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Determination of biogenic and fossil CO_2 emitted by waste incineration based on $^{14}CO_2$ and mass balances

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Abstract

A field application of the radiocarbon (^{14}C) method was developed to determine the ratio of biogenic vs. fossil CO_2 emissions from waste-to-energy plants (WTE). This methodology can be used to assign the Kyoto relevant share of fossil CO_2 emissions, which is highly relevant for emission budgets and emission trading. Furthermore, heat and electricity produced by waste incinerators might be labelled depending on the fossil or biogenic nature of the primary energy source. The method development includes representative on-site CO_2 absorption and subsequent release in the laboratory. Furthermore, a reference value for the ^{14}C content of pure biogenic waste ($f_{M,bio}$) was determined as 1.130 ± 0.038. Gas samples for $^{14}CO_2$ analysis were taken at three WTEs during one month each. Results were compared to an alternative approach based on mass and energy balances. Both methods were in excellent agreement and indicated a fraction of biogenic CO_2 slightly above 50%.

Keywords: ^{14}C method; Balance method; Biogenic CO_2 emission; Waste incineration; Waste-to-energy plant

1. Introduction

Waste incineration is gaining importance in European countries, mainly because of environmental protection and resource management (Wilson, 2007). In Switzerland, over 99% of combustible waste is currently incinerated (Hügi and Gerber, 2006). Although waste incineration is superior to landfilling regarding its overall environmental impact, it leads to significant CO_2 emissions which have to be considered in the national greenhouse gas inventory. Furthermore, waste incinerators produce heat and electricity, which might be labelled depending on the fossil or biogenic nature of the primary energy source. CO_2 emissions relevant to the Kyoto Protocol can be estimated from the total amount of waste being incinerated, its water and carbon content, the oxidation factor and the fractions of fossil and biogenic carbon (Sabin Guendehou et al., 2006). While ranges for CO_2 emission factors per ton of waste are quite readily available, its fossil vs. biogenic distribution is usually only a rough estimate.

The most common methods to determine the biogenic content of municipal solid waste (MSW) or solid recovered fuel (SRF) are the selective dissolution and manual sorting (CEN, 2006a). The selective dissolution method is based on the faster oxidation and dissolution of biomass in concentrated sulphuric acid and hydrogen peroxide while non-biomass carbon is not dissolving. However, certain products of fossil carbon, like polyurethane (PUR) are dissolved, and others of biogenic origin, such as charcoal

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are not. In addition, this method requires representative sampling of a few grams out of a waste bunker of hundreds of tons (CEN, 2006b, c). For the manual sorting method, mixed wastes such as MSW or SRF have to be separated into several fractions (e.g. wood, glass, plastics) which are attributed to biogenic, fossil or inert matter. Composite materials are often disregarded. Both, selective dissolution and manual sorting are cost- and labour-intensive, and yield rather uncertain values due to their systematic limitations.

Consequently, alternative approaches are attracting interest. One is the "balance method", developed at the Vienna University of Technology, which calculates the proportion of biogenic to fossil carbon from a set of mass and energy balances (Fellner et al., 2007). Input parameters are retrieved from literature (e.g. chemical composition of moisture-and-ash-free biomass) and from operation data measured at the waste incinerator.

Another alternative approach is the ^{14}C method. It links the biogenic carbon content of wastes to the concentration of the radioactive isotope carbon-14 (^{14}C, half-life: 5780 years) in the carbon dioxide released during combustion. Thereby it allows a distinction of fossil carbon, in which the originally existing ^{14}C is completely decayed, and modern (biogenic) carbon, which exhibits the current ^{14}C level. Thus the biogenic fraction is proportional to its ^{14}C content and can be determined. The wide interest in this topic is reflected in the activities of the CEN/TC 343 working group (WG 3) which is preparing a technical specification for the laboratory analysis of the biomass content in SRF (CEN, 2007). An American test method for the analysis of the bio-based content of carbon containing materials with the ^{14}C method has been published (ASTM, 2006). In contrast to our approach, ^{14}C laboratory analysis of mixed wastes, however, requires labour- and cost-intensive sampling. A European patent suggests the application of the ^{14}C method for an on-line determination of the ratio of renewable to non-renewable energy sources (Kneissl, 2005). A preliminary investigation was carried out by Hämäläinen et al. (2007), who analysed ^{14}C in flue gases of different power plants based on short samples collected in Tedlar bags. However, this only represents a snap-shot and a validation of this approach is still missing. Furthermore, no methodology is given so far to determine the ^{14}C content of pure biogenic waste ($f_{\mathrm{M,bio}}$), as a reference value, which is one of the key elements of the method. Finally, it was also considered that the ^{14}C approach could be biased by disposed ^{14}C labelled materials.

