On 14C-based methods for measuring the biogenic carbon fraction in fuels and flue gases
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Chapter 1

Introduction –

$^{14}$C-based methods for measuring the biogenic carbon fraction in fuels and flue gases
1.1 A global interest to distinguish biogenic from fossil carbon

This thesis is about a method to determine the biogenic carbon fraction in different kinds of materials, in particular flue gases and fuel gases. The radioactive carbon isotope $^{14}$C (also called radiocarbon) is used in this method to distinguish the biogenic and fossil carbon fractions.

The current interest to distinguish between biogenic and fossil carbon fractions in the production and combustion of certain (fuel) products is related to policy measures that have been taken over the last 10-20 years, to reduce the dependence on fossil carbon materials and to decrease the amount of fossil fuel CO$_2$ emissions into the atmosphere. European Union (EU) Directive 2009/28/EC for instance describes the promotion of the use of energy from renewable sources. The use of biogenic carbon materials or mixed bio-fossil waste materials as alternative for fossil carbon materials is encouraged and financially stimulated. Also from an ethical point of view, biogenic carbon products are marked to consumers as positive ‘green’ products and stated to be ‘better for the environment’. Producing biogenic carbon products or ‘green’ energy (from biogenic carbon materials or waste) therefore sells, even if the consumer has to pay a higher price. And these products can in several cases be more profitable for industrial companies and agricultural companies (farmers) than producing fossil-based products or food products, respectively.

The international political wish to decrease fossil fuel CO$_2$ emissions is caused by concerns about the increase of the global average atmospheric CO$_2$ concentration over the last century. CO$_2$ is a ‘greenhouse gas’ (like CH$_4$, CO, H$_2$O and N$_2$O) and the molecules absorb a large fraction of the thermal infrared radiation that is emitted from the earth’s surface, and the higher the concentrations of the greenhouse gases are, the larger this fraction becomes. This causes an unbalanced situation in which less energy (through radiation) is leaving Earth than is taken up (from sunlight) and an average global increase of the temperature of the lower atmospheric layer occurs: global warming. Over the last century different greenhouse gas concentrations, especially CO$_2$, CH$_4$ and N$_2$O have increased. Long-term temperature records at different locations on Earth show a trend of increasing average temperatures. It is almost certain that this global warming is related to the increase of the greenhouse gas effect. Global warming is expected to induce non-equally distributed temperature and climate changes on Earth and might have severe effects on (human) life already in the coming century. Extensive information about greenhouse gases and global warming can be found in the IPCC 2013 report of working group I (IPCC, 2013; chapter 2 by Hartmann et al., 2013).

Due to this threat of global warming, international policy measures are taken to reduce anthropogenic greenhouse gas emissions and/or stop a further increase of atmospheric greenhouse gas concentrations. Examples of policy measures within the
European Union (EU) concerning the reduction of (fossil) CO₂ emissions and other greenhouse gas emissions, are directive 2009/29/EC about the greenhouse gas emission allowance trading scheme of the EU community, combined with decisions 2007/589/EC and 2011/540/EU to establish guidelines for the monitoring and reporting the emissions of CO₂ and other greenhouse gases.

The increase of the global average CO₂ concentration in the atmosphere over the last century is mainly due to the use and combustion of fossil fuels such as coal, natural gas, lignite and gasoline, and fossil (waste) products from petroleum (such as plastics). The use of these fossil materials has increased over the last century. After World War II the use of fuels increased significantly in Europe and the United States of America. Due to the continuously increasing world population combined with the further economical development of several (large) countries in the world (such as China, Brazil and India), the use of fossil carbon materials is currently still increasing (IEA, 2014a; 2014b).

Fossil carbon materials are stored in the deep underground and do not have interaction with the carbon exchanging reservoirs on Earth (atmosphere, oceans and biosphere), at least not on a “human” time scale of centuries to millennia. The fossil carbon materials are therefore not part of the global carbon cycle in which a relatively balanced uptake and release of carbon between the atmosphere and the oceans and biosphere takes place (in a cycle of approximately 100 years). Without anthropogenic activities, natural carbon exchange processes determine atmospheric CO₂ concentrations in time. However, the combustion of the fossil materials causes fossil CO₂ emissions into the atmosphere, and so this fossil carbon becomes part of the global carbon cycle. The fossil CO₂ is initially mixed with the atmospheric CO₂, but is then divided over the different carbon reservoirs. Currently about 35% of the emitted (mainly fossil) CO₂ amount is taken up by the oceans and about 15% by the biosphere. The atmospheric CO₂ increases therefore in time with an amount that equals ≈50% of the added (fossil) CO₂. Detailed information about the global carbon cycle and fossil CO₂ emissions can be found in IPCC report 2013 (chapter 6; Ciais et al., 2013).

