



Fossil and biogenic CO₂ from waste incineration based on a yearlong radiocarbon study

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ABSTRACT

We describe the first long-term implementation of the radiocarbon (¹⁴C) method to study the share of biogenic (%Bio C) and fossil (%Fos C) carbon in combustion CO₂. At five Swiss incinerators, a total of 24 three-week measurement campaigns were performed over 1 year. Temporally averaged bag samples were analyzed for ¹⁴CO₂ by accelerator mass spectrometry. Significant differences between the plants in the share of fossil CO₂ were observed, with annual mean values from 43.4 ± 3.9% to 54.5 ± 3.1%. Variations can be explained by the waste composition of the respective plant. Based on our dataset, an average value of 48 ± 4%Fos C was determined for waste incineration in Switzerland. No clear annual trend in %Fos C was observed for four of the monitored incinerators, while one incinerator showed considerable variations, which are likely due to the separation and temporary storage of bulky goods.

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1. Introduction

Solid waste or solid recovered fuels (SRF) contain resources that can be recovered as material or energy. Although re-use and recycling should be favored as they lead to reduced energy consumption and less environmental impact, combustion of mixed or non-recyclable material streams in efficient waste-to-energy plants is part of an integrated waste management system (Tyskeng and Finnveden, 2010). Furthermore, heat and electricity production from the incineration of biogenic waste is considered as a renewable energy source, while fossil CO₂ emissions are non-renewable and have to be included in the national greenhouse gas inventory (Sabin Guendehou et al., 2006). As a consequence of these regulations and their financial implications, there is a growing interest in analytical techniques for the determination of the share of biogenic and fossil carbon in SRF.

Three normative methods for the determination of the biomass fraction in SRF are specified in a recent European standard (CEN, 2011a): selective dissolution, manual sorting, and the analysis of the ¹⁴C content. However, the explanatory power of these techniques, if applied on singular waste samples (CEN, 2011b,c), is limited. Furthermore, the applicability of the selective dissolution and manual sorting method is restricted by systematic limitations (CEN, 2011a; Staber et al., 2008). Correspondingly, significant

discrepancies in the biogenic carbon content were observed applying both techniques on different SRF fractions (Séverin et al., 2010).

In contrast to selective dissolution and manual sorting, the ¹⁴C method directly links the biogenic carbon content of waste to the measurand, i.e. the concentration of the radioactive isotope carbon-14 (¹⁴C, half-life: 5730 years). Thereby it allows the distinction between fossil carbon, in which the originally existing ¹⁴C is completely decayed, and modern (biogenic) carbon, which exhibits the current ¹⁴C level (ASTM, 2011; CEN, 2011a; ISO, 2011). It is an inherent advantage of the ¹⁴C method that it can be applied on representative gas samples, which allows the temporal integration over the entity of the combusted waste. The wide interest in this topic is reflected in the current activities of the ISO/TC 146/SC 1 working group (WG 26) which prepared a draft standard for the analysis of the biomass (biogenic) and fossil-derived CO₂, including sampling strategy and ¹⁴C laboratory analysis (ISO, 2011).

Until today, full-plant applications of the ¹⁴C method on combustion CO₂ are limited to short-term methodological investigations (Calcagnile et al., 2011; Hämäläinen et al., 2007; Palstra and Meijer, 2010) or inter-comparison studies (Mohn et al., 2008). Remaining limitations are mainly due to contamination problems with ambient CO₂ (Calcagnile et al., 2011; Palstra and Meijer, 2010), the required sophisticated and labor-intensive ¹⁴C laboratory analysis (CEN, 2011a), and the ongoing discussions on an appropriate ¹⁴C reference value for the pure biogenic waste fraction (Mohn et al., 2008). As a consequence of the nuclear bomb tests, the ¹⁴C content of atmospheric CO₂ was doubled in the early 1960s and declined since then to nearly the level of the reference

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year 1950 due to atmospheric exchange and fossil CO₂ emissions (Levin et al., 2010). Correspondingly, the ¹⁴C reference value for pure biogenic waste ($f_{M,bio}$; f_M “fractions of modern carbon” in relation to 1950) depends on the ¹⁴C content of atmospheric CO₂ during biomass growth, and thus mainly on its age and felling year (Lewis et al., 2004). Existing standards disagree on the correct calculation of $f_{M,bio}$: while the American test method (ASTM, 2011) and the ISO draft standard (ISO, 2011) employ the current atmospheric ¹⁴CO₂ level (1.05) which is only representative for fresh biomass, the European standard DIN EN 15440 (CEN, 2011a) suggests a significantly higher default value for $f_{M,bio}$ of 1.12. This value agrees with the ¹⁴C content of the biogenic waste fraction of mixed household, commercial and bulky waste (1.113 ± 0.038) determined by Mohn et al. (2008) for Switzerland in 2010. The Swiss reference value is supported by an intercomparison study at three incinerators (Mohn et al., 2008), where the ¹⁴C method was in excellent agreement to an alternative approach based on mass and energy balances (Fellner et al., 2007; Staber et al., 2008). For current European waste a higher value of 1.156 ± 0.034 for $f_{M,bio}$ was calculated by Fellner and Rechberger (2009) following a similar approach as Mohn et al. (2008).

In the present project we describe the first yearlong implementation of the ¹⁴C method on combustion CO₂ combining collection of temporally averaged exhaust gas samples with precise ¹⁴CO₂ analysis by direct-inlet accelerator mass spectrometry (AMS). At five incinerators in Switzerland, a total number of 24 three-week measurement campaigns were executed to obtain a robust mean value for the share of biogenic and fossil CO₂ from Swiss waste incineration. Based on this extensive data set, we also analyze differences in the share of biogenic and fossil CO₂ between plants and their annual variability.