In the present study the development and successful implementation of the ^{14}C method for field measurements at three waste-to-energy (WTE) plants is reported. Additionally, inter-comparison measurements were performed using the balance method as a completely independent approach. Both methods determine the ratio of biogenic to fossil CO_2 emissions by employing the entire WTE plant as an "analytical tool". Thus, these analyses integrate over thousands of tons of waste being incinerated and are therefore superior to standard waste analyses which are based on small and singular samples.

2. Methods

2.1. Field campaign

All three waste incinerators were located in the vicinity of Zurich (Switzerland). The plants are referred to by the letters A, B and C. Field campaigns were executed at WTE A from October–November 2006, at WTE B from November–December 2006 and at WTE C from January–February 2007. Average operating parameters for the relevant periods are given in Table 1. A schematic representation of the field setup is shown in Fig. 1.

2.2. ^{14}C method

2.2.1. On-site CO_2 sampling and release in the laboratory

On-site sampling at all three WTE plants was done by collecting 9–10 CO_2 samples each integrating over 3–4 days in a period of approximately one month (Fig. 1). A constant flow of 10 sccm of particle-free, hot and humid flue gas was sucked through two consecutive washing bottles (A and B), each filled with 100 ml 4 M aqueous KOH solution ($K_2CO_3 \leqslant 0.6\%$). Potassium hydroxide was preferred over the typically used NaOH because of the better solubility of the potassium carbonates compared to the corresponding sodium compounds. After passing a drying sorbent, gas flows were controlled using a mass flow controller (Voegtlin Instruments, CH) followed by a diaphragm pump (KNF Neuberger, CH). A CO_2 sensor (MSA Auer, Germany) was placed behind the pump to detect a potential CO_2 breakthrough. Thorough leak tests were performed before and after every sampling period to exclude the contamination with ambient CO_2.

CO_2 of six randomly selected absorption samples was released in the laboratory by acidification of <1 ml solution with 1 ml 4 M phosphoric acid. For three samples, CO_2 of the second washing bottle (B) was expelled separately to check the absorption rate. After removal of water vapour

Table 1
Average operating parameters of the incineration plants during the field campaign

Incinerator	Measurement period	Waste throughput ($t\,d^{-1}$)	Flue gas volume (dry) ($Nm^3\,h^{-1}$)	CO_2 concentration (%)
A	October–November 2006	350	106 000	9.3
B	November–December 2006	140	37 500	9.1
C	January–February 2007	340	83 300	10.2

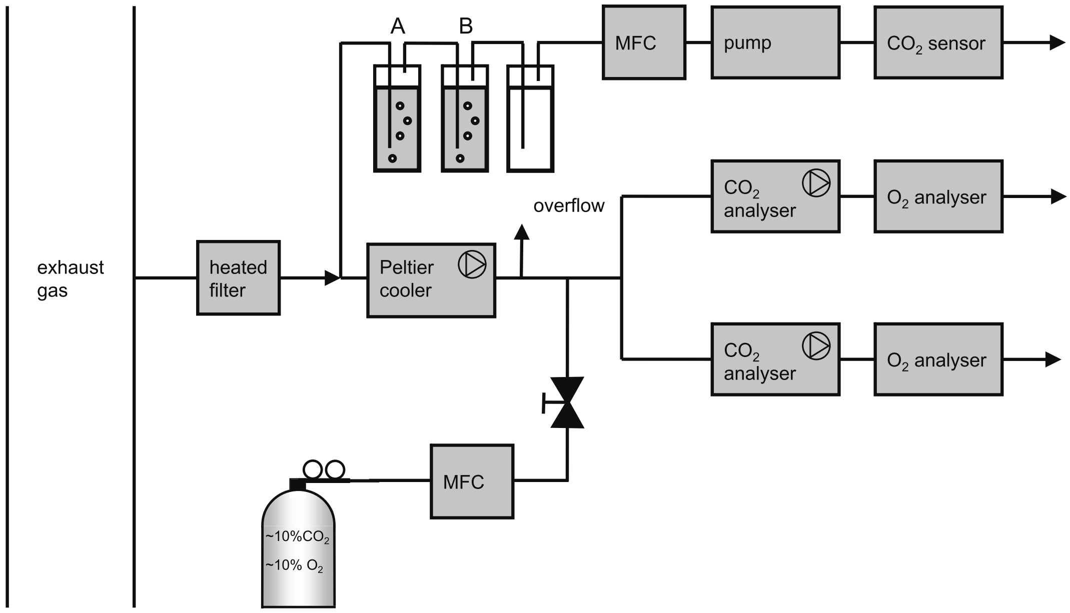


Fig. 1. Schematic drawing of the field setup for CO_2 absorption (^{14}C method). Additionally, two sets of gas analyzers for O_2 and CO_2 were operated in parallel to obtain reliable data sets for the balance method.

