Radiocarbon measurement of fossil CO_2 emissions from waste incineration plants

A monitoring tool for CO_2 trading in Denmark and Sweden

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In Denmark and Sweden:

WtE plants under the CO_2 Emission Trading System since 1 January 2013

Methods used for determination of annual fossil CO2 emissions from WtE plants in DK and SE

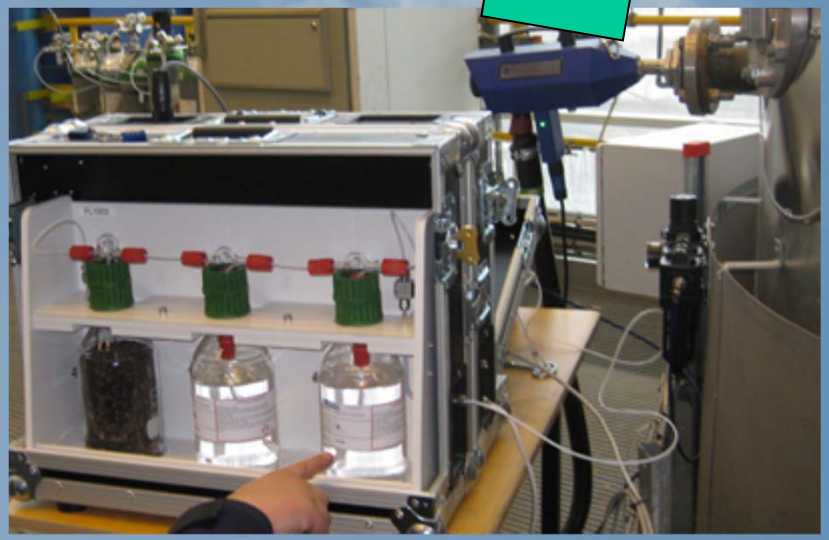
Plant cate-gory	Emission of fossil CO_2 (tonnes/ year)	Method for deter-mination	Methodology permitted	Max. uncer-tainty
A	< 50,000	Calculation approach	Standard, country specific emission factors used for fossil CO_2 emission: **Denmark:** 37.0 ton fossil CO_2 per TJ fuel. **Sweden:** - 30.2 ton fossil CO_2 per TJ fuel (household waste). - 36.8 ton fossil CO_2 per TJ fuel (industrial waste).	± 7.5 % (95 CI)
B	≥ 50,000	Monitoring approach	**Denmark:** 1. Carbon 14 based measurement method 2. Mass balance method **Sweden:** No guidelines given with respect to approved/permitted methods. The main two methods used are the carbon-14 method and the mass balance method.	± 7.5 % (95 CI)

