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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