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## Carbon-14 based determination of the biogenic fraction of industrial CO<sub>2</sub> emissions – Application and validation

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### ABSTRACT

The <sup>14</sup>C method is a very reliable and sensitive method for industrial plants, emission authorities and emission inventories to verify data estimations of biogenic fractions of CO<sub>2</sub> emissions. The applicability of the method is shown for flue gas CO<sub>2</sub> samples that have been sampled in 1-h intervals at a coal- and wood-fired power plant and a waste incineration plant. Biogenic flue gas CO<sub>2</sub> fractions of 5–10% and 48–50% have been measured at the power plant and the waste incineration plant, respectively. The reliability of the method has been proven by comparison of the power plant results with those based on carbon mass input and output data of the power plant. At industrial plants with relatively low biogenic CO<sub>2</sub> fraction (<10%) the results need to be corrected for sampled <sup>14</sup>CO<sub>2</sub> from atmospheric air.

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### 1. Introduction

The current net increase of atmospheric CO<sub>2</sub>, which enhances global warming and related changes in the Earth's climate system (IPCC, 2007), is mainly due to the combustion of fossil fuels, because its carbon was not part of the Earth's present day carbon cycle before it was combusted. Biomass carbon, on the contrary, is part of the carbon cycle and the combustion of biomass material does therefore not result in a significant net increase of CO<sub>2</sub> in the atmosphere as long as new biomass is grown again.

The interest in the use of biomass materials as fuels for different industrial plants, like power plants, has increased in the previous years. In many countries around the world governments have implemented financial incentives (subsidies, CO<sub>2</sub> trading system (2003/87/EC, 2003), emission taxes), especially for industrial plants, to discourage the emission of CO<sub>2</sub> due to the combustion of fossil fuels, while the combustion of biomass has been made attractive. A consequence of these kinds of regulations, and their financial implications and interests, is that emission data have to be quantified, monitored and reported annually by the companies involved. Moreover, these data should be verifiable by the emission authorities. This requires accurate, reliable and verifiable methods enabling the CO<sub>2</sub> emissions of fossil fuels and biomass to be quantified separately. At an industrial plant, the most direct way to determine the partition of the biogenic and fossil CO<sub>2</sub> emissions is to investigate the flue gas CO<sub>2</sub> itself. If the composition of the

fuel mixture is completely unknown it is in fact the only reliable way. Quantification of the biogenic and fossil CO<sub>2</sub> fractions in flue gas has been demonstrated in the literature by using the <sup>14</sup>C method (Mohn et al., 2008; Reinhardt et al., 2008; Staber et al., 2008) and the balance method (Fellner et al., 2007).

The <sup>14</sup>C-based method to determine the biogenic and fossil carbon fractions in samples has been investigated and described since the 1950s for different research fields like atmospheric research (atmospheric carbonaceous gases and aerosols) (Clayton et al., 1955; Currie et al., 1994; Zondervan and Meijer, 1996) and food authenticity research (Simon et al., 1968). It is based on the principle that biogenic and fossil carbon sources have very different <sup>14</sup>C values. Fossil carbon sources, like natural gas, coal, mineral oil and its products, do not contain the radioactive <sup>14</sup>C (half-life 5730 years) anymore due to their age (millions of years). Recent (<200 years) biogenic carbon sources, like biomass, have well measurable <sup>14</sup>C values that equal the average <sup>14</sup>C value of atmospheric CO<sub>2</sub> of the time-period in which the specific organisms lived. The relation between the fraction of biomass in a sample and its <sup>14</sup>C value is linear. This relation is used to determine the biogenic carbon fraction of many different sample types by measuring <sup>14</sup>C.

Regarding the principal simplicity of the use, the well-established analysis of <sup>14</sup>C in CO<sub>2</sub> (of any source) and the routine extraction, validation of the method is from a scientific point of view superfluous. However, industrial applications of the <sup>14</sup>C method for this purpose, especially with legal consequences, require proper standardization. Examples of industrial applications are the <sup>14</sup>C analysis of solid recovered fuels (CEN/TR15591, 2007), petrol and flue gas CO<sub>2</sub> (European patent by Kneissl (2002) and ASTM

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D6866-08 (2008)). So far, very little data has been published in scientific papers about the validation, reliability and applicability of the  $^{14}\text{C}$  method for flue gas samples of industrial plants (Mohr et al., 2008; Staber et al., 2008). More studies have been performed, but these have, unfortunately, not been officially published for a wide audience (Fichtner, 2007; Raber, 2003). Hämäläinen et al. (2007) have investigated the  $^{14}\text{C}$  values in flue gas  $\text{CO}_2$  samples of different power plants in Finland, but did not calculate the biogenic  $\text{CO}_2$  fraction. The American test method ASTM D6866-08 (2008) is currently the only available standard that can be used for the  $^{14}\text{C}$ -based determination of the biogenic fraction of flue gas  $\text{CO}_2$ . The  $^{14}\text{C}$  method to quantify the biogenic  $\text{CO}_2$  fraction of industrial  $\text{CO}_2$  emissions using flue gas  $\text{CO}_2$  is therefore still not widely recognized in the field of potential users.

This paper shows the results of a project in which the biogenic fraction of sampled flue gas  $\text{CO}_2$  of a power plant and a waste incineration plant in the Netherlands have been determined based on  $^{14}\text{C}$  analyses. The reliability of the  $^{14}\text{C}$  method has been validated by comparing the  $^{14}\text{C}$ -based biogenic  $\text{CO}_2$  fractions of the power plant samples with those based on known carbon in- and output mass data of the power plant. On the basis of the results and experiences of this project, the applicability and reliability of the used  $^{14}\text{C}$  method to determine the biogenic fraction of industrial  $\text{CO}_2$  emissions are discussed.

## 2. Methods

In this chapter the method is described, which has been used to determine the biogenic fraction of  $\text{CO}_2$  emissions of a power plant and a waste incineration plant based on the  $^{14}\text{C}$  analysis of flue gas  $\text{CO}_2$  samples. The method can be divided into three parts: (1) the sampling of the flue gas  $\text{CO}_2$ , (2) the off-line  $^{14}\text{C}$  analysis, including sample pre-treatment and (3) the calculation of the biogenic  $\text{CO}_2$  fraction.

### 2.1. Sampling

Flue gas  $\text{CO}_2$  has been sampled in cooperation with staff members of the Energy research Centre of the Netherlands (ECN), at the Dutch power plant “Amercentrale-08” of energy company Essent in Geertruidenberg from 26–27 August 2008 and at the Dutch waste incineration plant “AVI AZN Moerdijk” in Moerdijk from 28–29 August 2008.

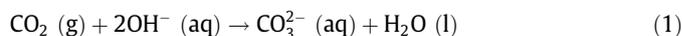
At the power plant, pulverized coal is combusted together with grinded wood pellets from two separately supplying biomass units. Before the flue gas from the combustion of coal and biomass is released into the atmosphere via a chimney, it has been washed to remove pollutants (e.g.  $\text{SO}_2$ ) and it has been reheated to prevent flue gas condensation in the chimney. The flue gas is reheated by adding, from three different inlets, flue gas from a natural gas fired

gas turbine into the coal/biomass–flue gas flow. All inlets are located 40 m before the chimney. This addition of (fossil)  $\text{CO}_2$  increases the  $\text{CO}_2$  emission of the power plant with approximately 4%. Flue gas has been sampled a few meters from the location where flue gas enters the chimney. Hence, a mixture of flue gas  $\text{CO}_2$  from the combustion of coal, biomass and natural gas has been sampled.