Radiocarbon method for determination of the annual emission of fossil CO_2

AMS AMS

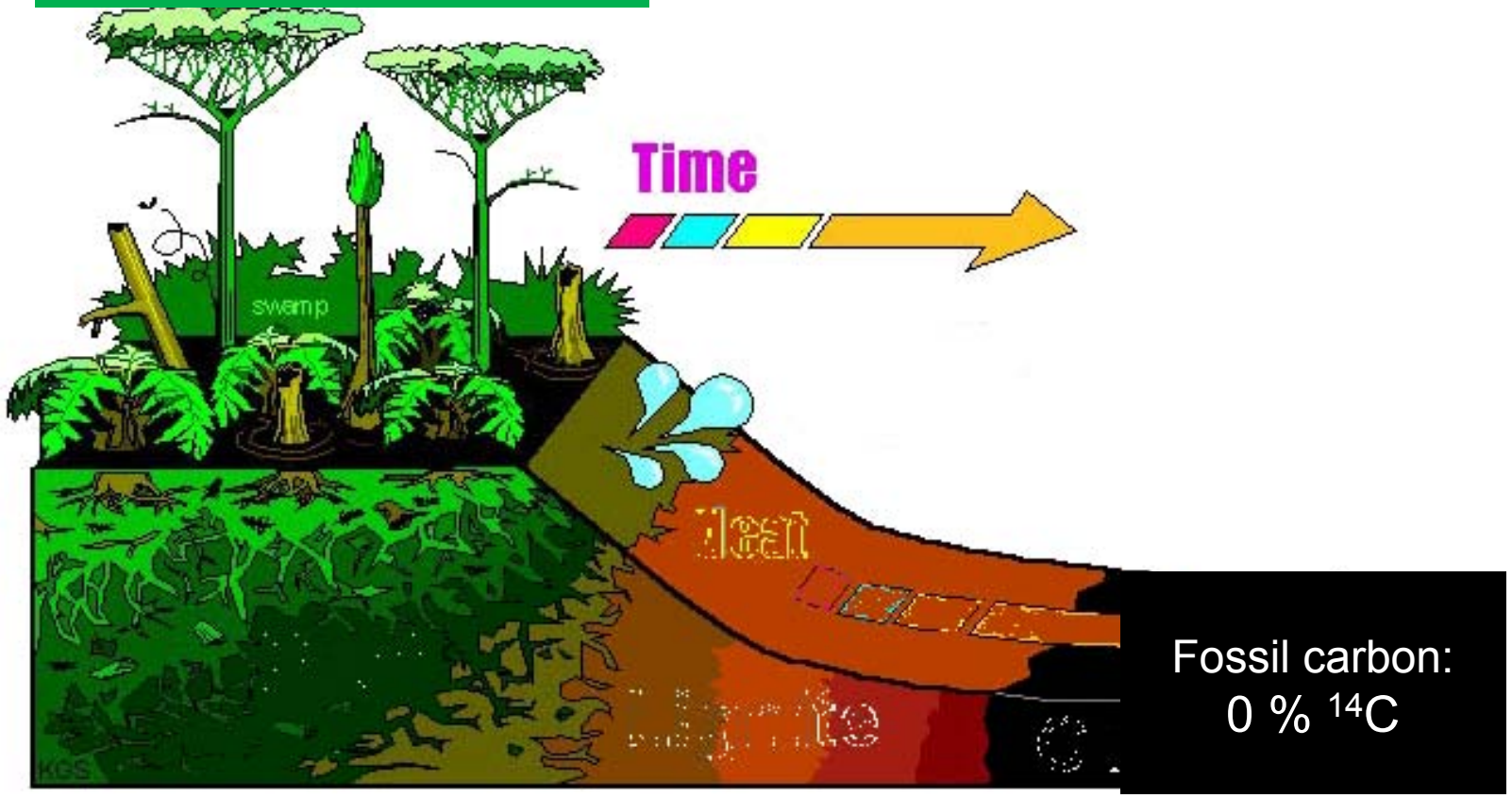
$$E, fCO_2 = fCO_2 \cdot totCO_2 \cdot Q(stack\ gas)$$

^{14}C



Content of carbon-14 in biogenic and fossil carbon

Fresh biomass: 100 % ^{14}C



Wood, straw, paper, cardboard, waste food etc.

Plastics, paint, oil products

Emission of fossil CO_2 from waste incineration plants

More fossil carbon in the waste → less ^{14}C in the emitted CO_2

Methodology described in EN ISO 13833

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN ISO 13833

April 2013

ICS 13.040.40

English Version

Stationary source emissions - Determination of the ratio of biomass (biogenic) and fossil-derived carbon dioxide - Radiocarbon sampling and determination (ISO 13833:2013)

Émissions de sources fixes - Détermination du rapport du dioxyde de carbone de la biomasse (biogénique) et des dérivés fossiles - Échantillonnage et détermination du radiocarbone (ISO 13833:2013)

Emissionen aus stationären Quellen - Bestimmung des Verhältnisses von Kohlendioxid aus Biomasse (biogen) und aus fossilen Quellen - Probenahme und Bestimmung des radioaktiven Kohlenstoffs (ISO 13833:2013)

This European Standard was approved by CEN on 1 March 2013.

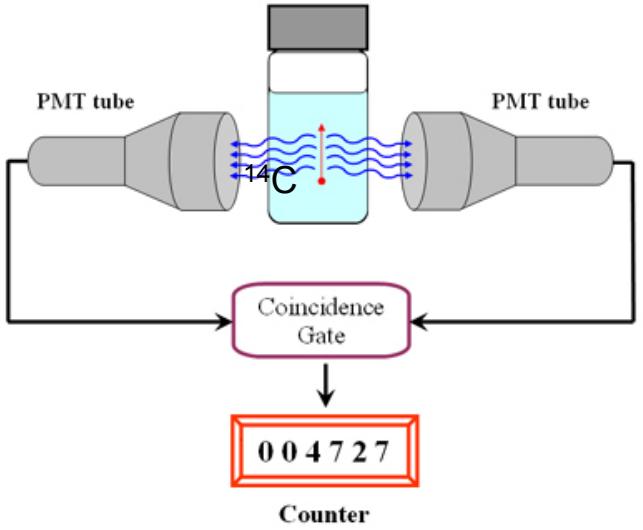
CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

Long term sampling and analysis of ^{14}C by Liquid Scintillation Counting (LSC)

Sampling of CO_2 from stack gas (4 or 8 weeks/sample)