in a cryotrap (dry ice/ethanol), CO_2 was cryofocused in a calibrated test tube. The total amount of CO_2 was determined manometrically according to the ideal gas law. The amount of CO_2 expected in the absorbing solution was estimated based on the sampled gas volume and the CO_2 concentration determined by the gas analysers. The recovery rate, which was calculated as the ratio of the CO_2 volume released in the laboratory and the CO_2 volume expected in the absorbing solution, was on average higher than 95%. Therefore, effects of CO_2 absorption and release on the $^{14}CO_2$ concentration can be excluded.

2.2.2. ^{14}C determination by accelerator mass spectrometry (AMS)

The ^{14}C content of the CO_2 samples was analyzed at the PSI/ETH AMS (Synal et al., 1997) and reported in relation to the reference year 1950 in terms of "fractions of modern carbon" (f_M) by comparison to a standard (Stuiver and Polach, 1977):

$$f_{M,\mathrm{sample}} = \frac{(^{14}C/^{12}C)_{\mathrm{sample}}}{(^{14}C/^{12}C)_{\mathrm{AD1950}}} \qquad (1)$$

2.2.3. Calculation of biogenic/fossil CO_2 emissions

While $f_{M,\mathrm{sample}}$ is the directly measured parameter, the fraction of biogenic or fossil carbon (%Bio C, %Fos C) has more practical relevance:

$$\%\mathrm{BioC} = 100\% - \%\mathrm{FosC} = (f_{M,\mathrm{sample}}/f_{M,\mathrm{bio}}) * 100\% \qquad (2)$$

Because ^{14}C in fossil material is completely decayed, the fraction of biogenic carbon (%Bio C) is directly proportional to the ^{14}C content in the emitted CO_2. However, for the calculation of %Bio C, the f_M value of the pure biogenic fraction of the incinerated wastes ($f_{M,\mathrm{bio}}$) is needed as a reference. $f_{M,\mathrm{bio}}$ depends on the ^{14}C content of atmospheric CO_2 during biomass growth and thus mainly on its age and felling year (Lewis et al., 2004). As a consequence of the nuclear bomb tests, the ^{14}C content of atmospheric CO_2 reached a maximum of approx. 2.0 in the early 1960s, related to the reference year 1950, and declined since then to about 1.0 due to atmospheric exchange and fossil CO_2 emissions (Levin and Kromer, 2004; Levin et al., 2003). A strategy for the calculation of the reference value $f_{M,\mathrm{bio}}$, of the biogenic waste fraction is given in Section 3.1. The overall uncertainty (95% confidence) of %Bio C is calculated from the uncertainty in the reference value $f_{M,\mathrm{bio}}$ and, as minor contribution, the uncertainty of the AMS measurement result $f_{M,\mathrm{sample}}$ (<1%, relative uncertainty 1σ) using the laws of error propagation.

2.3. Balance method

An alternative approach for determining biogenic and fossil CO_2 emissions from waste incineration is the so-called balance method (Fellner et al., 2005). It combines standard data on the chemical composition of biogenic and fossil organic matter with routinely measured operating data of the incineration plant and has been described in Fellner et al. (2007) and Rechberger et al. (2007). Therefore, in this paper only a short introduction of the balance method is given.

The concept is based on five mass balances and one energy balance. The result of each balance describes a certain waste characteristic (e.g. carbon content, calorific value, ash content). The balances represent a set of equations which is mathematically over-determined (more equations than unknowns). All required input data for the equations are considered with their respective uncertainty,