About 10 flue gas  $\text{CO}_2$  samples have been sampled at the power plant (four on the first day and six on the second day) by using a sample probe, a flue gas sampling set and a flue gas  $\text{CO}_2$  sampler developed by ECN. The sampling set-up is schematically shown in Fig. 1.

The sample probe entered approximately 15 cm into a large flow gas tunnel (of approximately 8 m deep and high). The filtered, cooled and dried flue gas passed three different analyzers that were placed serially (first to analyze  $\text{O}_2$ , then  $\text{CO}_2$  and  $\text{CO}$  and finally  $\text{NO}_2$  and  $\text{NO}$ ). The  $\text{CO}_2$  concentration (of main interest compared to the other measured components) has been continuously measured on the two sampling days with an ABB URAS 26 NDIR Analyzer and was on average 11% v/v.

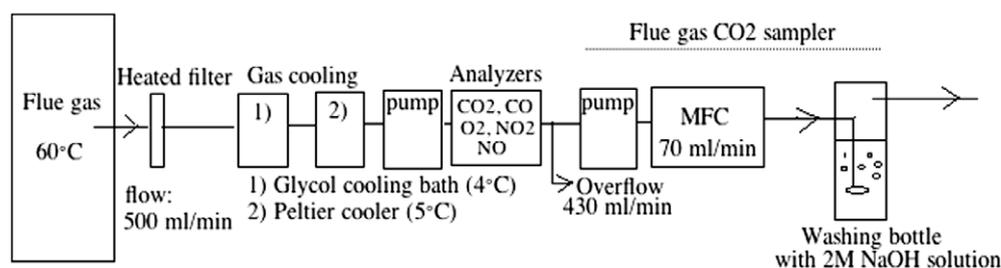
For the sampling of flue gas  $\text{CO}_2$ , flue gas has been sucked with a flow of 70–80 ml flue gas/min through a washing bottle that contained 200 ml 2 M NaOH solution. A sampling interval of 45 min has been chosen for each sample. The flue gas  $\text{CO}_2$  dissolves in the NaOH solution according to:



At the investigated waste incineration plant waste materials from different and variable sources, but mainly municipal waste (75% m/m), are combusted in four separate ovens at. 13 samples of flue gas  $\text{CO}_2$  (eight on the first day and five on the second day) have been sampled from emission pipe number 2 using the flue gas  $\text{CO}_2$  sampler of ECN. This flue gas  $\text{CO}_2$  sampler (pump, MFC and washing bottle with NaOH solution as shown in Fig. 1) has been connected to a tubing in which flue gas flowed that had already been filtered, cooled, dried and measured (without changing the carbon composition of the flue gas) by devices of Multi Instruments Analytical B.V. This company performs continuous measurements at AZN Moerdijk of several compounds (e.g.  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{CO}$ ,  $\text{O}_2$  and  $\text{CO}_2$ ) in flue gas. The flue gas  $\text{CO}_2$  has been sampled with the same flow (70–80 ml/min), sampling time (45 min) and NaOH volume (200 ml) as at the power plant.

### 2.2. $^{14}\text{C}$ analysis

Each 200 ml NaOH sample with dissolved flue gas  $\text{CO}_2$  has been stored in a closed plastic bottle before it was pre-treated and analyzed on  $^{14}\text{C}$  at the CIO laboratory. The pre-treatment of each NaOH sample consisted of the extraction of  $\text{CO}_2$  in a vacuum pumped system by addition of a few millilitres of sample to a few millilitres of



**Fig. 1.** Schematic overview of the used sampling set-up at the power plant to sample flue gas  $\text{CO}_2$ . The flue gas  $\text{CO}_2$  sampler, which is integrated in this figure, has been used at the waste incineration plant as well to sample flue gas  $\text{CO}_2$ . The sampler has been developed by ECN and consists, beside some electronics and a computer device, of a pump, a mass flow controller (MFC) and a washing bottle with NaOH solution. The washing bottle contains a borosilicate filter to obtain small flue gas bubbles in the solution and by that encourages the dissolution of the  $\text{CO}_2$  in the NaOH solution.

H<sub>3</sub>PO<sub>4</sub> (85% v/v). Water vapour and CO<sub>2</sub> were released in the chemical reaction between the acid and the sample. The water vapour has first been removed (cryogenic with dry ice/ethanol) and then the CO<sub>2</sub> has been cryogenically (liquid nitrogen) trapped in a calibrated volume. The CO<sub>2</sub> volume has been determined with a manometer and was then transferred into a special glass device.

For the <sup>14</sup>C analysis a <sup>14</sup>C-dedicated Accelerator Mass Spectrometer (AMS; High Voltage Europa Tandetron) (van der Plicht et al., 2000) has been used. For this analysis method the carbon from only 4 ml CO<sub>2</sub> is needed per sample. All CO<sub>2</sub> samples have been graphitized and pressed into targets as described by Aerts-Bijma et al. (1997, 2001), before they were analyzed on <sup>14</sup>C, <sup>12</sup>C and <sup>13</sup>C with the AMS.

The <sup>14</sup>C content of a sample, the so-called ‘activity’ <sup>14</sup>A<sub>corr</sub> (%), is by convention (Stuiver and Polach, 1977) expressed relative to the <sup>12</sup>C content of the sample and relative to the <sup>14</sup>C/<sup>12</sup>C ratio of standardized oxalic acid samples (“OxII”). Oxalic acid samples have been measured in the same batch as our flue gas CO<sub>2</sub> samples. The measured results have been corrected for isotope fractionation to a standardized δ<sup>13</sup>C value of −25‰ (relative to standard “VPDB”). In this paper ‘<sup>14</sup>A<sub>corr</sub>’ is meant if ‘<sup>14</sup>C value’ is written.

### 2.3. <sup>14</sup>C-based quantification of the biogenic CO<sub>2</sub> fraction

In this section the calculation method to quantify the biogenic CO<sub>2</sub> fraction of a flue gas sample based on the <sup>14</sup>C analysis of flue gas CO<sub>2</sub> will be explained. The calculation method as published or used by others so far (Mohn et al., 2008; Reinhardt et al., 2008; Staber et al., 2008), is not complete for those samples that contain also CO<sub>2</sub> from other sources than the biogenic and fossil carbon sources from the combustion process in the industrial plant. The calculation method for these samples will therefore be shown as well.

The <sup>14</sup>C value of a CO<sub>2</sub> sample is determined by the <sup>14</sup>C value and the CO<sub>2</sub> fraction, ‘*f*<sub>sourceCO<sub>2</sub></sub>’ (relative to the total carbon: <sup>12</sup>C, <sup>13</sup>C and <sup>14</sup>C in the sample), of each CO<sub>2</sub> source in the sample:

$$^{14}\text{C}_{(\text{sampleCO}_2)} = ^{14}\text{C}_{(\text{bioCO}_2)} \cdot f_{(\text{bioCO}_2)} + ^{14}\text{C}_{(\text{fosCO}_2)} \cdot f_{(\text{fosCO}_2)} + ^{14}\text{C}_{(\text{xCO}_2)} \cdot f_{(\text{xCO}_2)} \quad (2)$$

and

$$f_{(\text{sampleCO}_2)} = f_{(\text{bioCO}_2)} + f_{(\text{fosCO}_2)} + f_{(\text{xCO}_2)} = 1 \quad (3)$$