Anthropogenic activities in which biogenic carbon materials are used and combusted and CO₂ is released into the atmosphere have a different effect on the global average CO₂ concentrations in time than CO₂ from fossil materials. Plants, trees, animals and manure are examples of biogenic carbon sources. The products made from these materials are sometimes also called ‘bio-based products’. These materials and products contain carbon that was recently taken up from the atmosphere by photosynthesis of CO₂ (in general for plant-based materials <10 years ago and tree-based materials <50 years ago). The anthropogenic activities in which bio-based products are used will cause a certain release of CO₂ into the atmosphere in time again, by for instance combustion and decomposition. If the average yearly rate of CO₂ uptake by plants and trees equals the average yearly
release of CO₂ from biogenic carbon materials into the atmosphere (such that the biogenic carbon reservoir on land remains constant in size), then these specific anthropogenic activities (influencing both CO₂ uptake and CO₂ release) will not change the average global atmospheric CO₂ concentration. The use of biogenic carbon materials is therefore promoted as alternative for fossil materials: as a way to stop a further increase of the atmospheric CO₂ concentrations (so-called ‘climate neutral’ or ‘CO₂-neutral’ measures).

Besides the climate aspect, biogenic carbon materials are currently also promoted as an alternative for fossil materials to decrease the dependency on fossil carbon materials in the global geopolitical trading arena. The production of bio-based materials and products is therefore currently also a booming business in developed countries, as it gives industrial and agricultural companies and farmers in those countries new economic perspectives.

Figure 1.1 gives an example of the increased use of biogenic fuels in power generation from biogenic materials since 2006 and with predictions for the period 2014-2018 (IEA, 2013). A further increase in the production and use of biogenic fuels is expected for the coming years.


Despite this increase, the fraction of biofuels and waste in the total primary energy supply of the world is still the same as it was in 1973: only 10%, while the worlds total primary energy supply increased from 256 EJ (6106 Mteo) in 1973 to 560 EJ (13371 Mteo) in 2012. This 10% also includes the use of wood materials as fuel for domestic purposes (heating, cooking), mainly in undeveloped countries. Trees used for these domestic purposes are not always replaced by new ones and the 10% of ‘bio’-energy is therefore
not necessarily 100% CO₂-neutral. It is expected that the world primary energy demand will further increase in the coming future with in average 1.2% per year until (at least) 2035 (IEA, 2014b). The share of the fossil fuels decreased from 87 to 82% in the period 1973-2012, mainly due to the relative increased contributions of nuclear power and hydropower (IEA, 2014a) and some scenarios predict a further decrease to approximately 76% in 2035 (2014b). Fossil fuel use will nevertheless still increase in absolute numbers. These numbers about primary energy supply and demand give insight in the large and increased amount of fossil fuels that are used in the world. The numbers explain the ongoing increase in atmospheric CO₂ concentrations (expected: 0.7% per year for the period 2012-2035; IEA 2014b) and show the large dependency on fossil energy sources. The numbers also show the challenge to replace these high calorific fossil carbon sources with other, sustainable, CO₂-neutral and non-carbon energy sources as alternatives.

The ethical and financial values of products and flue gas CO₂ emissions increase with increasing biogenic carbon fraction. For producers of (partly) bio-based products, it can therefore be of interest to determine the biogenic carbon fraction in a produced product, for instance if such a product is to be sold with a certain specified biogenic carbon content. If a production process starts with mixed input materials it may be worthwhile to investigate in what ratio the biogenic and fossil carbon fractions end up in the final products. For authorities it can be of interest to check (for fraud investigation) products on the market that are sold as ‘100% bio-based’, but could also have been made from (usually cheaper) fossil carbon or mixed bio-fossil waste materials.

In EC decisions 2007/589/EC and 2011/540/EU to establish guidelines for the monitoring and reporting the emissions of CO₂ and other greenhouse gases by large (industrial) companies, a distinction is made between biogenic and fossil CO₂ emissions. Only the biogenic CO₂ can be emitted ‘for free’. Industrial companies have to report their biogenic and fossil CO₂ emission to national emission authorities. As soon as the combustion of biogenic carbon materials becomes financially profitable, these industrial companies might want to know their biogenic CO₂ emissions exactly. The emission authorities might want to verify reported biogenic and fossil CO₂ emission to prevent fraud.

In all these cases, especially with unknown biogenic composition of the ingredients of products and of combusted fuels, a determination method is needed which can distinguish between biogenic and fossil carbon fractions and which can accurately quantify the biogenic carbon fraction in the product, fuel or flue gas CO₂. To serve fraud identification purposes the method should also be independent: the analysis data should be obtained independent from the producer.
The biogenic carbon fraction of (fuel) products or flue gas CO$_2$ can in some cases be determined or approximated based on the use of statistics or specific data about the biogenic or fossil carbon origin and carbon content of the ingredients of (combusted) products. For flue gas CO$_2$ the biogenic carbon fractions can also be determined based on combustion parameters, which are different for biogenic and fossil carbon materials ("Balance method", Fellner et al., 2007). The biogenic carbon fraction of solid waste materials is sometimes determined with the so-called ‘selective dissolution method’ (Staber et al., 2008). However, especially for legal verification and certification purposes, for bio-fossil carbon partitioning investigations in production process, and if unknown and variable mixtures of biogenic and fossil carbon materials are used (like in waste materials), these indirect determination methods essentially lack the accuracy and reliability or cannot be used at all. Instead, a method is required in which the biogenic and fossil carbon fractions can be directly and independently distinguished based on carbon characteristics of the carbon atoms themselves. Methods using the carbon isotope $^{14}$C as tracer for biogenic carbon are so far the only of such atom-scale measurement methods.
1.2 $^{14}$C as tracer for biogenic and fossil carbon fractions