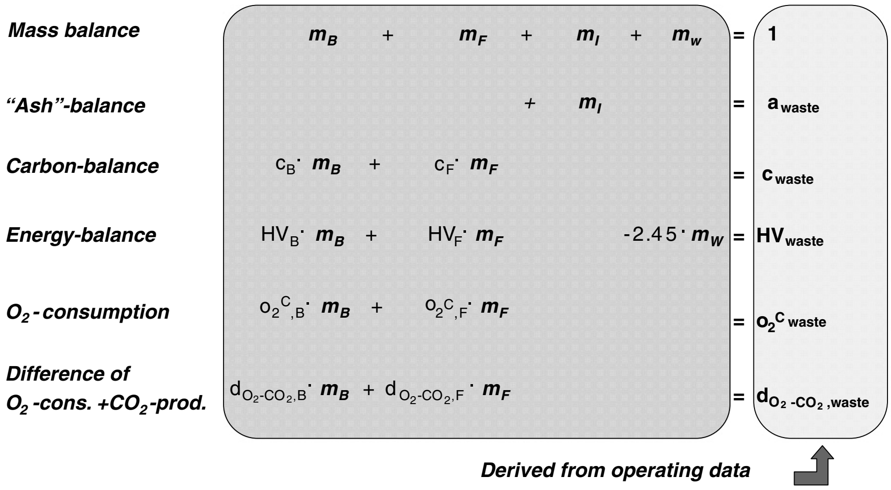
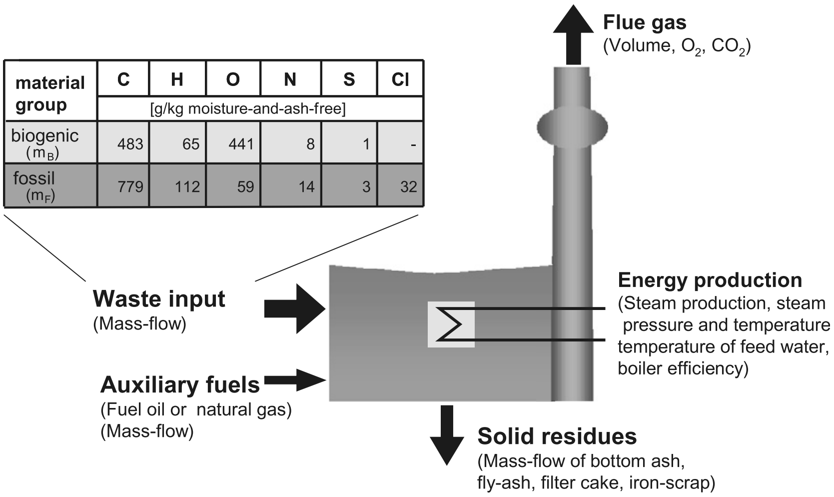


Fig. 2. Set of equations of the balance method (simplified), the four unknowns m_B, m_F, m_I, and m_W are to be determined (m_B mass of biomass, m_F mass of fossil matter, m_I mass of inert fraction, m_W mass of water) (Fellner et al., 2007).



material group	C	H	O	N	S	Cl
	[g/kg moisture-and-ash-free]					
biogenic (m_B)	483	65	441	8	1	-
fossil (m_F)	779	112	59	14	3	32

Fig. 3. Required input data for the balance method (Fellner et al., 2007).

which means that all assumptions, analytical uncertainties are reflected in the final result. In order to solve the mathematical problem error propagation and non-linear data reconciliation are applied. The calculated result is given by a mean value (most probable value) and a mathematically–statistically derived uncertainty range (e.g. a 95% confidence interval).

In particular, the approach is based on the following balances: mass balance, ash balance, carbon balance, energy balance, balance of O_2 consumption, and balance of difference between O_2 consumption and CO_2 production. Fig. 2 shows a simplified structure of the set of equations. A detailed mathematical description of each equation is given in Fellner et al. (2007) and Rechberger et al. (2007).

The input data required for the balance method comprise routinely recorded operating data of the incineration plant and basic information about the chemical composition of biogenic and fossil organic waste materials which are taken from literature (see Fig. 3). For example, the mean composition of biomass and its variation are well known. Once the unknowns (m_B, m_F, m_I, *and* m_W) are determined, the ratio of energy, and the carbon content of biogenic and fossil materials in the waste feed are calculated.

It is noteworthy that the balance method allows a temporal resolution of the result down to daily mean values, and that simultaneously to the fraction of biogenic carbon, the ratio of energy sources of the waste can be determined.

3. Results and discussion

In Section 3.1 a strategy for the calculation of the ^{14}C content of the pure biogenic fraction of the incinerated wastes ($f_{M,bio}$) is given. Based on this reference value and the ^{14}C analysis of emission CO_2 in Section 3.2 an apportionment of biogenic and fossil CO_2 emissions was performed for three WTE plants and compared to results obtained by the balance method as an independent approach.