In these two equations the following CO<sub>2</sub> sources can be distinguished: (1) biogenic CO<sub>2</sub> (‘*bioCO<sub>2</sub>*’), (2) fossil CO<sub>2</sub> (‘*fosCO<sub>2</sub>*’), and (3) CO<sub>2</sub> from other sources than the fuel materials involved in the combustion process of the industrial plant (‘*xCO<sub>2</sub>*’). An example of the ‘*xCO<sub>2</sub>*’ source is the CO<sub>2</sub> originally present in atmospheric air, which is used in the combustion process and ends up in the emitted flue gas of an industrial plant. Since <sup>14</sup>C<sub>(fosCO<sub>2</sub>)</sub> = 0, Eq. (2) can be re-written as:

$$^{14}\text{C}_{(\text{sampleCO}_2)} = ^{14}\text{C}_{(\text{bioCO}_2)} \cdot f_{(\text{bioCO}_2)} + ^{14}\text{C}_{(\text{xCO}_2)} \cdot f_{(\text{xCO}_2)} \quad (4)$$

The <sup>14</sup>C values, <sup>14</sup>C<sub>(bioCO<sub>2</sub>)</sub> and <sup>14</sup>C<sub>(xCO<sub>2</sub>)</sub> are source dependent and consist of a mixture of different ‘*bio*’ or ‘*x*’ carbon sources respectively with different <sup>14</sup>C values, such as biogenic materials in waste (Fellner and Rechberger, 2009; Mohn et al., 2008).

$$^{14}\text{C}_{(\text{bioCO}_2)} = \sum_{i=1}^n (^{14}\text{C}_{(\text{bioC}_i)} \cdot f_{(\text{bioC}_i)}) \quad (5)$$

$$^{14}\text{C}_{(\text{xCO}_2)} = \sum_{i=1}^n (^{14}\text{C}_{(\text{xC}_i)} \cdot f_{(\text{xC}_i)}) \quad (6)$$

In Eqs. (5) and (6), *f*<sub>(bioC<sub>*i*</sub>)</sub> and *f*<sub>(xC<sub>*i*</sub>)</sub> are the carbon fractions of ‘*bio*’ or ‘*x*’ sources ‘*i*’ within the total of all ‘*bio*’ or ‘*x*’ carbon, respectively.

The <sup>14</sup>C value of recent biogenic material depends on the time-period in which the particular biomass has been formed from atmospheric CO<sub>2</sub> (directly or indirectly). In the last century the atmospheric <sup>14</sup>C value has shown significant changes over time (Levin and Hesshaimer, 2000). Suess (1955) noticed a small decreasing trend in the atmospheric <sup>14</sup>C values in the 1950s. This trend is related to the increasing combustion of fossil fuels. The main changes in the <sup>14</sup>C values of the atmosphere were, however, due to aboveground nuclear bomb tests in the 1960s. These bomb tests doubled the <sup>14</sup>C value in the atmosphere within 5 years. After 1963 the aboveground tests were banned and the atmospheric <sup>14</sup>C value decreased again, due to carbon exchange between the atmosphere, the biosphere and, most importantly, the oceans. The atmospheric <sup>14</sup>C level is currently close to the level of before the beginning of the nuclear bomb tests and decreases now (again) mainly due to the combustion of fossil fuels. The CO<sub>2</sub> from atmospheric air, a ‘*xCO<sub>2</sub>*’ source in flue gas CO<sub>2</sub> samples, will in general have a <sup>14</sup>C value that is very close to the ambient atmospheric <sup>14</sup>C value.

Derived from Eqs. (4)–(6) the biogenic CO<sub>2</sub> fraction, *f*<sub>(bioCO<sub>2</sub>)</sub>, in a sample can be calculated as following:

$$f_{(\text{bioCO}_2)} = \frac{^{14}\text{C}_{(\text{sampleCO}_2)} - ^{14}\text{C}_{(\text{xCO}_2)} \cdot f_{(\text{xCO}_2)}}{^{14}\text{C}_{(\text{bioCO}_2)}} = \frac{^{14}\text{C}_{(\text{sampleCO}_2)} - ((\sum_{i=1}^n (^{14}\text{C}_{(\text{xC}_i)} \cdot f_{(\text{xC}_i))}) \cdot f_{(\text{xCO}_2)})}{\sum_{i=1}^n (^{14}\text{C}_{(\text{bioC}_i)} \cdot f_{(\text{bioC}_i)})} \quad (7)$$

Since <sup>14</sup>C<sub>(xCO<sub>2</sub>)</sub> · *f*<sub>(xCO<sub>2</sub>)</sub> = ((∑<sub>*i*=1</sub><sup>*n*</sup> (<sup>14</sup>C<sub>(xC<sub>*i*</sub>) · *f*<sub>(xC<sub>*i*</sub>)</sub>)) · *f*<sub>(xCO<sub>2</sub>)</sub> can be simplified to <sup>14</sup>C<sub>(xCO<sub>2</sub>)</sub> · *f*<sub>(xCO<sub>2</sub>)</sub> = ∑<sub>*i*=1</sub><sup>*n*</sup> (<sup>14</sup>C<sub>(xCO<sub>2</sub>)</sub> · *f*<sub>(xCO<sub>2</sub>)</sub>), where *i* is the particular CO<sub>2</sub> source with a certain <sup>14</sup>C value and a certain CO<sub>2</sub> fraction in the total CO<sub>2</sub> of the sample (in this project: the CO<sub>2</sub> absorbed in a NaOH solution), Eq. (7) can also be written as:</sub>

$$f_{(\text{bioCO}_2)} = \frac{^{14}\text{C}_{(\text{sampleCO}_2)} - ^{14}\text{C}_{(\text{xCO}_2)} \cdot f_{(\text{xCO}_2)}}{^{14}\text{C}_{(\text{bioCO}_2)}} = \frac{^{14}\text{C}_{(\text{sampleCO}_2)} - \sum_{i=1}^n (^{14}\text{C}_{(\text{xCO}_2)} \cdot f_{(\text{xCO}_2)})_i}{\sum_{i=1}^n (^{14}\text{C}_{(\text{bioC}_i)} \cdot f_{(\text{bioC}_i)})} \quad (8)$$

If there is no significant CO<sub>2</sub> contribution of other carbon sources than biogenic and fossil CO<sub>2</sub> from the combustion process, *f*<sub>(xCO<sub>2</sub>)</sub> = 0 and:

$$f_{(\text{bioCO}_2)} = \frac{^{14}\text{C}_{(\text{sampleCO}_2)}}{^{14}\text{C}_{(\text{bioCO}_2)}} = \frac{^{14}\text{C}_{(\text{sampleCO}_2)}}{\sum_{i=1}^n (^{14}\text{C}_{(\text{bioC}_i)} \cdot f_{(\text{bioC}_i)})} \quad (9)$$

Eq. (9) has been used so far in other studies.

## 3. Results

### 3.1. Biogenic CO<sub>2</sub> fraction of flue gas samples

Tables 1 and 2 show the biogenic CO<sub>2</sub> fractions, *f*<sub>(bioCO<sub>2</sub>)</sub>, (in percent) determined in flue gas samples of the investigated Dutch power plant and waste incineration plant respectively, based on <sup>14</sup>C measurements of flue gas CO<sub>2</sub> as described in Section 2. The uncertainty in each *f*<sub>(bioCO<sub>2</sub>)</sub> value has been calculated using error propagation (Monte Carlo simulation).