In $^{14}$C-based methods to distinguish biogenic and fossil carbon fractions, the carbon isotope $^{14}$C is used as a tracer for biogenic carbon. Carbon consists almost exclusively of the stable isotopes $^{12}$C (≈99%) and $^{13}$C (≈1%). Less than $10^{-10}$% of the global carbon atoms is radioactive $^{14}$C ($t_{1/2} = 5730$ a). These atoms are continuously produced in the high stratosphere by nuclear reactions between cosmic ray neutrons and $N_2$ at a relatively constant rate. $^{14}$C from the stratosphere is then oxidized to $^{14}$CO$_2$ and mixed with $^{12}$CO$_2$ and $^{13}$CO$_2$ in the lower atmospheric layers.

Plants and trees take up atmospheric CO$_2$, a mixture of site-specific fractions of $^{12}$CO$_2$, $^{13}$CO$_2$ and $^{14}$CO$_2$, by photosynthesis. Biogenic carbon materials (here defined as carbon taken up < 200 years ago from the atmosphere) therefore contain a certain carbon fraction of $^{14}$C. As soon as an organism dies the uptake of $^{14}$C atoms stops and the $^{14}$C fraction decreases in time (the rate of decay is used in dating materials). Due to this decay, fossil carbon materials, with ages of millions of years, contain no $^{14}$C anymore. Biogenic carbon therefore has a certain $^{14}$C fraction that represents 100% biogenic carbon, while fossil carbon contains no $^{14}$C and represents 0% biogenic carbon. If biogenic and fossil carbon components are mixed the $^{14}$C fraction of the biogenic carbon is diluted with the $^{14}$C-free fossil carbon fraction. The $^{14}$C fraction in the mixed material will then be between zero and the $^{14}$C fraction of the biogenic carbon, proportional to the biogenic carbon fraction. This dilution principle is used to calculate the biogenic carbon fraction in sample materials.

$$^{14}C_{\text{sample}} = ^{14}C_{\text{bio}} \times f_{\text{Cbio}} + ^{14}C_{\text{fos}} \times f_{\text{Cfos}}$$

(1.1)

In this equation 1.1, $^{14}C_{\text{sample}}$, $^{14}C_{\text{bio}}$ and $^{14}C_{\text{fos}}$ represent the fractions of $^{14}$C in the carbon of the sample, the biogenic carbon and the fossil carbon respectively, as measured, calculated and expressed in a certain way, as explained in section 1.3.2. $f_{\text{Cbio}}$ and $f_{\text{Cfos}}$ are the biogenic and fossil carbon fractions respectively, in the total carbon fraction of the sample. Combining equation 1.1 with $f_{\text{Cfos}} = 1 - f_{\text{Cbio}}$ gives the equation for the determination of the biogenic carbon fraction:

$$f_{\text{Cbio}} = (^{14}C_{\text{sample}} - ^{14}C_{\text{fos}})/(^{14}C_{\text{bio}} - ^{14}C_{\text{fos}})$$

(1.2)

As the $^{14}$C value of the fossil carbon, $f_{\text{Cfos}}$, is zero this equation can be simplified to:

$$f_{\text{Cbio}} = ^{14}C_{\text{sample}}/^{14}C_{\text{bio}}$$

(1.3)

Hence, to quantify the biogenic carbon fraction in a sample, the $^{14}$C value of the sample material should be measured and then divided with the $^{14}$C value of the biogenic carbon fraction in the sample, $^{14}$C$_{\text{bio}}$. 
1.3 Determination of $^{14}\text{C}_{\text{sample}}$ and $^{14}\text{C}_{\text{bio}}$

To calculate the biogenic carbon fraction, the values of $^{14}\text{C}_{\text{sample}}$ and $^{14}\text{C}_{\text{bio}}$ need to be determined. The values are obtained from carbon isotope measurements of the carbon fraction in a sample combined with specific calculations to normalize and calibrate the measured signals to a certain $^{14}\text{C}$ quantity.

To measure the carbon of interest, sample materials are first pretreated to obtain a pure carbon fraction (as graphite or CO$_2$). The applied pretreatment depends on the type of sample material and the used $^{14}\text{C}$ measurement technique. In general, solid and liquid fuels can be combusted directly to CO$_2$. Gas samples can be combusted directly to CO$_2$ as well, depending on the composition of the gas and the research question. In case of gases with large CO$_2$ and CH$_4$ fractions (raw biogas) for instance, these fractions can first be separated before combustion of the CH$_4$ fraction to analyze the fractions separately. Flue gas CO$_2$ can be sampled in an alkaline solution or in a specific solid absorber and the CO$_2$ fraction can be measured after removal from the absorber material. If flue gas is sampled in a gasbag, the CO$_2$ fraction in this gas sample first needs to be separated from the other gas components before it can be further pretreated and/or analyzed. In chapters 2-4 different pretreatment methods as applied by the Centre for Isotope Research for fuels and flue gas CO$_2$ are explained in more detail.

