true biogenic carbon fraction, if the isotope fractionation correction (based on ¹³C_sample = ¹³C_bio) is not applied.
The effects are indicated for different biomass(-based) materials. Some $^{14}\text{C}$ laboratories, mainly LSC laboratories, do not have equipment (IRMS) to measure $\delta^{13}\text{C}$ values and therefore report uncorrected $^{14}\text{C}_{\text{sample}}$ values if the $\delta^{13}\text{C}$ value of the biogenic carbon in the material is not known (or estimated) otherwise. Especially CO$_2$ and CH$_4$ fractions of (raw) biogas have relatively large errors in the calculated biogenic carbon fractions if the isotope fractionation correction is not applied. Absolute systematic errors are maximal for 100% biogenic materials and can then be maximal -10% for the CH$_4$ fraction. The relative systematic error in the determined biogenic carbon fraction of the CO$_2$ fraction of biogas samples, not indicated in figure 5.2, can be between +1 and +5% if no isotope fractionation correction is applied.

Only if the $^{14}\text{C}_{\text{bio}}$ value of the biogenic carbon fraction in a sample material can be separately determined, the size of the isotope fractionation correction will be almost equal to the correction of the measured $^{14}\text{C}_{\text{sample}}$ value. In those cases these two isotope fractionation correction factors cancel each other in the calculation of the biogenic carbon fraction and isotope fractionation correction can be neglected. In practise, $^{14}\text{C}_{\text{bio}}$ values are based on given ‘standard’ values or otherwise based on atmospheric $^{14}\text{CO}_2$ measurements and these values need to be corrected for isotope fractionation (as the atmosphere has different $\delta^{13}\text{C}$ values compared to most biogenic carbon materials).

In the calculation of the biogenic carbon fraction (eq. 1.3) the $^{14}\text{C}_{\text{sample}}$ value should only represent the carbon of interest and contributions of other carbon sources to the measured $^{14}\text{C}$ value should be left out as explained in section 1.3.3 (eq. 1.9). Examples of these kinds of corrections were demonstrated in chapter 2 for combustion air and contamination (section 2.2.3; eq. 2.2 and eq. 2.3). In those cases $^{14}\text{C}_{\text{sample}}$ is not identical to $^{14}\text{C}_{\text{sample measured}}$.

### 5.3.4 Representative determination of $^{14}\text{C}_{\text{bio}}$

As explained in section 1.3.3 and demonstrated in chapter 3 (sections 3.4.4 and 3.4.5), the $^{14}\text{C}$ reference value for 100% biogenic carbon, $^{14}\text{C}_{\text{bio ref}}$, in the investigated sample material can vary considerably between different (mixtures of) biomass materials, due to an annual decrease in average atmospheric $^{14}\text{CO}_2$ values over the last 60 years. In section 3.4.5 we introduced an approach to approximate the $^{14}\text{C}_{\text{bio}}$ value if this value cannot be determined by analysis of the biogenic carbon material itself. This approach aims to reduce systematic errors in the determined biogenic carbon fraction and results in lower uncertainty ranges. For this approach additional independent information about the origin of the biomass is essential. This information is, however, not always available and the approach requires additional knowledge and understanding of the $^{14}\text{C}$ method. Some standards, as ASTM 6866 and ISO 13833, therefore use one $^{14}\text{C}_{\text{bio}}$ value for simplicity,
regardless of the (average) harvest time and the (average) period of growth. This chosen value represents an average atmospheric $^{14}$CO$_2$ value as measured in one particular recent year and the idea (by those involved in making and revising the standards) is to adjust this value in the standards approximately every 5 years, to keep the reference value in line with the decreasing trend in the atmospheric $^{14}$CO$_2$ values.

Figure 5.3 shows the absolute systematic errors in the determined biogenic carbon fraction if a recent atmospheric $^{14}$CO$_2$ value of 101 pMC is used as $^{14}$C$_{bio}$ value, while the true average $^{14}$C$_{bio}$ value of the sample equals a certain atmospheric $^{14}$CO$_2$ value in the period 1975-2013. This is demonstrated for samples with 100%, 50% and 10% biogenic carbon.