3.1. Reference value for the ^{14}C content of pure biogenic waste – ^{14}C method

Because ^{14}C is completely decayed in fossil material, the biogenic waste fraction is directly proportional to the f_M value in emitted CO_2 (see Section 2.2.3). The proportionality constant ($f_{M,bio}$), which is the average ^{14}C content in biogenic waste, is calculated from the ratio of characteristic biogenic waste fractions α and their respective ^{14}C content ($f_{M,bio}$):

$$f_{M,bio} = \sum \alpha_{\text{waste fraction}} \times f_{M,bio,\text{waste fraction}} \tag{3}$$

To establish $f_{M,bio}$ from Eq. (3), the following steps will be described below: (i) determination of the relative contribution and their variability for the main biogenic waste fractions: wood, paper and fresh biomass (Section 3.1.1); (ii) evaluation of the age distribution for each waste fraction to estimate their ^{14}C content (Section 3.1.2); and (iii) calculation of $f_{M,bio}$ according to Eq. (3) using a Monte Carlo simulation by randomizing the percentages of waste fractions and their radiocarbon contents within their uncertainty limits (Section 3.1.3).

The assumption that $f_{M,bio}$ corresponds to the ^{14}C content of fresh biomass (ASTM, 2006) would lead to an overestimation of the biogenic fraction because ambient ^{14}C content was higher in the past, a signature that is conserved in wood and its products which contribute significantly to the biogenic fraction of mixed wastes. In the following, therefore the contribution and $f_{M,bio}$ of the most important biogenic waste fractions will be analyzed. In order to account for limited information on the waste composition and their variability, uncertainties are attributed to all input parameters. These uncertainties were assumed to describe a rectangular distribution and to have rather large values. This is considered to be a conservative approach which, as the results below will show, still leads to plausible, robust results and an acceptable overall uncertainty.

3.1.1. Relative contribution of biogenic waste fractions

The input to waste incinerators is mainly composed of municipal solid waste (MSW and bulky waste), building and demolition waste (BDW), special waste mainly from industrial production processes, and a small contribution of sewage sludge (SL). In Switzerland, MSW and bulky waste dominate the input with a contribution of 81.7%. The other components amount to 12.0% for BDW, 3.8% for special waste and 2.5% for sewage sludge (Hügi and Gerber, 2006; Steiger, 2003). For the calculation of $f_{M,bio}$, MSW, BDW and SL were considered, which cover more than 95% of combustible waste. To account for variations in water and ash content, the contribution of the biogenic waste fractions is given in %daf in Table 2, i.e. on a dry and ash-free base (Kost, 2001).

The biogenic part of BDW is predominantly made up of wood from dismantled buildings and renovations, while sewage sludge primarily consist of fresh biomass, respectively (Arioli and Haag, 2001). MSW has a more heterogeneous composition with three major fractions; paper/cardboard, fresh biomass and wood, mainly from furniture (Steiger, 2003). It is composed of a dominant domestic waste fraction (around 60%), and of waste with similar composition from industrial sources (Hügi and Gerber, 2006). Since no detailed information is available, a comparable composition for the domestic and industrial fraction is assumed.

Accordingly, the percentages of the three main biogenic waste fractions paper/cardboard, fresh biomass and wood are 43.2%daf (α_{paper}), 21.6%daf ($\alpha_{\text{fresh biomass}}$) and 35.2%daf ($\alpha_{wood}$). For single incinerators and three day averaging intervals maximum deviations described by a rectangular probability distribution, were estimated with ±20% for the fractions paper/cardboard and wood and ±10% for fresh biomass. The ^{14}C content of the individual fractions will be discussed in the following sections.

3.1.2. ^{14}C content of biogenic waste fractions

3.1.2.1. Paper/cardboard. The main part of the biogenic waste fraction is paper/cardboard, which is composed of numerous products, e.g. from newspapers and magazines to kitchen towels. Because the market for paper and cardboard as well as its raw materials is very open, biomass, i.e. wood used for production of paper/cardboard treated in Swiss incinerators, originates from different countries or even continents.

