Estimation of annual CH_4 and N_2O emissions from fluidised bed combustion: an advanced measurement-based method and its application to Finland

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Abstract

The aim of this study was to develop and apply an advanced, measurement based method for the estimation of annual CH_4 and N_2O emissions and thus gain improved understanding on the actual greenhouse gas (GHG) balances of combustion of fossil fuels, peat, biofuels and REF. CH_4 and N_2O emissions depend strongly on combustion conditions, and therefore the emission factors used in the calculation of annual emissions contain significant uncertainties. Fluidised bed combustion (FBC) has many good properties for combustion of different types of fuels and fuels of varying quality, e.g., biofuels and wastes. Therefore, it is currently increasing its market share. In this study, long term measurements (up to 50 days) were carried out at seven FBC boilers representing different size classes, loadings and fuel mixes. Both decreasing load and increasing share of coal in fuel mix increased N_2O emissions. Measurement results from different loading levels were combined with the common loading curves of similar plants in Finland to estimate annual emissions. Based on the results, recommendations for emission factors for the Finnish GHG emission inventory are given. The role of FBC as a potential technology for the utilisation of biofuels and wastes with future GHG reduction requirements is discussed.

1   Introduction

The most important greenhouse gas (GHG) source is carbon dioxide (CO_2) from combustion of fossil fuels (IPCC, 2001a). These emissions can be rather accurately estimated based on information on the amount of fuel combusted and fuel-specific emission factors, as nearly all carbon in the fuel is typically oxidised in combustion. According to the IPCC (2000), uncertainties in CO_2 emission factors for traded fuels are smaller than ±5% (bounds of 95% confidence interval relative to the mean value expressed as percent). There are also other direct greenhouse gases that are formed in combustion, namely methane (CH_4) and nitrous oxide (N_2O), which are powerful GHGs. Estimates of CH_4 and N_2O emissions usually contain significant uncertainties. The IPCC (2000) estimates that uncertainties in CH_4 emission factors are ±50-150% and those of N_2O even an order of magnitude. The large uncertainties are due to the formation mechanisms of these gases in combustion.

CH_4 is typically formed due to incomplete combustion - e.g. poor mixing and early quenched oxidation reactions in the combustion process. Methane emissions of several mg/MJ occur rarely in well operating large furnaces, but are more common in small-scale combustion, e.g. in heating stoves and open fireplaces (IPCC, 2006).

N_2O emissions occur in combustion at low (<950°C) temperatures, and they are affected by fuel type and various other conditions, like fraction of excess air and catalytic activity of char and mineral matter (Kilpinen & Hupa, 1991; Kramlich & Linak, 1994; Löffler et al., 2002). Both the amount of nitrogen in fuel and fuel-O/fuel-N ratio have an effect on N_2O emissions (Hämäläinen & Aho, 1996). N_2O is formed from volatile nitrogen species (e.g. HCN) originating from fuel nitrogen but also from nitrogen of char and by heterogeneous reactions on char surface (Åmand et al., 1991). Therefore also amount of char may have a significant effect on N_2O emissions. Due to these properties, N_2O emissions are usually larger for geologically older fuels, i.e. larger for coal than for peat, and larger for peat than for wood when other combustion conditions are equal. N_2O emissions are not formed in temperatures above 950°C or below 500°C. The peak of N_2O formation occurs around 700°C (IEA GHG R&D, 2000). In furnace areas where

temperature is above $950^{\circ}C$, N_2O molecules that were formed earlier in the combustion process are decomposed. In large boilers, it is assumed that 50 - 80% of N_2O formed in the bottom of the boiler is decomposed before it exits the boiler (Moritomi et al., 1999). The greater the furnace temperature, the larger the share of N_2O that is decomposed in enlarged hot areas.

Fluidised bed combustion (FBC) as a combustion technology is increasing its share in many countries due to its advantages. Moist fuels like biomass, wastes and sludge can be efficiently combusted by FBC. Technology is suitable especially for REF (recycled fuel, also called SRF or RDF) co-firing with other fuels. FBC is a proven technology for efficient CHP (combined heat and power) production in large and small scale, and in-process capture of SO_2 and small NO_x emissions are also important advantages. With the future requirements of more stringent GHG reductions after the first Kyoto protocol period of the United Nations Framework Convention on Climate Change (UNFCCC, 1998), increasing electrification of developing countries and the growing utilisation of various-grade biofuels and waste, it can be expected that FBC will continue to increase its global market share considerably.