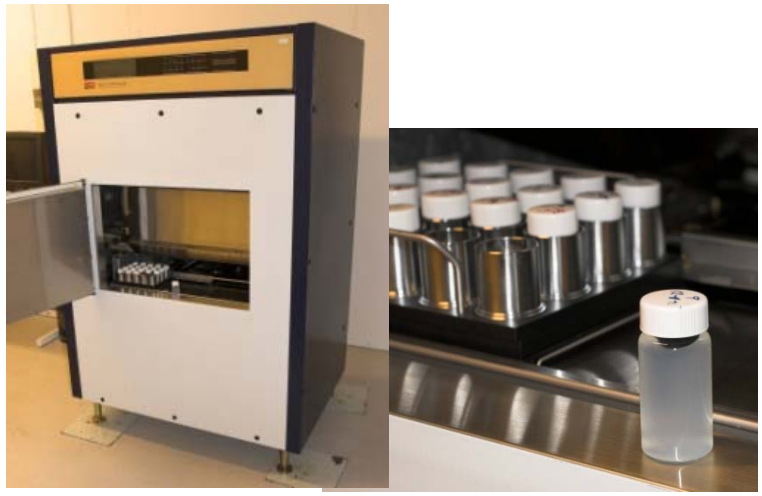
Transfer of CO_2 from sample to scintillation cocktail

Analysis by LSC



The ratio of biogenic CO_2 is calculated on the basis of analyses of reference materials:

- Zero (fossil CO_2), e.g. K_2CO_3
- 100% bio-CO_2
- All samples are spiked with known amounts of ^{14}C (traceable to NIST standard)



Calculation of the ratio of biogenic carbon to total carbon in the sample

$$pmC_{sample}\,[\%] = \frac{\left(DPM_{sample} - DPM_{background}\right)}{\varepsilon \cdot M_{CO2,sample}\,[g] \cdot C_{ratCCO2} \cdot C\left[\frac{dpm}{g}\right]} \cdot \frac{100}{pmC_{ref}} \cdot 100[\%]$$

Where

pmC_{sample} = the percentage of carbon in the sample that is of biomass origin, relative to the total mass of carbon in the sample

DPM_{sample} = the number of disintegrations per minute measured during LSC for the sample [min^{-1}]

$DPM_{background}$ = the number of disintegrations per minute measured during LSC for a sample 100% fossil carbon (without carbon of biomass origin)[min^{-1}]

ε = the total counting efficiency of the LSC detection, measured by spiking the sample with a reference sample of known ^{14}C abundance (including all quenching and geometry effects)

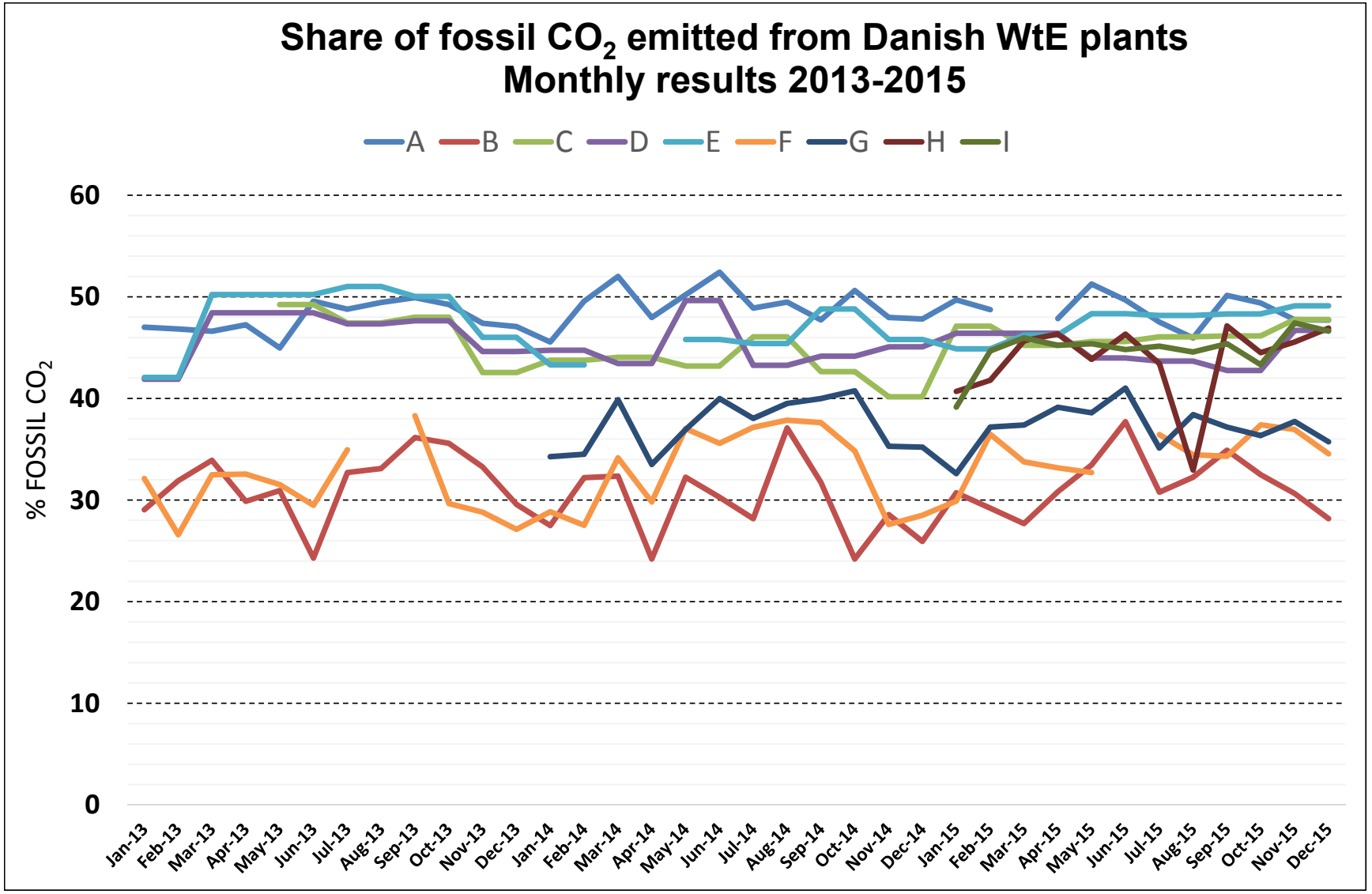
$M_{CO2,\ sample}$ = mass of carbon dioxide in the sample [g].