Based on a survey including several pulp manufacturers and wood experts (personal communications), the average age composition of wood used for paper/cardboard

Table 2
Prominent waste categories burnt in Swiss incinerators and the share of the main biogenic waste fractions therein, related to the weight of total biogenic waste on a dry and ash-free base (%daf)

Waste category	Weight content[a,b]	Paper/cardboard	Fresh biomass	Wood
Municipal solid waste (MSW)	78.9%daf (81.7%)	43.2%daf	19.8%daf	15.9%daf
Building and demolition waste (BDW)	19.3%daf (12.0%)			19.3%daf
Sewage sludge (SL)	1.8%daf (2.5%)		1.8%daf	
	100%daf	43.2%daf	21.6% daf	35.2%daf

[a] Due to its varying composition the category special waste was not considered.
[b] Numbers in parentheses are related to the wet total weight.

production was determined (Table 3). Around 20% each of biomass used for paper production was assumed to stem from 10 and 20 year old trees, mainly from first forest thinning and wood chips from timber production. The main part, viz. 40%, is derived from 40 year old biomass from later thinning. Mature trees with 65 and 85 years originating from regeneration, i.e. final cuttings, represent approximately 10% of total biomass. Felling was assumed in 2002 ± 3. The ^{14}C content of single wood fractions with age between 5 and 100 years and felling from 1999 to 2005 was computed using the Chapman–Richards growth model ($\tau = 50$; $m = 3$) as published by Lewis et al. (2004) and presented in Fig. 4.

Using a Monte Carlo simulation method, the ^{14}C content of different biomass fractions and the average reference value for the fraction paper/cardboard ($f_{\mathrm{M,bio,paper}}$) were calculated (Table 3). $f_{\mathrm{M,bio,paper}}$ as well as its uncertainty were computed by summing up the ^{14}C content of wood fractions weighted by their relative share as 1.153 ± 0.024 (uncertainty 1σ, normal distribution). The uncertainty includes variations in age and relative share of the biomass fractions and variations in the ^{14}C content of atmospheric CO_2.

3.1.2.2. Fresh biomass. Fresh biomass is made up of kitchen slops, eatables, and garden as well as balcony plants, etc., which are grown in recent years. Therefore, their ^{14}C content can be approximated by the ^{14}C value of current atmospheric CO_2 being 1.053 ± 0.015 ($f_{\mathrm{M,bio,fresh\ biomass}}$) for 2006 (uncertainty 1σ, normal distribution). The uncertainty includes variations in the ^{14}C content of atmospheric CO_2 and a conservative estimate of the fresh biomass age.

3.1.2.3. Wood. The wood fraction in waste consists in approximately equal shares of construction timber from dismantling and renovations and disposed furniture in the bulky waste. Logs used for these applications are usually between 50 and 100 years old. Their year of felling can be approached by the production year of the furniture or the construction year of the buildings presently broken down. While the main part of construction timber from dismantling and renovations is more than 40 years old (Arioli and Haag, 2001), the life cycle of furniture is usually shorter.

Table 3
Age, relative share and ^{14}C content of biomass fractions used for paper/cardboard production; felling assumed between 1999 and 2005

Age[a] (year)	Relative share[a] (%)	^{14}C content[b] $f_{\mathrm{M,bio}}$
10 ± 2.5	20 ± 10	1.084 ± 0.016
20 ± 2.5	20 ± 10	1.102 ± 0.018
40 ± 10	40 ± 20	1.176 ± 0.046
65 ± 10	10 ± 5	1.246 ± 0.014
85 ± 10	10 ± 5	1.208 ± 0.017
		1.153 ± 0.024

[a] Rectangular probability distribution.
[b] Uncertainty 1σ (normal distribution).

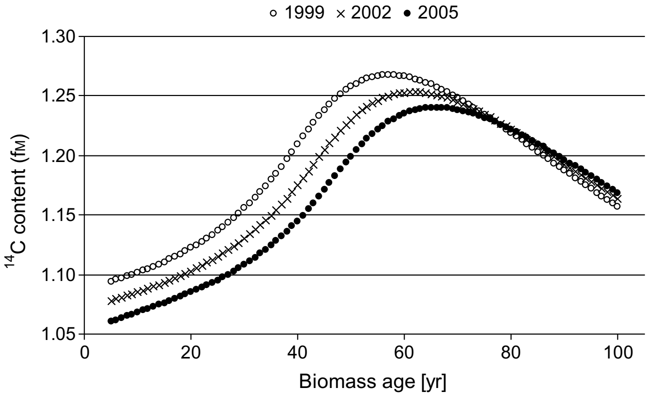


Fig. 4. ^{14}C content of 5–100 year old biomass harvested between 1999 and 2005; calculated according to Lewis et al. (2004) based on annual mean $^{14}CO_2$ concentrations at the research station Schauinsland (Levin, 2007; Levin and Kromer, 2004) and derived from tree ring data (Stuiver and Quay, 1981).