![Figure 5.3. Absolute error in the determined biogenic carbon fraction for the case where $^{14}$C$_{bio}$ is set to a value of 101 pMC while the true average value of a biomass material is equal to a certain average atmospheric $^{14}$CO$_2$ value as measured by CIO at monitoring stations Smilde (Netherlands; 1975-2002) and Lutjewad (Netherlands; 2003-2013) between 1975 and 2013. The 2020-value shows an example of the deviation observed in 2013-biomass from a depleted (urbanized) region ($^{14}$C$_{sample}$ value of 99 pMC). The majority of the currently used annual-plant biomass materials origin from the time period marked with the green box.](image)
Wood-based materials investigated at CIIO over the last years (as solid wood, flue gas and raw SNG) showed $^{14}$C values between 110 and 130 pMC. Studies by Mohn et al. (2008) and Fellner and Rechberger (2009) about average $^{14}$C values of waste-materials and wood-based materials also showed this range of values. They calculated average values for waste and wood-based materials between 113-117 pMC. This value was also found in our biogas study for biogas from an old landfill site (section 4.4.4). Waste and wood-based materials show systematic higher $^{14}$C values than the $^{14}$C values of current harvest years. For these kinds of materials the $^{14}$C$_{bio}$ value should therefore not be based on current atmospheric $^{14}$C values, as errors in the biogenic carbon fraction can be up to +30% if 100% biomass materials are determined. If a biogenic carbon fraction of for example 110% is calculated this way, one cannot be sure that this material is 100% biogenic, as this biogenic carbon fraction can in principle be 85% wood carbon with a $^{14}$C value of 130%, mixed with 15% of fossil carbon. Also, true biogenic carbon fractions of 50% or 10% will be determined as 58% and 12%, respectively. Hence: sample materials will appear to be containing more biogenic carbon than they actually do. The fraction of fossil carbon is then underestimated.

The use of representative $^{14}$C$_{bio}$ values in $^{14}$C-based methods is thus essential for reliable determination and verification of the biogenic carbon fraction. The studies by Mohn et al. (2008) and by Fellner and Rechberger (2009) have given reliable $^{14}$C values and uncertainty ranges for waste and wood-based materials that could be used as reference $^{14}$C value. The European standard for SRF/waste materials (CEN/TS 15440) uses an average $^{14}$C value for waste that is relatively similar to the average value determined by Mohn et al. (2008). Several other international standards however, which could in principle be used for a wide variety of materials including wood-based and mixed (waste) materials (like ASTM 6866, ISO 13833 and CEN/TS 16640), use only one recent harvest-year $^{14}$C$_{bio}$ value. If those standards are used for these particular materials, the obtained biogenic carbon fractions can deviate substantially from the true values. Standards using recent harvest-year $^{14}$C$_{bio}$ values only are not suitable for accurate biogenic carbon fraction determination of waste and wood-based materials.

The majority of the biomass from annual plants that is used in fuels and other bio-based materials were harvested less than 10 years ago, probably mostly even less than 5 years ago. Errors in the biogenic carbon fraction are then maximal 5% (for 100% biogenic carbon), and in general below 2%, if a very recent harvest year is used as $^{14}$C$_{bio}$ value.

For composite bio-based materials (different bio-based ingredients that were used in the production of the material), other than waste, the (proportional) average $^{14}$C value can vary substantially as well. This can result in errors in the biogenic carbon fraction if either the reference value for waste or a more recent harvest year value is used. The $^{14}$C$_{bio}$
value for these kinds of materials depends on the overall $^{14}$C value of each bio-based carbon fraction and the size of this fraction in the total bio-based carbon fraction in the sample. If for instance products are made from a mixture of wood and recent annual plant materials, the range of possible $^{14}$C$_{bio}$ values is relatively large and depends mostly on the sizes of the fractions of wood-carbon and plant-carbon in the material. For samples with these kinds of bio-based mixtures, a sample-specific approximation of the $^{14}$C$_{bio}$ value, using independent information about the used bio-based ingredients, is essential to minimize systematic errors in the calculated biogenic carbon fraction.