Tables 3 and 4 show the values of <sup>14</sup>C<sub>(sampleCO<sub>2</sub>)</sub>, <sup>14</sup>C<sub>(bioCO<sub>2</sub>)</sub>, <sup>14</sup>C<sub>(xCO<sub>2</sub>)\_air</sub> and *f*<sub>(xCO<sub>2</sub>)\_air</sub> that were needed to calculate the biogenic fraction *f*<sub>(bioCO<sub>2</sub>)</sub> in flue gas CO<sub>2</sub>, according to Eq. (8). Because in this study part of the CO<sub>2</sub> that was extracted from each NaOH sample, did, abusively, not origin from the sampled flue gas CO<sub>2</sub> alone, but also from a CO<sub>2</sub> contamination in the used NaOH solution, this contamination has been taken into account in the calculation of *f*<sub>(bioCO<sub>2</sub>)</sub> as well by the addition of “−<sup>14</sup>C<sub>(CO<sub>2</sub>-NaOH)</sub> · *f*<sub>(CO<sub>2</sub>-NaOH)</sub>” to the numerator of Eq. (8):

$$f_{(bioCO_2)} = \frac{{}^{14}C_{(sampleCO_2)} - {}^{14}C_{(xCO_2,air)} \cdot f_{(xCO_2,air)} - {}^{14}C_{(CO_2,NaOH)} \cdot f_{(CO_2,NaOH)}}{{}^{14}C_{(bioCO_2)}} \quad (10)$$

The fraction of the CO<sub>2</sub> contamination in the extracted CO<sub>2</sub> amount of each sample,  $f_{(CO_2)NaOH}$ , and the <sup>14</sup>C value,  ${}^{14}C_{(CO_2)NaOH}$ , (shown in Tables 3 and 4) have been quantified by the extraction and <sup>14</sup>C measurement of CO<sub>2</sub> from two blank NaOH solutions (0.046 ± 0.006 ml CO<sub>2</sub>/ml extracted 2 M NaOH solution). Only after the two sampling expeditions had taken place, it was discovered

**Table 1**

Biogenic CO<sub>2</sub> fraction (%),  $f_{(bioCO_2)}$ , with 95% confidence interval (2σ) of power plant flue gas, determined by the <sup>14</sup>C analysis of flue gas CO<sub>2</sub> (<sup>14</sup>C method).

Sampling date	Sampling interval (time)	Sample name	$f_{(bioCO_2)}$ (%)
26.08.2008	14:45–15:30 (45 min)	PP_1	10.4 ± 1.1
	15:32–16:17 (45 min)	PP_2	9.8 ± 1.1
	16:19–17:10 (51 min)	PP_3	–
	17:12–17:58 (46 min)	PP_4	–
27.08.2008	9:05–9:50 (45 min)	PP_5	10.4 ± 0.9
	9:52–10:37 (45 min)	PP_6	8.6 ± 0.8
	10:40–11:20 (40 min)	PP_7	5.3 ± 0.7
	11:25–12:10 (45 min)	PP_8	5.0 ± 0.6
	12:13–13:00 (47 min)	PP_9	5.1 ± 0.6
	13:02–13:47 (45 min)	PP_10	5.0 ± 0.6

**Table 2**

Biogenic CO<sub>2</sub> fraction (%),  $f_{(bioCO_2)}$ , with 95% confidence interval (2σ) of waste incineration plant flue gas, determined by the <sup>14</sup>C analysis of flue gas CO<sub>2</sub> (<sup>14</sup>C method).

Sampling date	Sampling time interval	Sample name	$f_{(bioCO_2)}$ (%)
28.08.2008	9:26–10:10 (44 min)	WL_1	48.0 ± 3.3
	10:17–11:02 (45 min)	WL_2	47.7 ± 3.2
	11:07–11:52 (45 min)	WL_3	46.9 ± 3.2
	11:53–12:35 (42 min)	WL_4	46.0 ± 3.1
	12:40–13:25 (45 min)	WL_5	48.0 ± 3.2
	13:26–14:11 (45 min)	WL_6	48.0 ± 3.3
	14:13–14:58 (45 min)	WL_7	49.7 ± 3.4
	15:00–15:45 (45 min)	WL_8	49.0 ± 3.3
	Average day 1		47.9 ± 3.3
29.08.2008	8:56–9:41 (45 min)	WL_9	49.4 ± 3.3
	9:43–10:28 (45 min)	WL_10	50.9 ± 3.4
	10:30–11:15 (45 min)	WL_11	51.2 ± 3.5
	11:17–12:02 (45 min)	WL_12	49.4 ± 3.3
	12:05–12:50 (45 min)	WL_13	49.8 ± 3.4
	Average day 2		50.1 ± 3.4

**Table 3**

Used <sup>14</sup>C values for  ${}^{14}C_{(bioCO_2)}$ ,  ${}^{14}C_{(xCO_2,air)}$  and  ${}^{14}C_{(CO_2)NaOH}$ .

Carbon source	<sup>14</sup> C (%) ± 2σ	Reference
${}^{14}C_{(bioCO_2)}$ , biomass power plant (n = 1)	116 ± 8 <sup>a</sup>	Measured at CIO lab
${}^{14}C_{(bioCO_2)}$ , biomass waste incineration	113 ± 8	Mohn et al. (2008)
${}^{14}C_{(xCO_2,air)}$ , atmospheric air	100 ± 10	Estimated <sup>b</sup>
${}^{14}C_{(CO_2)NaOH}$ , (n = 2), contamination	101 ± 8	Measured at CIO lab

<sup>a</sup> 10 g of wood pellets have been combusted. It has been treated as any organic sample for routine <sup>14</sup>C measurement (Mook and Streurman, 1983).

<sup>b</sup> The used <sup>14</sup>C value has been based on <sup>14</sup>CO<sub>2</sub> measurements at the Dutch measurement station Lutjewad of the CIO in 2008. The atmospheric <sup>14</sup>C value at Lutjewad was 104% in average in the period July–September. Since the used atmospheric air is obtained from the surrounding areas of the power plant and waste incineration plant respectively, the specific air might be depleted in <sup>14</sup>C due to the fossil fuel CO<sub>2</sub> emissions. A <sup>14</sup>C value of approximately 100% is therefore not unlikely.

**Table 4**

Measured  ${}^{14}C_{(sampleCO_2)}$  value and the fractions of CO<sub>2</sub> from atmospheric air ( $f_{(xCO_2,air)}$ ) and NaOH contamination ( $f_{(CO_2)NaOH}$ ) in the total extracted CO<sub>2</sub> amount of power plant samples (“PP”) and waste incineration plant samples (“WI”).

Sample name	${}^{14}C_{(sampleCO_2)} \pm 2\sigma$ (%)	$f_{(xCO_2,air)}$ (%) ± 2σ	$f_{(CO_2)NaOH}$ (%) ± 2σ
PP_1	16.66 ± 0.34	0.31 ± 0.06	4.3 ± 0.8
PP_2	16.71 ± 0.34	0.31 ± 0.06	5.0 ± 0.9
PP_5	14.97 ± 0.34	0.35 ± 0.06	2.6 ± 0.5
PP_6	13.03 ± 0.34	0.35 ± 0.06	2.7 ± 0.5
PP_7	9.18 ± 0.34	0.35 ± 0.06	2.7 ± 0.5
PP_8	8.39 ± 0.34	0.33 ± 0.06	2.2 ± 0.4
PP_9	8.55 ± 0.34	0.32 ± 0.06	2.3 ± 0.4
PP_10	8.56 ± 0.34	0.32 ± 0.06	2.5 ± 0.5
WI_1	57.01 ± 0.50	0.32 ± 0.03	2.4 ± 0.5
WI_2	56.59 ± 0.50	0.32 ± 0.03	2.3 ± 0.4
WI_3	55.95 ± 0.50	0.32 ± 0.03	2.6 ± 0.5
WI_4	55.22 ± 0.50	0.32 ± 0.03	2.9 ± 0.5
WI_5	56.89 ± 0.50	0.32 ± 0.03	2.3 ± 0.4
WI_6	57.17 ± 0.50	0.32 ± 0.03	2.5 ± 0.5
WI_7	59.11 ± 0.50	0.32 ± 0.03	2.6 ± 0.5
WI_8	57.89 ± 0.50	0.32 ± 0.03	2.1 ± 0.4
WI_9	58.64 ± 0.50	0.32 ± 0.03	2.5 ± 0.5
WI_10	60.22 ± 0.50	0.32 ± 0.03	2.4 ± 0.5
WI_11	60.46 ± 0.50	0.32 ± 0.03	2.2 ± 0.4
WI_12	58.53 ± 0.50	0.32 ± 0.03	2.4 ± 0.4
WI_13	58.93 ± 0.50	0.32 ± 0.03	2.3 ± 0.4

that abusively a wrong batch of NaOH that had already absorbed atmospheric air CO<sub>2</sub> had been used, instead of the clean batch that is normally used at the CIO laboratory for these kinds of sampling applications. The use of extra pure NaOH solution that has not been in contact with atmospheric air/CO<sub>2</sub> (before flue gas sampling) is an important factor in the correct application of this method. Although this is easy to achieve, performing a CO<sub>2</sub> extraction of blank NaOH solution before and after the use of a particular batch of NaOH solution for flue gas CO<sub>2</sub> sampling is nevertheless recommended.