The ^{14}C content of different wood fractions 50–100 years old and felling between 1900 and 2000 was calculated according to Lewis et al. (2004) and plotted in Fig. 5. Because, particularly the composition of building and demolition waste may strongly change due to big mono-assortments for $f_{\mathrm{M,bio,wood}}$ a range from 0.98 to 1.32 was assumed with a rectangular probability distribution.

3.1.3. Monte Carlo simulation

In the preceding sections the relative contribution of the biogenic waste fractions and their ^{14}C content were estimated. Paper/cardboard, wood and fresh biomass represent 43.2 ± 20%daf, 21.6 ± 10%daf and 35.2 ± 20%daf of pure biogenic waste, respectively. Their ^{14}C content corresponds to 1.153 ± 0.024 for paper/cardboard, 1.053 ± 0.015 for fresh biomass, and 0.98–1.32 for wood. A rectangular probability distribution was assumed as a conservative estimate for the relative shares of the biogenic waste fractions and the ^{14}C content of wood. For the ^{14}C content of paper/cardboard and fresh biomass a normal distribution was adopted because this was judged to be the best

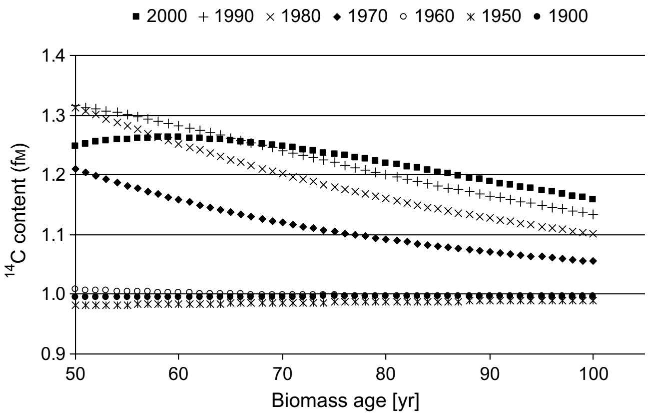


Fig. 5. ^{14}C content of 50–100 year old logs felt between 1900 and 2000; calculated according to Lewis et al. (2004).

representation for these large and heterogeneous fractions with a variable age distribution.

Using the above values, the average ^{14}C content of pure biogenic waste and its uncertainty (1σ, normal distribution) can be determined by a Monte Carlo simulation as

$$f_{\mathrm{M,bio}} = 1.130 \pm 0.038$$

Our reference value is distinctly higher than the value of 1.075 used in the American ASTM standard test method (2006). As can be inferred from the extensive discussion above, this is only appropriate for recently grown biomass. The German DIN report suggest reference values in the range from 1.075 to 1.18 (CEN, 2007). From our study it becomes clear that a realistic and sufficiently robust value for $f_{\mathrm{M,bio}}$ can be determined even if the composition of mixed waste is not known in every detail. The calculated reference value $f_{\mathrm{M,bio}}$ is only valid for the current biogenic waste fraction, and will decline in the future due to a constant decrease of the atmospheric ^{14}C content. For the years 2010 and 2015, $f_{\mathrm{M,bio}}$ was calculated to be 1.113 ± 0.038 and 1.092 ± 0.038, respectively, assuming a constant waste composition and a decrease in atmospheric $^{14}CO_2$ of 0.6% per year.

3.2. Intercomparison on determination of biogenic CO_2 emission fractions

The ^{14}C and the balance method were successfully applied at three different WTE plants in Switzerland. To limit the costs for ^{14}C analysis, for every WTE plant, out of the 9–10 time intervals of 3–4 days, six were randomly selected and the respective CO_2 samples processed and analyzed for ^{14}C by AMS. Moreover, the average ratio of biogenic CO_2 emissions was calculated for these intervals using the balance method (Table 4).

Excellent agreement between the ^{14}C and the balance method was observed with respect to single sampling intervals as well as for the average biogenic CO_2 emissions (%Bio C) of all WTE plants (Table 4). %Bio C determined by the ^{14}C method were on average 0.9% higher than values obtained by the balance method. However, differences between both methods are within their uncertainties. Based on this very consistent dataset there is no indication for any contamination with ^{14}C labelled waste. In Switzerland, the intensive use of ^{14}C isotopes, mainly for medical applications, must be approved by federal authorities, and contaminated waste should not reach normal waste incinerators.

For all WTE plants, %Bio C was slightly above 50% (Table 4). The fraction of biogenic CO_2 emissions was thus distinctly lower than 60%, which is used in the current Swiss greenhouse gas inventory (FOEN, 2007). However, the emphasis of our study was on the method development. Seasonal variations in waste composition would have to be taken into consideration to obtain a reliable annual average (Morf et al., 2004).