5.3.5 $^{14}$C-based biogenic carbon fraction

The previous sections demonstrated the different factors that affect the biogenic carbon fraction and its representativeness for the carbon under investigation. The described factors influence the reliability of the results and should therefore be taken into account in the application of $^{14}$C-based method. As the biogenic carbon fraction can be determined in a wide range of materials with different characteristics and features (solid, liquid, gas; waste, defined products; wood-based materials, annual plants), the influence of the different factors and its impact on the final determined biogenic carbon fraction varies therefore as well. Due to these observed differences between samples, the $^{14}$C-based methods must be employed in a sample-type specific way. Depending on the required level of accuracy, sample-type specific features need to be added to each $^{14}$C-based method.
5.4 Future use of $^{14}$C-based methods for fuels, flue gases and bio-based materials

The production and use of biomass-based materials is increasing for a wide range of products. Besides using biomass as fuel, it is used to an increasing extent as an ingredient in the production of for instance plastics and chemicals. A broad range of materials claimed as “100% bio” or produced from mixtures of biogenic and fossil carbon molecules is appearing on the consumer markets. Another development that is currently visible is the increased use of waste materials as fuel (waste-to-energy plants) or as ingredient for the production of new fuels (such as SNG production from waste: see reference “Swindon”).

$^{14}$C-based methods are mentioned in several regulations, such as a European Union (EU) regulation in which a distinction is made between biogenic and fossil CO$_2$ (2007/589/EC, 2007) or Mandate M/475 of the European Commission (development of CEN standard to guarantee bio-methane quality). In both cases $^{14}$C-based methods are mentioned as possible test methods to determine biogenic carbon fractions. It is, however, the question whether $^{14}$C-based methods will really be used for these purposes. This depends mainly on who has what kind of (financial) interest to know the biogenic carbon fraction. As long as suppliers of bio-methane (such as farmers or gasifier plants) or industrial plants with large CO$_2$ emissions (such as power plants) have already easier (and cheaper) methods to calculate the biogenic carbon content of their output products based on the information about their input materials, it is not likely that they will use $^{14}$C-based methods. Only if the input material has an unknown and variable composition, like waste materials from mixed fossil and biogenic origin, some producers of gas or CO$_2$ emissions, might be interested in specific determination methods, like the $^{14}$C-based methods. But this is probably only going to be the case if knowing the biogenic carbon composition is financially beneficial. In the EU Emissions Trading System for instance, current emission prices for fossil CO$_2$ emissions are very low, which does in the first place not enhance the use of alternatives for fossil fuels and secondly makes knowing the amount of biogenic CO$_2$ emissions (as these have no CO$_2$ emissions costs) less needed.

As $^{14}$C-based methods can be used to independently verify reported biogenic carbon fractions of fuels, flue gases and bio-based products (fraud investigation), authorities are potential users of these methods. Because verification procedures are very costly this application of $^{14}$C-based methods is probably only of interest if the financial benefits are larger than the costs to verify products and emissions. So far, the CIO laboratory has never received samples for bio/fossil carbon verification by authorities (except for cases concerning ingredients for food).
The main and increasing interest in using $^{14}$C-based methods to determine biogenic carbon fractions comes currently from (industrial) companies using biomass-based materials in the manufacturing of their products. If in production processes the biogenic/fossil carbon composition of the different ingredients is not known, or if bio-fossil partitioning might occur during the process, then the biogenic carbon fraction of the end product is unknown as well. $^{14}$C-based methods can then be very beneficial in giving insight in the composition of separate carbon input and output flows of the production process. Also, an independent determination of the biogenic carbon fraction of the output material gives the opportunity to verify claims of “100% bio” and certify to customers the biogenic character of certain products (some customers base their decision to buy a certain product on this biogenic aspect).

Current international standards for measurement of biogenic carbon fractions in specific sample materials try to facilitate producers with relatively simple and straightforward $^{14}$C-based methods. But, as already discussed in section 5.2, it is the question whether these standardized methods are in all cases accurate enough to certify and verify products. Especially for products with mixtures of different biogenic carbon sources, and also for unknown material mixtures, it can be quite difficult to achieve an accurate result, if no additional information and knowledge about the origin of the material and its ingredients are used.