The fraction of atmospheric air CO<sub>2</sub> in the total sampled flue gas CO<sub>2</sub> of the samples,  $f_{(xCO_2,air)}$ , (shown in Table 4) has been calculated from the fraction of atmospheric air CO<sub>2</sub> in the flue gas CO<sub>2</sub>. The latter has been determined as described in Section 3.2. In Eq. (8) the fraction  $f_{(xCO_2,air)}$  is in principle equal to the fraction of atmospheric air CO<sub>2</sub> in the flue gas CO<sub>2</sub>, while in Eq. (10) the fraction is slightly lower, due to contribution of CO<sub>2</sub> from the NaOH contamination ( $f_{(CO_2)NaOH}$ ) to the total CO<sub>2</sub> in each sample.

The biogenic CO<sub>2</sub> fraction of the power plant flue gas was nearly 10% on the first sampling day. The results of power plant samples “PP\_3” and “PP\_4” have been omitted because the sampling flow and therefore the sampled (absorbed) CO<sub>2</sub> amount of these samples had been much lower (by a factor 6) than for other samples. This has been discovered before the sampling of “PP\_5”. The connection of the tubing between the pump system and the washing bottle of the flue gas sampler (see Fig. 1) was not tightly connected and leaked flue gas. This leakage has been solved before the sampling of “PP\_5” and the following samples, but it had already affected the sampling of samples PP\_1 to PP\_4. This was confirmed when the CO<sub>2</sub> from all samples had been extracted: more sample volume had to be extracted from samples PP\_1 to PP\_4 to obtain the same amount of CO<sub>2</sub> in comparison to PP\_5 to PP\_10, while the flue gas CO<sub>2</sub> concentration was virtually constant (see Table 5). The results of PP\_1 and PP\_2 have not been omitted, because on the basis of the extracted CO<sub>2</sub> amount the leak was not severe yet for these samples.

On the second sampling day at the power plant, during the sampling of “PP\_6”, one of the two supplying biomass units of the power plant was stopped and the biomass carbon input reduced by 50%, resulting in a biogenic CO<sub>2</sub> fraction of 5% for the last four samples.

**Table 5**

CO<sub>2</sub> concentration (% v/v) in sampled flue gas, extracted sample amount (NaOH solution) and the amount of CO<sub>2</sub> released from this sample volume during the extraction procedure (Section 2.2).

Sample name	CO <sub>2</sub> flue gas (% v/v) <sup>a</sup>	Extracted sample volume (ml)	Extracted CO <sub>2</sub> (ml)
PP_1	11.8	5.7	6.0
PP_2	11.6	5.6	5.1
PP_3	11.5	16.6	4.6
PP_4	11.5	13.0	4.6
PP_5	10.8	3.0	4.1
PP_6	10.8	3.0	5.0
PP_7	10.9	3.0	5.0
PP_8	11.1	3.0	6.1
PP_9	11.4	2.7	5.2
PP_10	11.3	2.6	4.8
WL_1	11.8	3.0	5.7
WL_2	11.9	2.6	5.1
WL_3	11.5	2.7	4.7
WL_4	11.4	2.7	4.2
WL_5	11.5	2.7	5.3
WL_6	12.0	2.5	4.5
WL_7	11.5	2.7	4.7
WL_8	12.0	2.7	5.8
WL_9	12.4	2.5	4.6
WL_10	12.5	2.5	4.8
WL_11	12.6	2.5	5.1
WL_12	12.5	2.5	4.8
WL_13	12.2	2.7	5.3

<sup>a</sup> The CO<sub>2</sub> concentration has been measured continuously. Since the results were not logged to a computer, the average CO<sub>2</sub> concentration of each sample has been calculated from 3 to 4 different measurement results, which were read out during each sampling interval.

The biogenic CO<sub>2</sub> fraction of the waste incineration plant flue gas was in average 47.9 ± 3.3% on the first sampling day and 50.1 ± 3.4% on the second sampling day. The uncertainty in each  $f_{(bioCO_2)}$  value (including the uncertainty in the average values) of the waste incineration plant samples is largely determined (>90%) by the relatively high systematic uncertainty in the estimated average <sup>14</sup>C value of the biogenic waste fraction, <sup>14</sup>C<sub>(bioCO<sub>2</sub>)</sub> (Table 3). The random variation that can be observed in  $f_{(bioCO_2)}$  is due to random variations in <sup>14</sup>C<sub>(sampleCO<sub>2</sub>)</sub>. Since the measurement error in <sup>14</sup>C<sub>(sampleCO<sub>2</sub>)</sub> is relatively low (±0.25%, 1σ), the measured random variation in <sup>14</sup>C<sub>(sampleCO<sub>2</sub>)</sub> is real and must be due to variations in time in the composition of the combusted waste: random variation in fossil/biogenic carbon fractions and random variation in <sup>14</sup>C<sub>(bioCO<sub>2</sub>)</sub> (Eq. (5)).

### 3.2. Verification of <sup>14</sup>C-based biogenic CO<sub>2</sub> fractions

The <sup>14</sup>C-based biogenic CO<sub>2</sub> fractions of the power plant samples have been verified by comparison with biogenic CO<sub>2</sub> fractions calculated from carbon input and output mass data ('mass data method') of the specific power plant for the same sampling intervals as the flue gas CO<sub>2</sub> samples. For the mass data method the biogenic CO<sub>2</sub> fraction in the emitted flue gas CO<sub>2</sub> has been calculated according to:

$$f_{(bioCO_2)} = \frac{mC_{(bio)}}{mC_{(total)}} = \frac{mC_{(bio)}}{mC_{(bio)} + mC_{(coal)} + mC_{(natural\_gas)} + mC_{(air)}} \quad (11)$$

In Eq. (11)  $mC_{(...)}$  is the total carbon mass of each carbon source (biomass, coal, natural gas and atmospheric air CO<sub>2</sub>) in the flue gas emitted by the power plant during a specific sampling interval. It is assumed that the biogenic carbon fraction in flue gas (mass data method) equals the biogenic CO<sub>2</sub> fraction in the flue gas (<sup>14</sup>C meth-

od). Since CO<sub>2</sub> is by far the major carbon component in the flue gas, the relatively small amounts of CO and other carbon containing compounds in the mass data method can safely be ignored.