1.3.1 $^{14}\text{C}$ measurement

Currently there are three different $^{14}\text{C}$ measurement techniques to determine $^{14}\text{C}$ in carbon samples with natural (low-level) $^{14}\text{C}$ concentrations.

Proportional gas counters and liquid scintillation counters (LSC) measure signals induced by beta ions from $^{14}\text{C}$ decay. The size of the signal is proportional to the number of $^{14}\text{C}$ atoms in the detector, and depends on the total amount of carbon introduced into the detector (which needs to be determined accurately as well). Arnold and Libby (1949) were the first who investigated the measurements of beta ions from $^{14}\text{C}$ decay. They experimented with proportional gas counters for the measurement of beta ions from the decay of $^{14}\text{C}$ in bio methane and tried detectors in which the decay counts of solid carbon samples were measured. De Vries and Barendsen (1952) of the University of Groningen further improved the $^{14}\text{C}$-beta ion detection technique by developing gas proportional counters with purified sample CO$_2$ as counting gas and taking specific measures to reduce background counts. The Centre for Isotope Research of the University of Groningen has used this $^{14}\text{CO}_2$ measurement technique (with some adjustments in time) until 2011.

The LSC measurement technique to measure $^{14}\text{C}$ was also developed in the 1950s (Polach, 1992). In this technique the carbon of investigation is part of a liquid cocktail with a certain solvent and scintillator. After beta decay of $^{14}\text{C}$, the energy of the beta particles is taken up and re-emitted by the solvent molecules and by the scintillation molecules. The excited scintillation molecules emit photons, which are measured by photomultiplier
Introduction

Accelerator Mass Spectrometry (AMS) (Purser, 1992) is in use since the 1990s as $^{14}$C measurement technique. The technique has been adjusted and improved over the years (Synal, 2013). The carbon isotopes $^{12}$C, $^{13}$C and $^{14}$C in the investigated (and purified) carbon sample, either graphite or CO$_2$, are ionized and separated from each other and from other (molecular) ions based on differences in mass/charge ratio. The CIO laboratory operates since 1994 a $^{14}$C-dedicated AMS system based on a 2.5 MV Tandetron accelerator and built by High Voltage Engineering Europe (Wijma et al., 1996). The $^{14}$C analyses described in chapters 2, 3 and 4 are all measured with this AMS system. Figure 1.2 gives an overview of this particular AMS system, which is described in detail in Wijma et al. (1996).

![Schematic setup of the $^{14}$C-dedicated 2.5 MV Tandetron operated by the CIO laboratory.](image)

A carrousel with 59 targets with graphite samples is placed in the ion source. This source sputters Cs in a high intensity towards the graphite surface and produces a C$^-$ beam by irradiation of the graphite. During a sample run the graphite target is sputtered several times at different positions of the surface area. The ionized carbon enters the recombinator using specific focusing lenses and magnets. The very abundant $^{14}$N atoms, an isobar of $^{12}$C (similar mass), do not obtain a negative current and are removed from the carbon beam before entering the recombinator. In the recombinator the ions with masses 12, 13 and 14 are first separated and the relatively large $^{12}$C beam is then reduced with a factor of about 90. With magnets the separated masses are recombined and
Laser-based $^{14}$C measurement methods for low-level $^{14}$C applications are investigated since approximately 10 years. Two techniques have been proposed. The first is detection based on Cavity Ring Down Spectroscopy (CRDS), a highly sensitive optical technique that is nowadays commercially available for accurate on-line measurements for atmospheric trace gases and stable isotope ratios. One group is striving to reach the ultimate sensitivity needed for $^{14}$C detection at levels below those in present day material with the final goal to make the technique fully competitive with AMS. (Galli et al., 2013). Other groups have adapted the very successful Picarro commercial CRDS set-up for $^{14}$C detection, aiming at use for applications in pharmacy and biomedicine, where researchers use samples that are orders of magnitude enriched in $^{14}$C (McCartt et al., 2015; Genoud et al., 2015).