$^{14}$C-based methods are not easy to standardize, by using just one measurement and calculation procedure. Which procedure or exact method, should be used to accurately determine the biogenic carbon fraction of the carbon of interest, depends on the sample material under investigation. As discussed in section 5.3, several sample dependent factors can affect the final result and thus affect the final interpretations and conclusions. Very often, $^{14}$C measurements of the sample materials alone do provide a good indication of the biogenic carbon fraction, but not more than that. To give a really accurate answer to the question: “What is the biogenic carbon fraction in this particular material?” additional measurements and information about carbon components in the sample materials or in the production process are an essential part of the $^{14}$C method.

The unsurpassed quality of $^{14}$C-based methods for biogenic carbon fraction measurements is unnecessarily deteriorated, if ‘standardized’ methods are used that apply $^{14}$C-based methods in their most straightforward mode without mentioning the possible systematic uncertainty ranges of the final result and without mentioning how this uncertainty ranges could be improved (decreased) with additional measurements and/or data analyses.
Instead, for standards in which a $^{14}$C-based method is used for biogenic carbon fraction measurement, it is recommended to describe a procedure in which the following information will always be provided to the user of the method: 1) the quality of the data (uncertainty ranges), 2) how this quality can be related to the applied determination method (what factors have influenced the given uncertainty range) and 3) the available option, beyond the scope of the standard, to further improve or optimize the results by sample-specific method approaches. $^{14}$C-based methods can only be used in an optimal way by a broad range of users, if knowledge about these methods is shared as much as possible.
5.5 Future research of $^{14}$C-based methods to distinguish biogenic and fossil carbon sources

Over the last ten years many research studies were performed to show the use of $^{14}$C-based methods for biogenic carbon fraction measurement of different sample materials. Beside the studies as mentioned in the previous chapters in which $^{14}$C-based methods were investigated for different kinds of fuels and flue-gases, other studies focused on the use of $^{14}$C-based methods for several bio-based products (Norton et al. 2007; Funabashi, 2009; Kunioka, 2010; Quarta, 2013). Most of the aspects that influence the $^{14}$C-based results have already been identified and described in papers. It is, however, likely that in the coming years several studies will investigate the applicability of $^{14}$C-based methods for new types of materials and/or production processes. Other research topics that can be expected are more detailed investigations of specific aspects that influence the biogenic carbon fraction results. To investigate for instance the variability in results between different materials or between samples of the same material (validation research).

So far, the output of all these studies is only partly used in the international standards. This is probably because suggested new approaches based on the results from the several studies, make the standardized procedures in general less straightforward and ask more knowledge and expertise from the users of the standard. It is difficult to implement this knowledge in these standards.

This is a challenging part for researchers in this field as, due to the standards and the preference of industrial companies for working with accredited ('standardized') laboratories, the connection between (academic) research laboratories and the users of $^{14}$C-based data is not always a direct link and knowledge of the researchers is therefore not easily shared with these users. Following the recommendation described at the end of section 5.4 could be a first step to share more scientific information with the users of standards: information about the quality of the method results and about the option to improve the accuracy if desired with sample specific approaches.

Only if there is direct contact between customers of a $^{14}$C-based method and a research laboratory with knowledge about all features of this specific method, it is possible to follow a specific procedure with the aim to obtain results that are optimized for the sample material under investigation. This is the strength of academic research laboratories, as these are familiar with investigating on an experimental foundation and not following standardized procedures only. However, thorough research will be costly and time consuming. Therefore, it is expected that sample-specific approaches that can be performed very well by academic research groups, are most likely to be used in research projects of customers: when new products or production set-ups are investigated and tested. And it is also likely that for more regular tests of products, the international
standards and commercial laboratories will be used for quick and low-cost results. These results will be less accurate, but good enough for their purpose.

For future research of $^{14}$C-based methods, the challenge for the experienced research groups is to get into, and stay in contact with new users: producers of new bio-based materials and researchers of chemical (production) processes.