Most of the used data for the mass data method were obtained from measurements that were performed by the power plant company itself. Table 6 shows the  $mC_{(...)}$  values of the different carbon sources for the investigated sampling intervals.  $mC_{(bio)}$ ,  $mC_{(coal)}$  and  $mC_{(natural\_gas)}$  have been calculated from input flow data (kg/s) and the mass and carbon content (in dry and ash free material) of each carbon source. For the biomass and coal the amount of uncombusted carbon, based on the carbon content of the ash in time, has been taken into account. Since, according to the power plant company, more than 99% of the carbon from natural gas ends up as flue gas carbon, its uncombusted carbon part has not been taken into account.  $mC_{(air)}$  has been calculated from the carbon mass flow of atmospheric air. At the power plant atmospheric air ends up in flue gas because it is used in the combustion processes and it leaks into the flue gas during a heat exchange process in which air needed for the combustion is heated up by using the heat of flue gas. The carbon mass flow of atmospheric air was 7.65 ± 1.25 kg/min and has been calculated from the (given) air mass flow of 770 ± 30 kg/s (constant), the air density of 1.29 kg/m<sup>3</sup>, the CO<sub>2</sub> fraction in air of 400 ± 50 ppm (estimated, based on current atmospheric CO<sub>2</sub> levels), the molar volume of 0.0224 m<sup>3</sup>/mol and the molar carbon mass weight of 0.012 kg/mol.

The fraction of atmospheric air CO<sub>2</sub> in the flue gas CO<sub>2</sub>, which is needed in the <sup>14</sup>C-based determination of the biogenic CO<sub>2</sub> fraction (see Section 3.1), has been calculated for the power plant samples by using Eq. (11) ( $mC_{(bio)}$  is then replaced by  $mC_{(air)}$  in the denominator) and the data shown in Table 6. The particular fraction was on average 0.34 ± 0.06% for the power plant samples. For the waste incineration plant, where atmospheric air is added in the combustion process of the waste materials and it leaks into the flue gas during the transport of the flue gas from the combustion furnace, via the flue gas washing set-up, to the chimney, the fraction of atmospheric air CO<sub>2</sub> in flue gas CO<sub>2</sub> was 0.33 ± 0.03%. This fraction has been calculated as following for the waste incineration plant samples:

$$\text{fraction CO}_{2\_atmospheric\ air\ in\ CO}_{2\_flue\ gas} = \frac{\text{flow}_{atmospheric\ air} \cdot \text{CO}_2\ \text{concentration}_{air}}{\text{flow}_{flue\ gas} \cdot \text{CO}_2\ \text{concentration}_{flue\ gas}} \quad (12)$$

The data for  $\text{flow}_{atmospheric\ air}$  and  $\text{flow}_{flue\ gas}$  (dry) have been based on the average results from measurements and calculations that were performed by the waste incineration plant company. In general 25–30 ton waste/h is combusted in every oven of the particular waste incineration plant. The atmospheric air and dry flue gas flows are almost equal and are in general between 25 and

**Table 6**

Total carbon mass values ( $mC_{(...)}$  in Eq. (11)) of the different carbon sources in power plant flue gas for the investigated sampling intervals.

Sampling interval of:	Carbon mass in flue gas			
	Biomass C (kg) ± 9%	Coal C (kg) ± 9%	Natural gas C (kg) ± 7%	Atmospheric air C (kg) ± 16%
PP_1 (45 min)	10980	91795	3897	344
PP_2 (45 min)	10486	91772	3894	344
PP_3 (51 min)	11959	104309	4416	390
PP_4 (46 min)	10730	94250	3984	352
PP_5 (45 min)	10382	81057	3889	344
PP_6 (45 min)	7278	83852	3890	344
PP_7 (40 min)	4543	76101	3460	306
PP_8 (45 min)	4912	91798	3890	344
PP_9 (47 min)	5234	100375	4056	360
PP_10 (45 min)	5121	96251	3883	344

40 Nm<sup>3</sup>/s. The CO<sub>2</sub> concentration of the atmospheric air has been estimated similar to the power plant samples (400 ± 50 ppm, based on current atmospheric CO<sub>2</sub> levels). The average CO<sub>2</sub> concentration of the dry flue gas (12 ± 1% v/v) has been based on CO<sub>2</sub> concentration values measured at the waste incineration plant.

Fig. 2 shows the biogenic CO<sub>2</sub> fraction of the power plant samples determined with the <sup>14</sup>C method and the mass data method. The results of the '<sup>14</sup>C method' and 'mass data method' show very good agreement within the uncertainty intervals. The reduction of biomass combustion on the second day is very well visible in the results of both methods. The changes in the biomass input flow were due to problems with one of the biomass units and these problems caused non-stationary operating conditions, which have also negatively affected the monitoring of the biomass input flow during the same time-period and therefore have affected the results of the mass data method. This might explain the somewhat larger differences between both methods in the results of PP\_5 and PP\_6, in comparison to the other sample results. The error bars of the mass data method results in Fig. 2 show the relative measurement error (2σ) in the biogenic CO<sub>2</sub> fraction of each sample for a ±5% relative measurement error in all used data (fuel flows, carbon content in each fuel). If these relative measurement errors were ±1% the size of the error bars would be reduced by a factor of 5.

The good agreement between the results of the <sup>14</sup>C method and the mass data method for the power plant flue gas samples gives confidence in the <sup>14</sup>C results of the waste incineration plant as well. Mohn et al. (2008) report results of three different Swiss waste incinerators. The biogenic CO<sub>2</sub> fraction in the Swiss waste incinerators varied between 47% and 59% and was 52% on average for the 18 different flue gas CO<sub>2</sub> samples (six samples per waste incineration plant), which had been sampled each during 3 consecutive days within a total period of 4 months. Generally speaking, the same values have been found in the current project. Differences between the determined biogenic CO<sub>2</sub> fraction of the Dutch and Swiss waste incinerators can be expected, since Dutch municipal waste and Swiss municipal waste have slightly different compositions (Fellner and Rechberger, 2009) and the composition of waste also varies in time (for both countries).

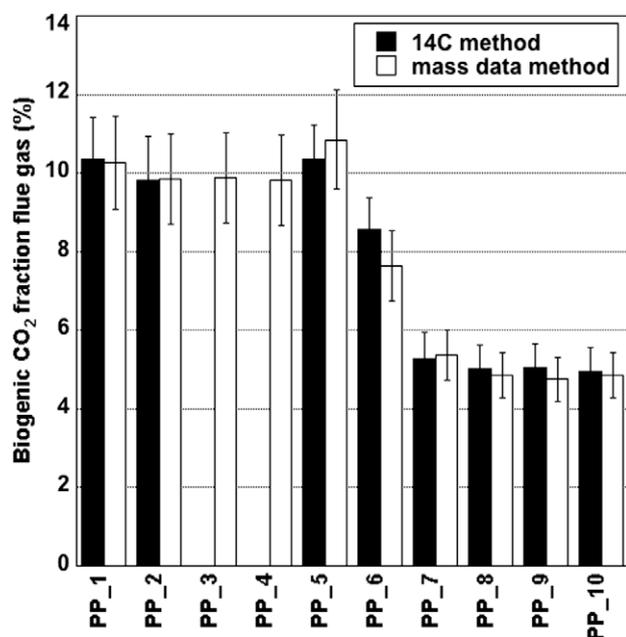


Fig. 2. Comparison of the biogenic CO<sub>2</sub> fractions determined at a power plant with the <sup>14</sup>C method and the mass data method. The error bars show the 95% confidence intervals (2σ).

## 4. Discussion

The applied <sup>14</sup>C method is very useful to determine the biogenic fraction of CO<sub>2</sub> emissions of different industrial plants. In this section the three stages of the <sup>14</sup>C method (sampling, off-line <sup>14</sup>C analysis and calculation of  $f_{(bioCO_2)}$ ) will be systematically discussed based on the results and experiences of this project, to give insight into the reliability of the method that has been applied. This study was the result of a first experience with the application for flue gas CO<sub>2</sub> sampled at industrial plants and the results are therefore not based on a routinely performed method, except for the <sup>14</sup>C analysis. Several improvements can still be made in the applied method and in its validation, in order to obtain a robust method for routine measurements. Recommendations for future users of the <sup>14</sup>C method for flue gas CO<sub>2</sub> are therefore part of this section.