The second technique is based on Intra-Cavity Opto-Galvanic Spectroscopy (ICOGS) and is in use for atmospheric tracer measurements and for $^{13}$C in breath analysis. In 2008 Murnick et al. announced to have caused a breakthrough in sensitivity. In this paper the group claimed to have reached a detection limit for $^{14}$C in atmospheric CO$_2$ that is comparable to AMS. Several groups then followed up on this, among which also the Centre for Isotope Research. To their disappointment, the results were not reproducible (Persson et al., 2013). Just recently Paul and Meijer (2015) in our group finally proved the technique to be not useful for $^{14}$C detection, not even for very enriched levels of $^{14}$C.
Introduction

1.3.2 Calculation of $^{14}$C values

The $^{14}$C value of a measured sample, $^{14}C_{\text{sample\_measured}}$, is calculated according to equation 1.4. The value is usually expressed in '%', but in the application for fuels and flue gases 'pMC' (percent Modern Carbon) is also used. The use of 'pMC' as unit for $^{14}$C values instead of '%' in bio-fossil carbon measurements can avoid confusion between reported $^{14}$C values and biogenic carbon fractions.

$$^{14}C_{\text{sample\_measured}} = ^{14}C_N \cdot \frac{^{14}A_N}{^{14}A_{RN}} = \frac{^{14}A_{sample}}{^{14}A_{RN}} \cdot \left[ \frac{1 + \delta^{13}C_{N}}{1 + \delta^{13}C_{sample}} \right] \cdot e^{\lambda (t_{1950}-t_s)} \quad (1.4)$$

This particular equation is, by convention, used by $^{14}$C laboratories to calculate atmospheric CO$_2$-based $^{14}$C values in carbon materials formed in the period after 1950AD, regardless the type of sample material, the used measurement technique, the variations in measurement efficiency and the time and location of measurement. More detailed information on the international conventions and their history can be found in Stuiver and Polach (1977) and Mook and van der Plicht (1999).

The given symbols (of 'a' and 'A') are equal to those suggested by Mook and van der Plicht (1999). The symbols '0', 'N', 'S' and 'R' refer to the application of normalization of the reference materials to $t_0 = 1950$ ('0'), normalization of the isotope fractionation ('N'), and decay correction ('S'), or indicates whether a measured abundance is from a reference material ('R'). The equation can be divided in three parts.

The first part, $^{14}A_{\text{sample}}$, is the main calibration part of the measured signals. It relates the sizes of measured $^{14}$C signals' in the sample ($^{14}A_{\text{sample}}$), to the measured signals of a reference material for which the $^{14}$C abundance is set equal to a certain fixed number ('standard activity', valid for 1950 AD), $^{14}A_{RN}$. For AMS measurements these measured signals are $^{14}$C/$^{12}$C (or sometimes $^{14}$C/$^{13}$C) ion count ratios, and for proportional gas counters and liquid scintillation counters these are beta decay counts (in Bq).

In this part of the equation the measured signal is standardized to obtain $^{14}$C amounts in the same (relative) unit, regardless the used measurement technique. It is also corrected for variations in $^{14}$C signal due to variations in measurement efficiency and for background counts of $^{14}$C contamination from the laboratory pre-treatment and noise signals of the instrument:

$$\frac{^{14}A_{\text{sample}}}{^{14}A_{RN}} = \frac{\left(^{14}A_{\text{sample}} - ^{14}A_{bg}\right) \cdot \text{meas eff}_{\text{sample}}}{x_{RN} \cdot \left(^{14}A_{\text{ref\_meas}} - ^{14}A_{bg}\right) \cdot \text{meas eff}_{\text{ref\_std}}} \quad (1.5)$$
If the sample and reference material are measured with the same measurement efficiencies, the efficiency factor ratio can be left out. $x_{RN}^0$ is a correction factor which consists of two parts:

$$x_{RN}^0 (ref) = \frac{1}{a_{RN\_ref}^{14}} \left[ \frac{1 + \delta^{13}C_N}{1 + \delta^{13}C_{ref}} \right]^2$$  \hspace{1cm} (1.6)

The first part, $\frac{1}{a_{RN\_ref}^{14}}$, normalizes the measured $^{14}$C amount in the reference material to the standard activity value as defined for 1950 AD. Most $^{14}$C laboratories use Oxalic Acid I (SRM 4990B) and/or Oxalic Acid II (SRM 4990C) as reference materials. Different reference materials have in general different $^{14}$C abundances. If not taken into account, the $^{14}$C abundance ratio of the measured sample material with the reference material would not only depend on the $^{14}$C abundance in the sample material (which is investigated), but would also depend on the measured reference material. The value of $^{14}$C$_{sample\_measured}$ should however not vary with used reference material and the measured $^{14}$C abundances of the reference standards are therefore normalized to a fixed standard activity value. $a_{RN\_ref}^{14}$ is the 1950 AD $^{14}$C abundance of the reference material relative to the standardized activity value: ($^{14}$A$_{ref\_meas}$ - $^{14}$A$_{biog}$/ $^{14}$A$_{RN}$ and its reciprocal value gives the correction factor to correct the value of the reference material to the standardized value. $\frac{1}{a_{RN\_ref}^{14}}$ is 0.95 for Oxalic Acid I (OXI) and 0.7459 for Oxalic Acid II (OXII).