The FBC can be divided into two categories. Bubbling Fluidised Bed (BFB) boilers have a lower velocity of primary air than Circulating Fluidised Bed (CFB) boilers and therefore the bed (e.g. mixture of sand, limestone and ash) of the BFB boiler is "bubbling". In CFB boiler, bed material is circulating in boiler and it is separated from flue gases by cyclone before returning back to furnace. Typically CFB boilers are larger than BFB boilers because CFB technology is often more suitable for very large plants (Teir, 2003). Low combustion temperatures of FBC reduce formation of NO_x emissions, but at the same time N_2O emissions increase, as temperatures are typically in the range where N_2O formation is notable. FBC typically dominates N_2O emission levels from large scale combustion in countries where the technology is widely used. For example, in Finland FBC caused approximately 60% of N_2O emissions from large scale combustion in 2002 even though about 20% of fuel [TJ] was combusted by FBC (Ministry of the Environment, 2004). Therefore, FBC is of special interest when developing more accurate estimates of N_2O emissions from stationary combustion in countries, where this technology is commonly used, namely USA, Finland and Sweden and to some extent, e.g., Japan, China, India, Poland and Germany.

According to the reporting requirements set by the UNFCCC, industrial countries are liable to estimate

and report GHG emissions annually. For this purpose, emissions are usually estimated by calculations, using activity data (e.g. amount of fuel combusted) and emission factors (emissions per unit activity). Because fuel type, combustion technology and conditions during the combustion have a significant effect on the CH_4 and N_2O emissions, it is challenging to develop representative emission factors for these gases. In addition, temperature in the furnace in FBC often decreases with decreasing load, leading to increased N_2O emissions. Therefore, loading of boilers has to be taken into account when estimating annual average emission factors for N_2O. Estimation of emissions based on measurement carried out during full load only may cause notable bias in the estimate.

This paper presents a method to estimate annual CH_4 and N_2O emissions from FBC, taking into account the effect of load changes. Estimates are based on measurements done in seven FBC boilers, and on a survey of loading conditions in Finnish plants. Measurements were carried out during rather long time periods (up to 50 days), to gain information on the effect of different conditions on resulting emissions. Measurement data presented in literature are typically collected during short periods compared to the measurements presented in this study. In addition, measurements in literature are often carried out during full load and stable conditions, representing optimal conditions rather than annual average emissions.

In this study, more weight was given to N_2O than to CH_4 due to the higher significance of N_2O. Annual estimated emissions from the stationary combustion (other than small scale combustion) in Finland were 4.62 Gg CH_4 and 2.40 Gg N_2O, according to the national GHG inventory submitted to the UNFCCC (Ministry of the Environment, 2004). The Global Warming Potential (GWP) that measures the climatic effect of the gas relative to CO_2 is 23 for CH_4 and 296 for N_2O (IPCC, 2001b). Therefore the annual emissions of the sector are 106 and 711 Gg CO_2-equivalent, respectively.

Section 2 in this article gives an overview of power and heat production in Finland. Section 3 describes the methods used, including both measurement methods and the survey of loading. Section 4 presents the results of measurements and the survey, and the recommended emission factors for Finland. Discussion and conclusions are in Section 5.

2 Power and heat production in Finland

Cold and varying weather during winter together with heavy and energy intensive industry set special requirements for the Finnish energy system. Due to the varying heating demand of buildings and energy consumption of forest and metal industry, both efficient CHP and a great adjusting capacity of heat production are typical features of the Finnish energy system. Because the country is sparsely inhabited and widely covered by forest, many different fuels are combusted in Finland. Small scale combustion of wood is common but a large amount of biomass is also combusted in large-scale applications, e.g. in FBC boilers and as black liquor in recovery boilers of forest industry. Co-combustion of biomass and peat by FBC is very common. In addition, smaller amounts of other fuels like coal, REF and sludge from pulp and paper mills are co-combusted with biomass and peat in many Finnish fluidised bed boilers (Mattila et al., 2001). In Finland, most of the methane emissions from combustion sector come from small scale combustion of biomass (Ministry of the Environment, 2004). However, this study concentrates on larger scale (> 5 MW_{fuel}) combustion. Most of these plants produce heat for district heating network and many of them also electricity to grid and/or steam to industry.