### 4.1. Reliability of flue gas CO<sub>2</sub> sampling

The most direct way, so far, to determine the biogenic and fossil fraction of industrial CO<sub>2</sub> emissions is by analyzing the composition of the flue gas CO<sub>2</sub> itself. A main aspect in the strategy to sample flue gas CO<sub>2</sub> is whether the sampled flue gas represents the composition (biogenic carbon fraction) of the emitted CO<sub>2</sub> for a specific time-period. In principle only homogeneously distributed flue gas should be sampled, but in practice it is sometimes not possible to sample flue gas at the ideal (optimal) sampling position. In this project flue gas has been sampled at the waste incineration plant that had been used for validated continuous measurements (by the waste incineration plant). Representative (homogeneous) sampling of flue gas is part of the validation (and evaluation) method for these measurements and is ascertained according to NEN-ISO 10396 (2007). At the power plant the homogeneity of the flue gas sampling has, for practical reasons, not been ascertained with flue gas flow measurements at different sampling locations. Instead, the sampling took place relatively close to (3 m below) a sampling point for continuous oxygen measurements where homogeneous sampling conditions can be expected and the flue gas has been sampled relatively far away (40 m) from the location where flue gas from the combustion of coal/biomass is mixed with flue gas from combusted natural gas. Since the natural gas flue gas is very well mixed with the coal/biomass-flue gas to heat up the latter one and its contribution is only 4% of the total carbon fraction in the flue gas (see Table 6), significant anomalies in the determined average biogenic CO<sub>2</sub> fractions are not to be expected. The good comparison of the <sup>14</sup>C method results with the mass data method results (Fig. 2) indicates that the sampled flue gas CO<sub>2</sub> has been representative for the CO<sub>2</sub> as emitted by the power plant. However, future users of the method are recommended to investigate the homogeneity of flue gas flows in time at the chosen sampling position if the measurements are needed for legal verification purposes.

To obtain samples that represent the relative total amount of the emitted CO<sub>2</sub> and its <sup>14</sup>C value during a specific sampling interval, the flue gas CO<sub>2</sub> samples should in principle be acquired by proportional sampling. Proportional sampling, by adjusting the sampling flow of flue gas CO<sub>2</sub>, is required when the biogenic CO<sub>2</sub> fraction changes during the sampling interval while at the same time the emission flow of the industrial plant changes as well. In this project flue gas CO<sub>2</sub> has been sampled in a NaOH solution with a constant flow rate during 45 min for each sample. During this relatively short time-period the CO<sub>2</sub> emission flows in the specific industrial plants have been relatively constant and proportional sampling was therefore not needed. So far, no studies have used proportional sampling. For longer sampling intervals (day–month), however, the use of a proportional flue gas CO<sub>2</sub> sampler is recom-

mended, because of the large chance of interruptions in the combustion processes (especially at waste incineration plants).

A factor that might alter the relative amount of  $^{14}\text{C}$  in the flue gas  $\text{CO}_2$  during the sampling is isotope fractionation. Isotope fractionation occurs if the efficiency of the dissolution of  $\text{CO}_2$  in the NaOH solution (or other dissolver or absorber of  $\text{CO}_2$ ) is not 100%. The part of flue gas  $\text{CO}_2$  that does not dissolve, will have relatively more  $^{14}\text{CO}_2$  than  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$ , because  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  dissolve more easily in NaOH than  $^{14}\text{CO}_2$ . Solution efficiencies lower than 100% might occur if the flue gas flow is too high and (consequently) the path length of the flue gas flow through the NaOH solution is too small. In the method used in this project the measured  $^{14}\text{C}$  amounts are corrected for isotope fractionation (a commonly used procedure in  $^{14}\text{C}$  analysis, see Section 2.2) and a dissolution efficiency of 100% is therefore not required to obtain reliable biogenic  $\text{CO}_2$  fractions from the  $^{14}\text{C}$  measurements. The dissolution efficiency in the currently used method set-up has not been checked. Methods to determine the dissolution efficiency, using additional washing bottles and/or measuring the  $\text{CO}_2$  concentration of the flue gas leaving the washing bottle, have been described by Mohn et al. (2008).

The amount of  $\text{CO}_2$  that can be absorbed in the NaOH solution during a specific sampling interval (dissolution capacity) is determined by the molarity and volume of the NaOH solution and by the sampling flow and should be taken into account in the measurement set-up to prevent saturation (and therefore non-representative sampling). In the current described experiments at most 10% of the maximum capacity for  $\text{CO}_2$  in the solution has been used.

#### 4.2. Reliability of sample pre-treatment and $^{14}\text{C}$ analysis

It is the task of the  $^{14}\text{C}$  laboratories to specify and control the reproducibility and accuracy of their measurements. The  $^{14}\text{C}$  analysis and the extraction of  $\text{CO}_2$  from a NaOH solution are well known techniques at the CIO laboratory from other applications (especially dating of materials). The reproducibility and accuracy of the AMS  $^{14}\text{C}$  analysis (in use since 1994) of the CIO laboratory are well known, based on the analyses (including graphitization) of different regularly measured international reference standards and on results in international inter-comparison tests.

The reproducibility of the  $^{14}\text{C}$  analysis including the extraction of  $\text{CO}_2$  from the NaOH solution has been investigated based on two measurements of a power plant sample and two measurements of a combusted wood-sample (the  $\text{CO}_2$  of this sample was dissolved in a NaOH solution after combustion). The two measurements of each sample (including the extraction of  $\text{CO}_2$ ) were performed under different conditions (different days and analysts). The two  $^{14}\text{C}$  values of the power plant sample (PP\_5) were 14.97% and 14.98% (both  $\pm 0.17\%$ ,  $1\sigma$ ) and the two  $^{14}\text{C}$  values of the wood-sample were 113.93% and 113.91% (both  $\pm 0.39\%$ ,  $1\sigma$ ). The two results of both samples are very well comparable. The reproducibility of the used sample pre-treatment and the  $^{14}\text{C}$  analysis method is good at both (relatively) high and low  $^{14}\text{C}$  level.

#### 4.3. Reliability of the calculated biogenic $\text{CO}_2$ fraction, $f_{(\text{bioCO}_2)}$

The reliability of a calculated biogenic  $\text{CO}_2$  fraction,  $f_{(\text{bioCO}_2)}$ , according to Eq. (8) depends, beside on the reliability of the flue gas  $\text{CO}_2$  sampling and the  $^{14}\text{C}$  measurement, also on the accuracy of the used values for  $^{14}\text{C}_{(\text{bioCO}_2)}$ ,  $f_{(\text{XCO}_2)}$  and  $^{14}\text{C}_{(\text{XCO}_2)}$ . In the present study, in which Eq. (10) has been used, the reliability of the calculated biogenic carbon fraction also depends on the accuracy of  $f_{(\text{CO}_2\text{-NaOH})}$  and  $^{14}\text{C}_{(\text{CO}_2\text{-NaOH})}$ .