$C_{ratCCO2}$ = the mass ratio between carbon and carbon dioxide in a CO_2 molecule (=0.2729).

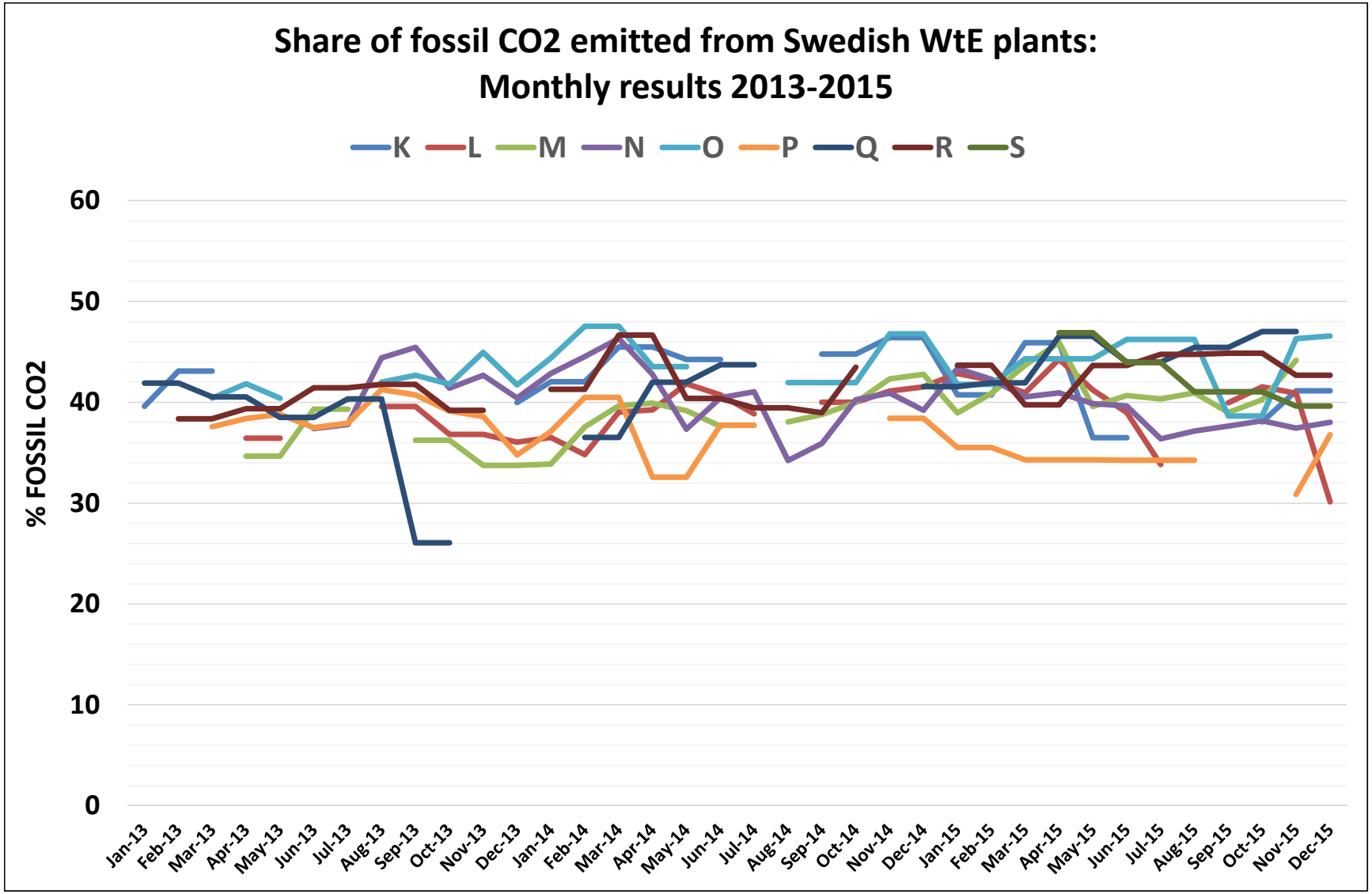
C = a constant representing the number of disintegrations per gram carbon of biomass origin = 13.65 [$min^{-1} \cdot g^{-1}$]