In the second parts of equations 1.4 and 1.6 ($\left[ \frac{1 + \delta^{13}C_N}{1 + \delta^{13}C_{sample}} \right]^2$ and $\left[ \frac{1 + \delta^{13}C_N}{1 + \delta^{13}C_{ref}} \right]^2$ respectively), the measured $^{14}$C abundances of the sample and reference material are corrected for isotope fractionation. The $^{14}$C/$^{12}$C abundance ratios of different carbon components show some variation due to mass-dependent chemical and physical reaction during the formation (production) of these compounds and during sampling, pretreatment and measurement of the carbon. This is called isotope fractionation (Mook, 2000). Measured $^{14}$C abundances in samples with the same biogenic carbon fraction and the same $^{14}$C$_{bio}$ value can therefore differ if the differences in isotope fractionation rate are not taken into account. This will undesirably result in the calculation of different biogenic carbon fractions, while these are in fact equal.
A correction for isotope fractionation is therefore applied. The rate of fractionation as measured in the sample is normalized to a fixed and standardized value. As the isotope fractionation rate of $^{14}$C is difficult to determine based on changes in the relatively small $^{14}$C measurement signals, the correction factor cannot be determined based on $^{14}$C measurements. The isotope fractionation correction factor of $^{13}$C on the other hand is well measurable. And because there is a relatively constant relation between the fractionation rates of $^{13}$C and $^{14}$C ($^{13}\alpha^2 = ^{14}\alpha$; Mook, 2000), the isotope fractionation correction factor for the measured $^{14}$C abundance, can be approximated based on $^{13}$C measurements and the relation in isotope fractionation rates between $^{13}$C and $^{14}$C.

In equations 1.4 and 1.6, $\delta^{13}C_{N}$ is the standardized isotope fractionation value. This value is -25‰ with respect to the international $^{13}$C calibration material VPDB (Gonfiantini, 1984) for sample materials and for reference material OXII. For reference material OXI the value for normalization is -19.2‰ (with respect to VPDB).

The isotope fractionation value of a sample, $\delta^{13}C_{sample}$, is determined by measuring the $^{13}$C/$^{12}$C ratio with Isotope Ratio Mass Spectrometry (IRMS) and/or with AMS. In both cases, the measured $^{13}$C/$^{12}$C ratio of the sample is calculated relative to the $^{13}$C/$^{12}$C ratio of VPDB:

$$\delta^{13}C_{sample} = \frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{VPDB}} - 1 \text{ (Usually expressed in ‰)} \quad (1.7)$$

This VPDB material is usually not measured. Instead, the measured $^{13}$C/$^{12}$C ratio of the sample is calculated relative to the measured $^{13}$C/$^{12}$C ratio of a local reference material, $\left(\frac{^{13}C}{^{12}C}\right)_{ref meas}$ (usually the average value of multiple analyses in the same measurement batch), that is calibrated with respect to VPDB, $\delta^{13}C_{ref}$:

$$\delta^{13}C_{sample} = \frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{ref meas}} \cdot \left(1 + \delta^{13}C_{ref}\right) - 1 \quad (1.8)$$

In this equation it is assumed that all variables that affected the $^{13}$C/$^{12}$C ratio of the reference material at a certain rate, like variations in measured signals and also isotope fractionation during pre-treatment and measurement of the reference material, did affect the $^{13}$C/$^{12}$C ratio of the sample material at least in the same rate. In that case the effects of these particular variables on measured signals of the sample and reference material are ruled out in equation 1.8. The measured $^{13}$C/$^{12}$C ratio of the reference material then directly represents the $\delta^{13}C_{ref}$ value of the reference material as determined (and
standardized to a certain value) relative to the VPDB standard. The $\delta^{13}\text{C}_{\text{ref}}$ values of reference materials OXI and OXII are 19.2 $\%_o$ and -17.8 $\%_o$, respectively, with respect to VPDB (Mann, 1983). As for OXI both $\delta^{13}\text{C}_N$ and $\delta^{13}\text{C}_{\text{ref}}$ are the same, the fractionation correction part of 1.6 can be left out (= 1).

In chapter 3 the isotope fractionation correction of the sample based on the measured $\delta^{13}\text{C}_{\text{sample}}$ value is discussed, because in some cases (especially with methane) anomalies are observed in the final calculated biogenic carbon fraction if the contribution of the fossil carbon fraction to the $\delta^{13}\text{C}_{\text{sample}}$ value is not left out.

The third part of equation 1.4, $e^{\lambda \cdot (t_{1950} - t_{s})}$, corrects the measured $^{14}\text{C}$ abundances of the sample and the reference material for $^{14}\text{C}$ decay since 1950 ($t_0$). As explained, the $^{14}\text{C}$ abundance of the reference material is corrected to a fixed standardized value that is valid for 1950 AD. A nowadays-measured reference material (with measurement time $t_m$), however, does not have the $^{14}\text{C}$ abundance anymore that was calculated for 1950 ($^{14}\text{CO}_2^{0 \text{RN, ref std}}$; eq. 1.6), due to decay. Hence, a decay correction needs to be applied to the measured $^{14}\text{C}$ abundance of the reference material to obtain the standardized 1950-value again: $e^{\lambda \cdot (t_m - 1950)}$. For sample material the $^{14}\text{C}$ abundance has decreased in the time period between sampling ($t_s$) and measurement ($t_m$). To obtain the $^{14}\text{C}$ abundance of the material direct after sampling a correction needs to be applied as well: $e^{\lambda \cdot (t_m - t_s)}$. As the sample and reference material correction factors are divided in equation 1.4, the net decay correction factor in this equation is $e^{\lambda \cdot (1950 - t_s)}$, with $\lambda = \ln 2 / t_{1/2}$. The half-life of $^{14}\text{C}$, $t_{1/2}$, is 5730 a (Godwin, 1962).