As mentioned before in Section 2.3, the  $^{14}\text{C}$  value of recent biogenic material is determined by the growing period in which the

particular biomass has been formed from atmospheric  $\text{CO}_2$  (directly or indirectly) and by its harvest year. The  $^{14}\text{C}$  value of biomass will in general vary between 105% and 125%. Since this is a relatively large variation, the value of  $^{14}\text{C}_{(\text{bioCO}_2)}$  should therefore be approximated for analyzed samples to minimize the uncertainties in  $^{14}\text{C}_{(\text{bioCO}_2)}$  and (consequently) in  $f_{(\text{bioCO}_2)}$ .  $^{14}\text{C}_{(\text{bioCO}_2)}$  has been determined for the power plant samples by  $^{14}\text{C}$  analysis of wood pellets (see Table 3) from the same batch as combusted when we sampled flue gas at the power plant. Since the whole batch of wood pellets (several tons of material) might originate from different trees with different growing periods and harvest years, the measured  $^{14}\text{C}_{(\text{bioCO}_2)}$  value of only 10 g of sample material might not have been fully representative for the average  $^{14}\text{C}_{(\text{bioCO}_2)}$  value of the combusted wood during the sampling of flue gas  $\text{CO}_2$  at the power plant. Because the uncertainty in representative sub-sampling has not been investigated, the uncertainty in the measured  $^{14}\text{C}_{(\text{bioCO}_2)}$  value has been estimated to be  $\pm 4\%$  ( $1\sigma$ ; absolute value). This is a relatively large uncertainty in comparison to the measurement uncertainty of  $\pm 0.4\%$  ( $1\sigma$ ) and it has increased the overall absolute uncertainty in the calculated biogenic carbon fraction  $f_{(\text{bioCO}_2)}$  of the power plant samples (Table 1) with 0.3% for samples PP\_1 and PP\_5, with 0.2% for samples PP\_2 and PP\_6 and with 0.1% for samples PP\_7 to PP\_10 respectively. Future users of the method (for similar cases) are recommended to investigate the variation in  $^{14}\text{C}_{(\text{bioCO}_2)}$  due to sub-sampling of the combusted biomass material, in order to decrease the uncertainty in the calculated biogenic  $\text{CO}_2$  fraction.

For the waste incineration plant samples a  $^{14}\text{C}_{(\text{bioCO}_2)}$  value has been used that was determined by Mohn et al. (2008) (see Table 3) based on estimations of the average composition of (municipal) waste. Fellner and Rechberger (2009) have confirmed this value for municipal waste of the Netherlands. Since waste materials are an unknown and variable mixture of different biogenic carbon sources in time, which are already mixed with fossil carbon sources, the  $^{14}\text{C}_{(\text{bioCO}_2)}$  value of these materials could, obviously, not be determined by  $^{14}\text{C}$  analysis. Due to the large variation in origin and composition of the biomass materials in waste in time, the uncertainty in the estimated  $^{14}\text{C}_{(\text{bioCO}_2)}$  value is still relatively large. This determines (both in the results of this study as in the results of Mohn et al. (2008)) the uncertainty in  $f_{(\text{bioCO}_2)}$  almost entirely.

In order to obtain reliable values for  $f_{(\text{bioCO}_2)}$  in flue gas, other  $\text{CO}_2$  sources than the combusted fuels, should be taken into consideration because their contributions can be relevant. In the present study the relative contribution of the atmospheric air  $\text{CO}_2$  to the measured  $^{14}\text{C}_{(\text{sampleCO}_2)}$  value is very small for the waste incineration plant samples and would have changed the calculated  $f_{(\text{bioCO}_2)}$  values with less than +0.7% (relative), if this contribution would have been ignored in the calculation. The relative contribution of the atmospheric air  $\text{CO}_2$  for the investigated power plant samples, is, however, significant and increases the  $f_{(\text{bioCO}_2)}$  value up to +7% (relative) if not taken into account in the calculation of  $f_{(\text{bioCO}_2)}$ . The relative contribution of the  $\text{CO}_2$  from the NaOH contamination in the present study was relevant for both the waste incineration plant samples and the power plant samples and changed  $f_{(\text{bioCO}_2)}$  significantly if not corrected for (up to +4% and +40%, respectively). This  $\text{CO}_2$  source can, however, be avoided in flue gas samples prior to the sampling of the flue gas  $\text{CO}_2$  (as explained in Section 3.1) and its contribution to the calculated  $f_{(\text{bioCO}_2)}$  value can therefore become negligible. The uncertainty in  $f_{(\text{bioCO}_2)}$  of the power plant samples (shown in Table 1) would have reduced with approximately 0.3% (absolute) if there had been no NaOH contamination. The uncertainty in the results of the waste incineration plant (Table 2) would not have changed significantly since it is mainly determined by the uncertainty in  $^{14}\text{C}_{(\text{bioCO}_2)}$ .

The very good agreement between the power plant results of the  $^{14}\text{C}$  method and the mass data method (Fig. 2) shows that a

reliable correction for other carbon sources than biomass and fossil fuels (like atmospheric CO<sub>2</sub>) in the <sup>14</sup>C method is successful. Only if unknown carbon sources in already mixed fuel materials (like waste) are combusted that are enriched with <sup>14</sup>C (on purpose or not), reliable verification of the biogenic fraction of CO<sub>2</sub> emissions using the <sup>14</sup>C method is not possible, because the determined  $f_{(bioCO_2)}$  value will be overestimated. Enriched <sup>14</sup>C materials are not very common and are governed by permits to deal with radioactive materials. They are mainly used in hospital or microbiological radioactivity laboratories and the waste will normally not end up as a fuel in industrial plants. A deliberate constant enrichment of the combusted fuel with <sup>14</sup>C will be very difficult and costly (and highly illegal by itself) and is therefore not very likely to occur. Nevertheless, both accidental and deliberate <sup>14</sup>C enrichment might be possible and should therefore be taken into account in the sampling strategy of flue gas CO<sub>2</sub> at industrial plants. Random sampling at industrial plants with different relatively short intervals (1 h – a few days), is therefore required in order to identify variations in the measured <sup>14</sup>C value in time which are not likely to be due to variations in the biogenic CO<sub>2</sub> fraction.

In industrial plants where peat is combusted the <sup>14</sup>C method to determine the biogenic carbon fraction of flue gas CO<sub>2</sub> can be difficult to apply, because peat has often a very variable and not a well defined <sup>14</sup>C<sub>(bioCO<sub>2</sub>)</sub> value (between 30% and 100%), due to its variable age (up to 9000 years). Due to its age, peat is in some regulations (like EU commission decision 2007/589/EC, 2007) not defined as biomass. If a mixture of biomass and peat materials is combusted, difficulties arise in determining the biogenic CO<sub>2</sub> fraction of a sample using the <sup>14</sup>C method, since part of the measured <sup>14</sup>C in the sample is from the ‘fossil’ peat. A correction is in that case needed in the calculation of the biogenic CO<sub>2</sub> fraction, comparable to the correction for atmospheric air as applied in this study. It might, however, be difficult to determine the fraction of peat carbon in sample material or to obtain a reliable (average) <sup>14</sup>C value for the combusted batch of peat materials. An attractive and realistic solution would be to define peat as only partly biogenic, with a percentage ‘biomass’ carbon corresponding to its <sup>14</sup>C value (age related). In that case, the <sup>14</sup>C contribution of the peat in the total <sup>14</sup>C amount of a sample is taken into account in the calculation of the biogenic CO<sub>2</sub> fraction, while only the combusted (recent) biomass materials determine the reference value for <sup>14</sup>C<sub>(bioCO<sub>2</sub>)</sub> in this calculation.

## 5. Conclusions

The <sup>14</sup>C method is a very useful method for industrial plants, emission authorities and emission inventories to verify data estimations of biogenic fractions of industrial CO<sub>2</sub> emissions. The method is reliable and sensitive and can be used to determine biogenic CO<sub>2</sub> fractions even below 5%. At industrial plants with biogenic CO<sub>2</sub> fractions below 10%, the presence of other CO<sub>2</sub> sources than the combusted biomass and fossil fuels, like atmospheric air CO<sub>2</sub>, should be taken into account in the calculation of the biogenic CO<sub>2</sub> fraction.

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