pmC_{ref} = a reference value representing the level of ^{14}C in the biomass used, given as an index value relative to the ^{14}C content in the atmosphere before 1950.

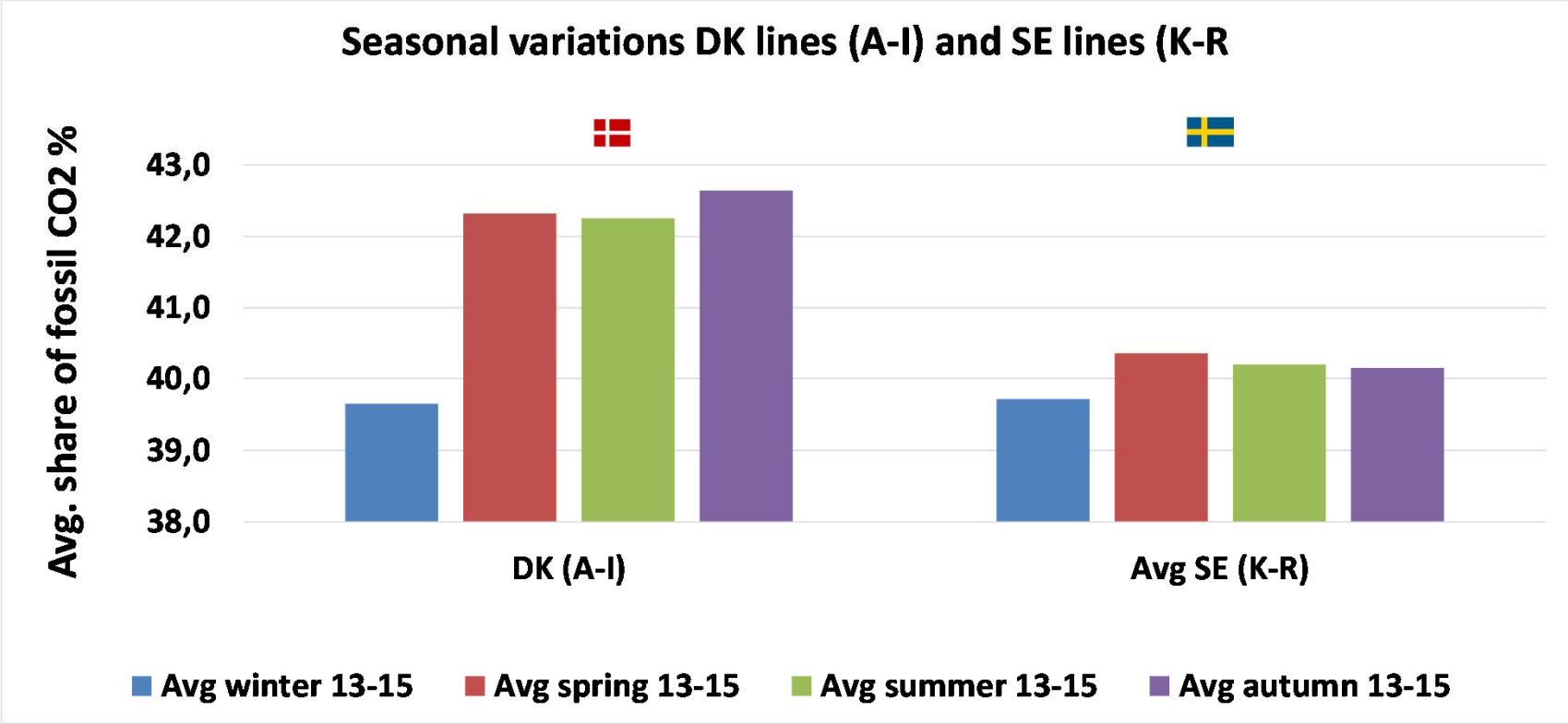
Monthly results from 9 Danish incinerator lines