If, in the calculation of the biogenic carbon fraction, both the biogenic carbon in a sample and the carbon representing 100% biogenic carbon have the same $t_s$ value, this decay correction will be similar for both $^{14}\text{C}_{\text{sample, measured}}$ and $^{14}\text{C}_{\text{bio}}$. In that case the decay correction factor cancels in the combined equations 1.3 and 1.4 and can be left out of the calculation. This can be of interest in case $t_s$ is not known and it is known that the biogenic carbon in the investigated sample has the same (time) origin as the carbon representing the $^{14}\text{C}$ value of 100% biogenic carbon. It should always be clear whether $^{14}\text{C}_{\text{sample}}$ values used in the calculation of the biogenic carbon fraction are corrected for decay or not.

Using symbols when reporting $^{14}\text{C}_{\text{sample}}$ can help to identify the applied calculation method: $^{14}\text{C}_{\text{sample}}$ symbolized with $^{14}\text{a}_N$ is only corrected for isotope fractionation, while symbolized with $^{14}\text{a}_N^5$ it is also corrected for decay correction (Mook and van der Plicht, 1999).
1.3.3 Definition of 0% biogenic carbon and determination of $^{14}$C$_{sample}$ and $^{14}$C$_{bio}$

Equation 1.3 is the general equation for the calculation of the biogenic carbon fraction in a sample. In this equation it is assumed that the fossil carbon fraction has not contributed to the $^{14}$C abundance of the measured sample carbon. In those cases, samples with 100% fossil carbon and thus 0% biogenic carbon have $^{14}$C abundances comparable to background samples. The practical detection limit of the current $^{14}$C measurement is $^{14}$C$_{sample\_measured} = 0.1 - 0.2 \%$. For dating purposes this would correspond to a dating limit of about 50 ka. This implies that all carbon with ages >50 ka is ‘fossil carbon’ (although not always millions of years old) and the measured $^{14}$C abundances in these carbon samples represent 0% biogenic carbon.

In general, the measured $^{14}$C value, $^{14}$C$_{sample\_measured}$, as calculated according to eq. 1.4 will be used as the value for $^{14}$C$_{sample}$ in the calculation for the biogenic carbon fraction. This value should, however, only represent the carbon of interest. In some cases other carbon sources, from the same sample material or contamination, have contributed to the measured $^{14}$C value. In those cases $^{14}$C$_{sample}$ is not equal to $^{14}$C$_{sample\_measured}$ as the contributions of the other carbon sources should be corrected for:

$$^{14}C_{sample} = \frac{^{14}C_{sample\_measured} - \Sigma(^{14}C_{(C_i)} \cdot f_{(C_i)})}{\sum f_{(C_{to\_be\_investigated})}}$$

(1.9)

In this equation $^{14}$C$_{sample}$ is the $^{14}$C value of the carbon for which the biogenic carbon fraction is determined; $^{14}$C$_{sample\_measured}$ is the measured $^{14}$C value in the sample (eq. 1.4); $f_{(C_{to\_be\_investigated})}$ is the carbon fraction of the carbon of interest in the measured carbon; $^{14}$C$_{(C_i)}$ and $f_{(C_i)}$ are the $^{14}$C$_{sample}$ value and carbon fraction in total measured carbon respectively, of each carbon source $i$ that should not be part of the biogenic carbon fraction determination.

Examples of these kinds of corrections and ways to determine the carbon fractions and $^{14}$C values of particular carbon sources that need to be left out are demonstrated in chapter 2 for combustion air and contamination (section 2.2.3; eq. 2.2 and eq. 2.3).

The $^{14}$C$_{bio}$ value should represent the $^{14}$C value of 100% biogenic carbon. Ideally, all biogenic carbon would have the same and known $^{14}$C value; then this value would be a known constant and only $^{14}$C$_{sample}$ should have to be determined for the biogenic fraction calculation. Unfortunately, this $^{14}$C$_{bio}$ value is not a constant, as it is determined by the $^{14}$CO$_2$ values in the atmosphere and these are very variable in time and space. Besides several natural variations, which are relatively small, the $^{14}$CO$_2$ level in the atmosphere has shown large variations over the last century due to different anthropogenic activities.