2. Materials and methods

2.1. Field campaign

Flue gas was sampled at five Swiss waste incinerators, referred to by plant codes A–E. The facilities offer one to four boilers and exhibit a waste throughput of 88,000–219,000 t year⁻¹ (Hügi, 2011). Field campaigns were executed between September 2010 and August 2011, with six measurement campaigns at waste-to-energy (WTE) plants A–C and three campaigns at plants D and E. Along with the gas sampling, data on the exhaust gas flow and the waste composition, in particular the shares of household waste, industrial waste and sewage sludge, were collected.

2.2. CO₂ sampling

Every measurement campaign, one representative gas sample was prepared based on three weekly integrating exhaust gas samples. During exhaust gas sampling (Fig. 1) a constant flow of around 200 sccm (standard cubic centimeter per minute) of flue gas was extracted from the duct, filtered by a heated out-stack quartz wool filter (120 °C, Koneth, Switzerland), and dried with a permeation dryer (70 °C, MD-070-24S, PermaPure Inc., USA). The main part of the dehumidified exhaust gas was applied under reduced pressure ($\Delta p = -600$ mbar; N010ST.18, KNF Neuberger, Switzerland) as purge gas for the permeation dryer. Alternatively, at WTE B, the sample was taken from the already filtered and dehumidified gas of the gas analysis system. For temporal integration, a constant flow (3 sccm) of particle-free and dried exhaust gas was pooled over 1 week in a 44 l aluminum lined gas bag (GSB-P/44, Ritter Apparatebau GmbH, Germany) applying a peristaltic pump (Ecoline VC-MS/CA 8-6 with Tygon LFL tubing ID 0.59 mm, Ismatec, Switzerland). This procedure is in accordance with the

current version of the ISO draft standard (ISO, 2011). Steady state sampling was applied as fluctuations of the exhaust gas flow rate (double standard deviation of daily average values) within a measurement campaign were generally below 10% (data not shown). In comparison, the ISO draft standard (ISO, 2011) indicates a limit of 55% above which flow rate proportional sampling should be implemented. At the beginning and at the end of every bag sampling the oxygen content in the sample gas was determined with a paramagnetic analyzer (Model 570A, Servomex, UK) and compared to the stack concentration analyzed by the continuous emission monitoring system of the plant to exclude significant leaks in the sampling setup. Additionally, the sample gas flow was determined (Optiflow 520, Humonics, USA) and was always within $\pm 10\%$ of the adjusted value (3 sccm). Integrity of weekly-average gas samples was assured, after transport to the laboratory, by CO₂ analysis employing a Nicolet Avatar 370 MCT FTIR spectrometer (Thermo Nicolet Corp., USA) equipped with a heated (40 °C) low-volume (50 ml) flow-through gas cell with 1 m pathlength (Model LFT-210, Axium Analytical Inc., USA) as in Mohn et al. (2010). Identical gas volumes of weekly gas samples of one campaign were pooled in a 5 l aluminum lined gas bag (GSB-P/5, Ritter Apparatebau GmbH, Germany) applying a mass flow controller (Vögtlin Instruments, Switzerland) and a gas tight membrane pump (PM25032-022, KNF Neuberger, Switzerland). The combined gas samples were processed as described in section 2.3. to determine the ¹⁴C value of CO₂ by AMS.

Suitability of the employed gas bags was assured by the absence of ¹⁴CO₂ analyzed ($f_{M,blank} = -0.003 \pm 0.008$, 95% confidence) in a gas bag (GSB-P/5, Ritter Apparatebau GmbH, Germany) filled with 100% fossil CO₂ standard gas (10% CO₂ in N₂, Messer Switzerland), and stored in ambient air over several weeks. This blank procedure guarantees that exhaust gas samples are not contaminated with ambient CO₂ during storage.

2.3. ¹⁴C analysis of CO₂ by AMS

After removal of water vapor from the pooled exhaust gas sample in a cryotrap (dry ice/ethanol) carbon dioxide was cryofocused applying liquid nitrogen, and the major air constituents as N₂ and O₂ were removed. The ¹⁴C content of the CO₂ samples was analyzed with the MICADAS system of the ETH Zürich (Wacker et al., 2010). The samples were introduced into the system as CO₂ using a direct gas inlet and a gas-capable ion source (Ruff et al., 2010, 2007; Wacker et al., 2012). Results are reported in relation to the reference year 1950 in terms of “fractions of modern carbon” (f_M) by comparison to a standard (SRM 4990B, $f_M = 1.0526$) (Stuiver and Polach, 1977):

$$f_{M,Sample} = (^{14}\text{C}/^{12}\text{C})_{\text{sample}} / (^{14}\text{C}/^{12}\text{C})_{\text{AD1950}} \quad (1)$$

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

$$\% \text{Bio C} = 100\% - \% \text{Fos C} = (f_{M,sample} / f_{M,bio}) \times 100\% \quad (2)$$

Because ¹⁴C in fossil material is completely decayed, the fraction of biogenic carbon is directly proportional to the ¹⁴C content in the emitted CO₂. No correction was applied for the ¹⁴CO₂ content in combustion air, as suggested by Calcagnile et al. (2011) as well as Palstra and Meijer (2010), as the exact effect is unknown but presumably smaller than 0.25%Fos C. This estimate is based on exhaust CO₂ concentrations of 10% ($f_{M,exhaust} \text{CO}_2 = 0.50-0.64$) and ambient CO₂ mixing ratios of 500 ppm ($f_{M,ambient} \text{CO}_2 = 1.05$). For the calculation of %Bio C, the $f_{M,bio}$ value of the pure biogenic fraction of the incinerated wastes ($f_{M,bio}$) is needed as a reference, which depends on the ¹⁴C content of atmospheric CO₂ during biomass

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