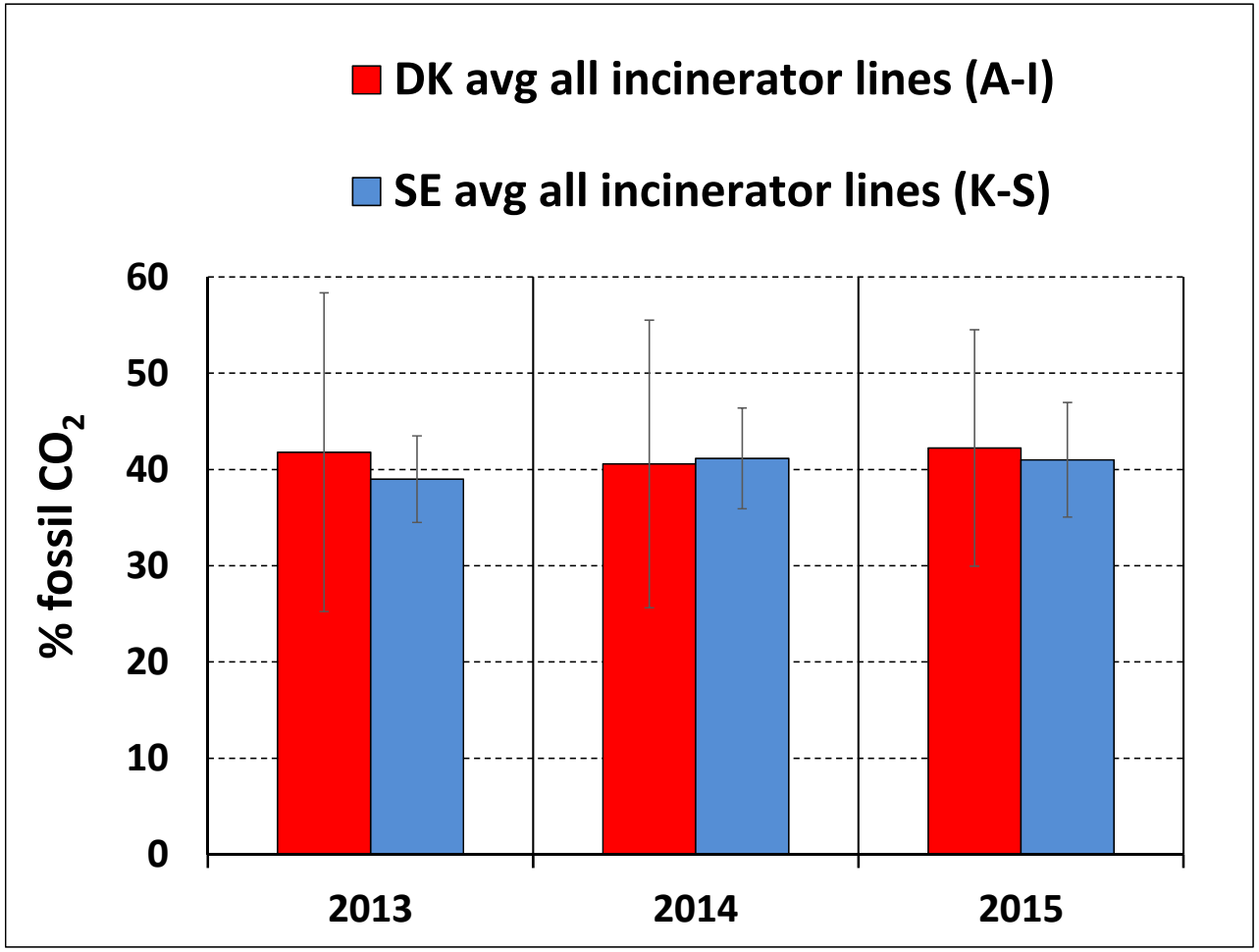
Monthly results from 9 Swedish incinerator lines