Temporal variations within the considered sampling periods are reflected by changes of biogenic emissions

Table 4
Fractions of biogenic CO_2 emissions for three WTE plants in Switzerland determined by the ^{14}C and the balance method with 95% confidence intervals

	Sampling interval		%Bio C (%)	
	Start	End	^{14}C method	Balance method
WTE A (2006)	09.10.06, 15:25	12.10.06, 15:25	54.8 ± 3.8	52.3 ± 4.5
	12.10.06, 16:45	15.10.06, 20:05	51.3 ± 3.5	50.1 ± 4.6
	16.10.06, 09:20	19.10.06, 06:45	53.4 ± 3.7	53.7 ± 4.5
	27.10.06, 09:25	30.10.06, 09:35	51.9 ± 3.6	51.2 ± 4.6
	31.10.06, 10:25	03.11.06, 12:40	53.0 ± 3.6	51.7 ± 4.6
	03.11.06, 13:30	06.11.06, 11:43	51.8 ± 3.6	52.8 ± 4.5
			52.7 ± 2.6	51.9 ± 2.6
WTE B (2006)	14.11.06, 14:30	17.11.06, 07:39	47.3 ± 3.3	50.1 ± 4.7
	17.11.06, 08:30	20.11.06, 09:10	52.2 ± 3.6	52.6 ± 4.6
	20.11.06, 10:05	24.11.06, 06:45	50.0 ± 3.4	49.9 ± 4.7
	27.11.06, 13:25	30.11.06, 09:55	50.1 ± 3.5	53.1 ± 4.8
	04.12.06, 08:55	08.12.06, 11:15	59.2 ± 4.0	51.7 ± 4.6
	08.12.06, 12:15	11.12.06, 11:45	53.6 ± 3.7	53.0 ± 4.6
			52.1 ± 8.2	51.8 ± 2.8
WTE C (2007)	16.01.07, 11:45	19.01.07, 07:45	49.0 ± 3.4	47.1 ± 4.6
	25.01.07, 23:15	29.01.07, 12:45	48.4 ± 3.3	49.1 ± 4.5
	29.01.07, 13:40	01.02.07, 13:20	55.6 ± 3.8	51.1 ± 4.4
	01.02.07, 14:05	05.02.07, 07:05	50.6 ± 3.5	50.8 ± 4.4
	05.02.07, 08:00	09.02.07, 08:20	48.2 ± 3.3	48.4 ± 4.5
	09.02.07, 09:00	12.02.07, 08:10	55.4 ± 3.8	51.7 ± 4.4
			51.2 ± 6.9	49.7 ± 3.6

between consecutive 3 and 4 day samples. The standard uncertainty (95% confidence) of the mean value for individual WTEs is therefore rather a measure for the variation of the average biogenic waste fraction and not for the precision of the analytical methods.

4. Conclusions

The present study demonstrates a successful development and implementation of the ^{14}C method for field measurements of biogenic vs. fossil CO_2 emissions at WTE plants. The ^{14}C method is based on a simple and demonstrative concept linking the biogenic content of mixed wastes to a characteristic property related to its origin. Because ^{14}C is completely decayed in fossil material, the biogenic waste fraction is directly proportional to the ^{14}C content in emission CO_2. The proportionality constant, which is the average ^{14}C content in the biogenic fraction of mixed wastes, is therefore of major importance.

Based on literature and expert communications input parameters for the ^{14}C reference value of the biogenic waste fraction were derived. In particular the share of characteristic waste fractions, its biomass age and year of felling as well as their uncertainties were estimated. A Monte Carlo simulation method was parameterised to obtain a robust and plausible reference value $f_{\mathrm{M,bio}}$ of 1.130 ± 0.038. ^{14}C analysis of emission CO_2 permitted the apportionment of biogenic and fossil CO_2 emissions to approximately 50% during the investigated period.

An inter-comparison measurement at three different WTE plants, using the balance method as a completely independent approach, resulted in an excellent agreement of both methods. Consequently, there is no indication for any contamination with ^{14}C labelled waste for these WTE plants. Biogenic emissions of all waste incinerators were higher than fossil CO_2 emissions but distinctly lower than current national estimates in Switzerland. Both methods allow representative sampling as well as long-term monitoring of biogenic vs. fossil CO_2 emissions and are thereby superior to standard techniques like selective dissolution and manual sorting. Additionally, the application of both methods is not restricted to waste incinerators but can be extended to industrial co-incineration plants such as cement kilns.

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