In Finland, district heating is the most commonly used heating system for residential, commercial and public buildings with a share of 20% of energy used for heating (Energy Statistics, 2004). District heating plants are adjusted by the heating demand, which is strongly influenced by outdoor temperature. A typical district heating network consists of larger plants (from 50 up to 600 MW_{fuel}) which supply the base load to the heating network often with their full capacity, and smaller plants which are used for adjusting the supply to demand and are therefore started up and shut down during winter one after another when the temperature changes. This recurs several times a year. Larger plants have at least one maintenance break every year, but many boilers are shut down more often. FBC is a typical solid fuel firing technology in CHP and district heating plants in Finland and therefore load changes are common in many Finnish FBC boilers.

Industry uses a major share of the energy used in Finland (50% of primary energy) but it has a lot of its own power and heat production by different kinds of boilers in the mills. For example, the recovery boilers of forest industry are used at high load during the whole year and shut down once or twice a year

for maintenance. According to loading data obtained from industry and expert interviews, fluidised bed boilers are often used to adjust steam supply to demand. Therefore FBC of forest industry may operate even more at partial load than public district heating boilers with corresponding capacity.

3 Methodology

3.1 Survey of load distributions

Extensive temperature and air supply data from all boilers of Finland were very difficult to get due to different data collection systems in plants. Therefore, a survey was conducted to obtain information on typical load distributions and fuels. The purpose was to get automatically collected data, e.g., hourly averages of the thermal input [MW_{fuel}] from the most of the combustion plants in Finland. Load changes affect N_2O emissions [mg/MJ_{fuel}] mainly due to changes in combustion temperature. The plant types considered were public heat or CHP producing plants, condensing power plants and industrial combustion plants.

In Finland, the largest category (according to the number of plants and the amount of fuel combusted) is heat and CHP production plants. Therefore, this study concentrated especially on these plants. Combustion plants were divided into different types based on their fuel type (solid / liquid or gas), size of heating network (village / small town / city) and purpose of plant in network (base load / adjusting / peak load / reserve), because each of these plant types may have different load distributions. Data for the most common plant types was obtained by contacting the combustion plants. By this method, enough loading data from all the significant plant types was obtained and it could be divided to categories according to different load distributions.

The loading data of many condensing power plants was available from Fingrid, the electricity transmission system operator of Finland. Fingrid collects electricity production data, which is well correlated with fuel load in the case of condensing power plants. This data is confidential at plant-level, but load distributions were converted into a form where specific plants could not be identified. The efficiency of electricity production decreases with load, but potential error caused to average load

distributions is insignificant when compared with other sources of uncertainty in developing national average emission factors.

For comparison, the load distributions from two BFB boilers from forest industry are presented. These boilers are used to adjust steam supply to mill because recovery boilers produce most of the steam needed and are adjusted by other parameters. Therefore the average share of partial load for boilers of industry may be larger than for other boilers.

Four loading levels, i.e. >80%, 60-80%, 40-60% and 0-40% energy input [MW_{fuel}] of the nominal capacity of the plant, were determined based on the data obtained. The share of each loading level of annual energy input was then calculated based on plant-specific data. Results of the survey are presented in Section 4.

3.2   Measurements and unit conversions

Continuous measurements were carried out in seven FBC plants. The aim was to find out the average N_2O and CH_4 emission factors [mg/MJ_{fuel}] for each of the loading levels given in Section 3.1. Measurement periods were long in order to include different load levels, start-ups, disorders etc. In addition, measurements were done for different fuels and fuel mixes. All measurements were taken from the stack or from the flue gas duct shortly before the stack.