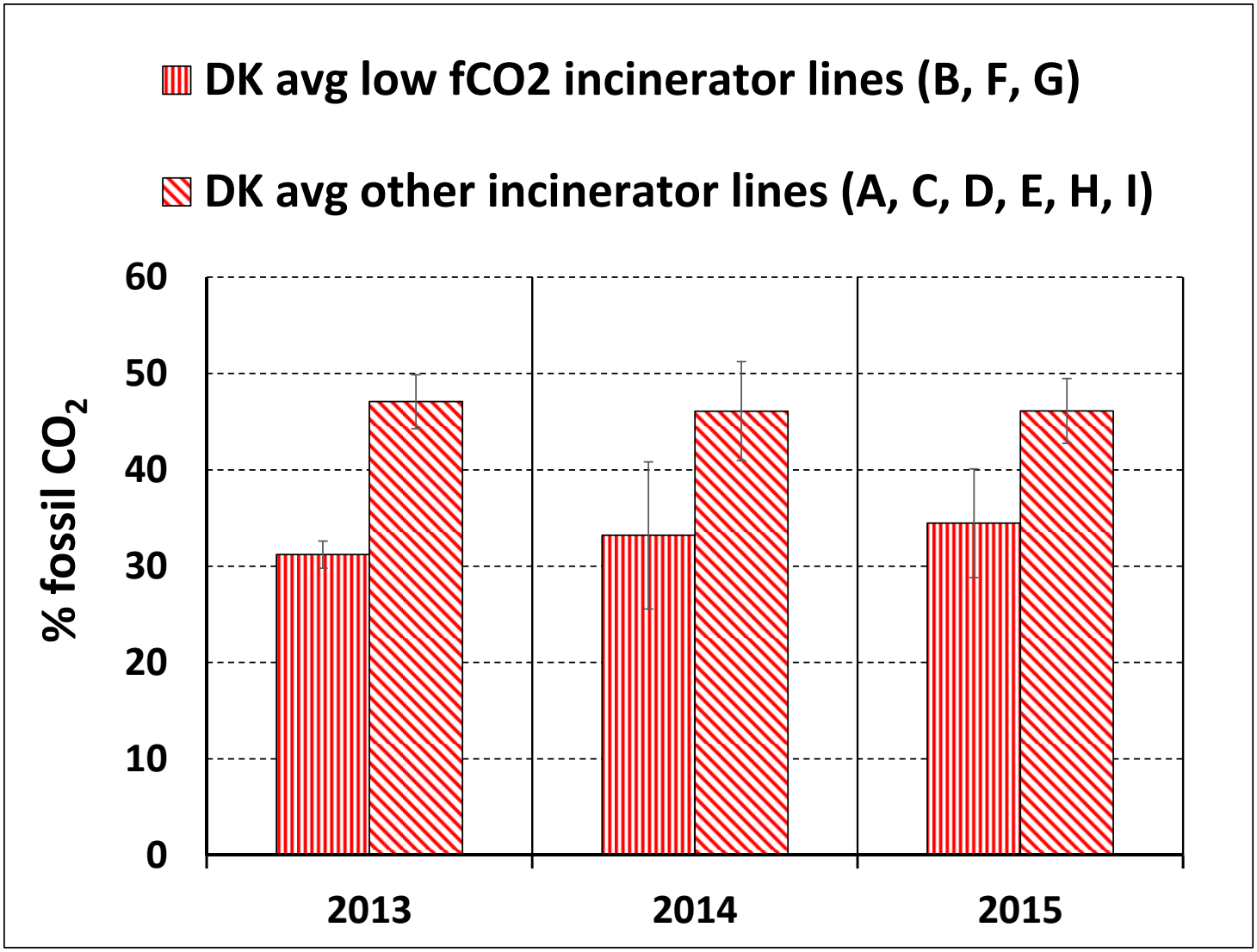
Seasonal variations?



Annual averages: DK and SE



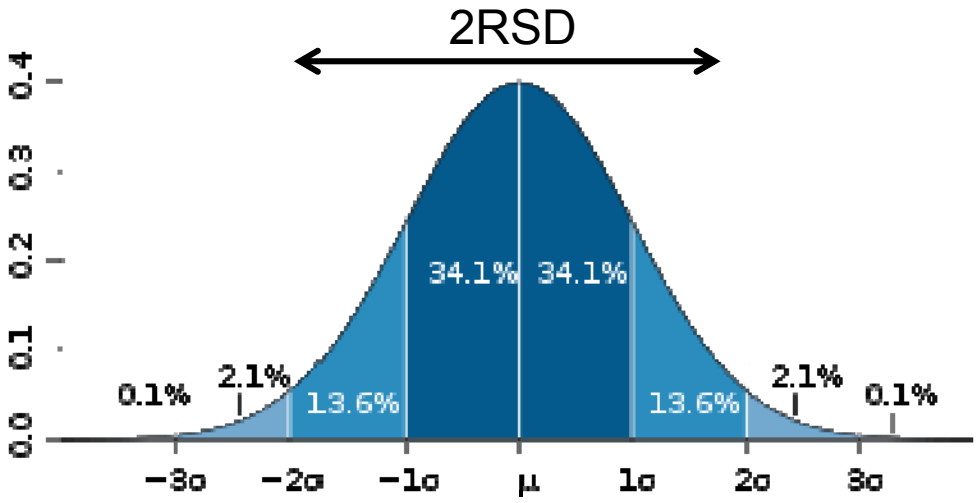
Annual averages DK: Low/high categories



Total uncertainty related to the annual emission of fossil CO_2

$$E, fCO_2 = fCO_2 \cdot totCO_2 \cdot Q(stack\ gas)$$

$$U(E, fCO_2) = \sqrt{U(fCO_2)^2 + U(totCO_2)^2 + U(Qstack\ gas)^2}$$



Uncertainty budget: FORCE C14 method

Uncertainty Budget: (*)