Introduction
(Levin and Hessheimer, 2000; Levin et al., 2010; Hua et al., 2013). Suess (1955) noticed a small decreasing trend in the atmospheric $^{14}$CO$_2$ values (measured in tree-rings) of the period 1875-1953. This trend is related to the increasing combustion of fossil fuels. The main annual changes in the $^{14}$CO$_2$ values of the atmosphere over the last 60 years, however, are related to aboveground nuclear bomb tests in the 1950s and 1960s. These bomb tests almost doubled the $^{14}$CO$_2$ values in the atmosphere within 5 years, time, with a maximum in 1963. In 1963 an international treaty banned the aboveground tests. Since then, the atmospheric $^{14}$CO$_2$ values decreased annually, mainly due to carbon exchange between the atmosphere and the oceans and biosphere. Current atmospheric $^{14}$CO$_2$ levels are close to the level before the nuclear bomb tests, but will further decrease with continuing fossil fuel-derived CO$_2$ emissions (‘Suess-effect’).

The $^{14}$C$_{bio}$ value of the biogenic carbon fraction in a sample therefore depends on the time period in which plants or trees (the original material of biogenic materials) have taken up $^{14}$CO$_2$ and depends also on the location (see Palstra et al., 2008 for an example of temporal and spatial variation in $^{14}$C values measured in wine-ethanol). If a sample material contains carbon from different biogenic materials originating from different batches of plants and/or different species, then the $^{14}$C$_{bio}$ value of a sample will be the average of all individual $^{14}$C$_{bio}$ values, weighted by their carbon share in the total material. Hence, $^{14}$C$_{bio}$ values are sample specific and need to be determined for each sample individually. The best way to determine $^{14}$C$_{bio}$ for a specific sample is, obviously, by measuring the $^{14}$C value of this biogenic carbon fraction. However, this biogenic carbon (mixture) is usually not separately available (e.g. in waste materials) or representatively measurable (e.g. mixtures of solid materials with variable $^{14}$C values). In these cases the $^{14}$C$_{bio}$ value of a sample needs to be approximated based on atmospheric $^{14}$CO$_2$ data, combined with information about the (time) origin of the biogenic carbon fraction. An approach for $^{14}$C$_{bio}$ determination is described and discussed in chapter 3.
1.4 Application of \( ^{14} \text{C} \)-based methods for fuels and flue gases

\( ^{14} \text{C} \)-based methods, in which \( ^{14} \text{C} \) measurements are used to determine the biogenic carbon fraction in a sample material, are investigated and applied since the 1950s in different research fields. The general principle of these methods is very straightforward and this makes it applicable for a wide range of sample materials. It is, for instance, used in atmospheric research for the investigation of atmospheric carbonaceous gases and aerosols (Clayton et al., 1955; Currie et al., 1994, Zondervan and Meijer, 1996) and in food authenticity research (Simon et al., 1968). With the increasing interest in the production and combustion of bio-based (fuels) products and quantification of biogenic CO\(_2\) emissions, a new application has been found. Approximately 10 years ago the first papers were published about the application of \( ^{14} \text{C} \)-based methods for the biogenic carbon fraction determination in different manufactured products (Norton et al., 2007; Kunioka et al. 2007), liquid fuels (Dijs et al., 2006), solid fuels (Staber et al., 2008) and flue gas CO\(_2\) from waste incinerators (Mohn et al., 2008). Since then, many other publications have followed.

Given the fundamental simplicity of the use, the well-established analysis of \( ^{14} \text{C} \) from any source and the available routine sample pre-treatments, methodological research of the \( ^{14} \text{C} \)-based methods might seem superfluous. The accuracy and reliability of a \( ^{14} \text{C} \)-based biogenic carbon fraction, however, depend on different aspects such as representative carbon selection and using an accurate \( ^{14} \text{C}_{\text{bio}} \) value. The importance of these aspects varies for different sample materials and therefore they need to be identified for each sample type, such that they can be taken into account if necessary. Whether these aspects should be taken into account in the measurement of the biogenic carbon fraction depends on the desired accuracy of the result and/or the purpose of the analyses: verification (and possible fraud detection) of product claims might require more accuracy than a quick product scan.

This thesis describes the results of three studies (Palstra and Meijer, 2010; Palstra and Meijer, 2014; Palstra et al., 2015) in which different methodological aspects of the \( ^{14} \text{C} \)-based biogenic carbon fraction measurement were investigated. The application of \( ^{14} \text{C} \)-based methods was investigated for different types of fuel gases and flue gases. In chapter 2 the results are given of a study in which the biogenic carbon fractions of flue gas CO\(_2\) samples were determined at a power plant and a waste incineration plant. The \( ^{14} \text{C} \)-based results of the power plant were, for verification of the applied \( ^{14} \text{C} \)-based method, compared with biogenic carbon fractions as calculated based on carbon composition and flow data of the separate biogenic and fossil fuel materials (wood and coal). Chapter 3 describes and quantifies the main uncertainty factors in the biogenic carbon fraction measurement for fuel gases (in particular methane). The application of a \( ^{14} \text{C} \)-based
method to quantify bio/fossil carbon partitioning in the production process of synthetic natural gas from a mixture of wood and lignite, is demonstrated in chapter 4. Finally, chapter 5 gives an overview of several methodological and practical aspects of $^{14}$C-based methods if used for flue gases, fuel gases and other (partly) bio-based products in general.