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Sensitivity Coefficient	Uncertainty Contribution	Index
DPM_{sample}	4.0690 dpm	0.0268 dpm	50	27	0.72 % bioC	23.2 %
$DPM_{background}$	1.7760 dpm	0.0333 dpm	50	-27	-0.90 % bioC	36.0 %
C	13.65 1/(min*g)					
epsilon	0.540000 -	$210 \cdot 10^{-6}$ -	50	-110	-0.024 % bioC	0.0 %
$M_{CO2sample}$	1.6364 g	0.0184 g	50	-38	-0.69 % bioC	21.5 %
$C_{ratCCO2}$	0.2729 -					
pmC_{ref}	113.00 % bioC	1.20 % bioC	50	-0.55	-0.65 % bioC	19.2 %
pmC_{sample}	61.65 % bioC	1.49 % bioC	190			

Result: Quantity: pmC_{sample}
Value: 61.6 % bioC
Expanded Uncertainty ±3.0 % bioC
Coverage Factor: 2.00
Coverage: manual

(*) GUM workbench software calculation

Uncertainty budget for total, annual fossil CO_2 emission from WtE plant (example)

	Based on samples with ≈ 38 % fCO2	Unit	Uncertainty (95 CI level)
r_{fCO2}	**U_{sample} bCO_2** = U_{sample} fCO_2 (2xSD) Absolute uncertainty for each monthly sample	pmC	± 3.0
r_{fCO2}	**U_{annual} bCO_2** = U_{annual} fCO_2 (2xSD) Absolute uncertainty for avg. of 12 samples = (U_{sample} fCO_2)/SQRT(12)	pmC	± 0.9
r_{fCO2}	**2xRSD f-CO_2** Relative uncertainty related to avg. of 12 samples	% relative	± 2.3
CO_2	**2xRSD totCO_2** (example)	% relative	± 5.0
Q_{stack}	**2xRSD Q(røggas)** (example)	% relative	± 5.0
fCO_2 TOTAL	**U(E,fCO_2)** Relative uncertainty related to calculated, total annual fCO2 emission	**% relative**	**± 7.4**

Requirement of max ±7.5% uncertainty fulfilled

Conclusions (1)

- Significant monthly variations of fCO_2 ratios observed for most incinerator lines
- fCO2 ratios generally lower in winter months
- The annual averages of fCO_2 ratios generally been constant
- The overall averages for all the Danish plants were similar to the Swedish overall annual averages.
- Low fCO_2 ratios observed at three Danish WtE lines.

Conclusions (2)

- The radiocarbon method defined in EN ISO 13833 proved to be a useful tool for WtE plants in Denmark and Sweden.
- The uncertainty of the reported, annual emissions met the ETS requirements of max. 7.5%.

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Long-term sampling of CO_2 from waste-to-energy plants: ^{14}C determination methodology, data variation and uncertainty

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Abstract

A dedicated sampling and measurement method was developed for long-term measurements of biogenic and fossil-derived CO_2 from thermal waste-to-energy processes. Based on long-term sampling of CO_2 and ^{14}C determination, plant-specific emission factors can be determined more accurately, and the annual emission of fossil CO_2 from waste-to-energy plants can be monitored according to carbon trading schemes and renewable energy certificates. Weekly and monthly measurements were performed at five Danish waste incinerators. Significant variations between fractions of biogenic CO_2 emitted were observed, not only over time, but also between plants. From the results of monthly samples at one plant, the annual mean fraction of biogenic CO_2 was found to be 69% of the total annual CO_2 emissions. From weekly samples, taken every 3 months at the five plants, significant seasonal variations in biogenic CO_2 emissions were observed (between 56% and 71% biogenic CO_2). These variations confirmed that biomass fractions in the waste can vary considerably, not only from day to day but also from month to month. An uncertainty budget for the measurement method itself showed that the expanded uncertainty of the method was ± 4.0 pmC (95 % confidence interval) at 62 pmC. The long-term sampling method was found to be useful for waste incinerators for determination of annual fossil and biogenic CO_2 emissions with relatively low uncertainty.