Measurements were done by FT-IR (Fourier Transform Infrared Spectrometer) technique. FT-IR is a sensitive, multicomponent analysis technique which has proven to be suitable for flue gas analysis in several different applications. The quantitative analysis is performed by comparing the fraction of radiation absorbed by an unknown sample to the absorption of samples of known concentration of the same components. When FT-IR technique is used, it is an advantage that measurements can be performed from hot and wet gases. Since there is no need for water removal, there are no risks for components to be lost in the condensate.

Measurement results obtained using FT-IR were given as average concentration of each minute [$ppm_{vol,}$

wet]. Temporal emission factors [mg/MJ_fuel]for figures 2, 3 and 4 were calculated by Equation [1]. Because e.g. flue gas flow and thermal input data were automatically collected by combustion plants usually as averages of each hour, the period mentioned after the Equation [1] was set to one hour for most of the measurements presented in this study.

$$EFi = c * \dot{V} * \rho / P \hspace{4cm} [1]$$

where EF_i is the emission factor for a certain period [mg/MJ_fuel], c is an average of measured concentrations during the period [ppm_vol, wet], $\dot{V}$ is an average flue gas flow of the period [m³n_wet/s], ρ is the density of the each gas [kg/m³n] and P is the average thermal input of the period [MW_LHV]. Densities were calculated by using the assumption of ideal gases. The corrections to normal temperature and pressure (NTP) were also made. The letter n in the units [m³n_wet/s] and [kg/m³n] stands for NTP.

The emissions of each hour [mg/h] were calculated by Equation [2].

$$Emissions = c * \dot{V} * \rho * 3600 \hspace{3cm} [2]$$

Emissions calculated by Equation [2] were divided into four groups according to the prevailing load (>80%, 60-80% etc.). Emissions of each of these groups were summed up and divided by the amount of energy [MJ], which was calculated from thermal input [MW = MJ/s] and also divided into these four groups and summed up. The average emission factor [mg/MJ] of each loading level was calculated by Equation [3].

$$EF_n = Emissions_n / Energy_n \hspace{3cm} [3]$$

where $Emissions_n$ is the sum of the emissions at this loading level [mg] and $Energy_n$ [MJ] is the sum of the energy content of the fuels fed in the furnace at this loading level.

To obtain annual emission factors for the typical Finnish plant types, emission factors for each loading

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level (EF_n) were combined with the loading data by Equation [4].

$$EF = (X_{80+} * EF_{80+} + X_{60-80} * EF_{60-80} + X_{40-60} * EF_{40-60} + X_{0-40} * EF_{0-40}) / 100 \qquad [4]$$

where EF is the average emission factor for plant type [mg/MJ$_{fuel}$], X_n is the annual share of the load level n [% of energy] and EF_n is the average measured emission factor for load level n [mg/MJ$_{fuel}$]. Values for X_n and EF_n are presented in the section 4.

4   Results

The results of the survey of combustion plants loadings are presented in Table 1.

Table 1. Perceptual share of each loading level of annual fuel consumption by plant type.

Category	Specification	Size category	Share of loading levels [%]			
			X_{80+}	X_{60-80}	X_{40-60}	X_{0-40}
Condensing power	Gas turbines	< 50 MW$_e$	40	34	13	13
	Others	< 50 MW$_e$	72	22	4	2
		> 50 MW$_e$	78	15	6	1
Forest industry	BFB boilers	All	29	38	25	8
District heating & CHP	Solid fuels	< 50 MW$_{fuel}$	33	39	17	11
		> 50 MW$_{fuel}$	85	9	5	0
	Other fuels	< 50 MW$_{fuel}$	16	28	16	41
		50–100 MW$_{fuel}$	76	12	8	6
		> 100 MW$_{fuel}$	91	8	1	0

The average loading distributions (Table 1) are defined for emission factor calculations and they are relatively uncertain. In addition, loading levels of combustion plants are plant and time dependent and vary from one plant to another. Therefore, this data should only be used as an average, not for single plants. In the case of industry, load distributions presented should be considered as examples rather than

averages, because sample size was small.

Figure 1 presents average temperatures in the measured boilers as a function of boiler load, and Table 2 gives an overview of the measurements carried out.
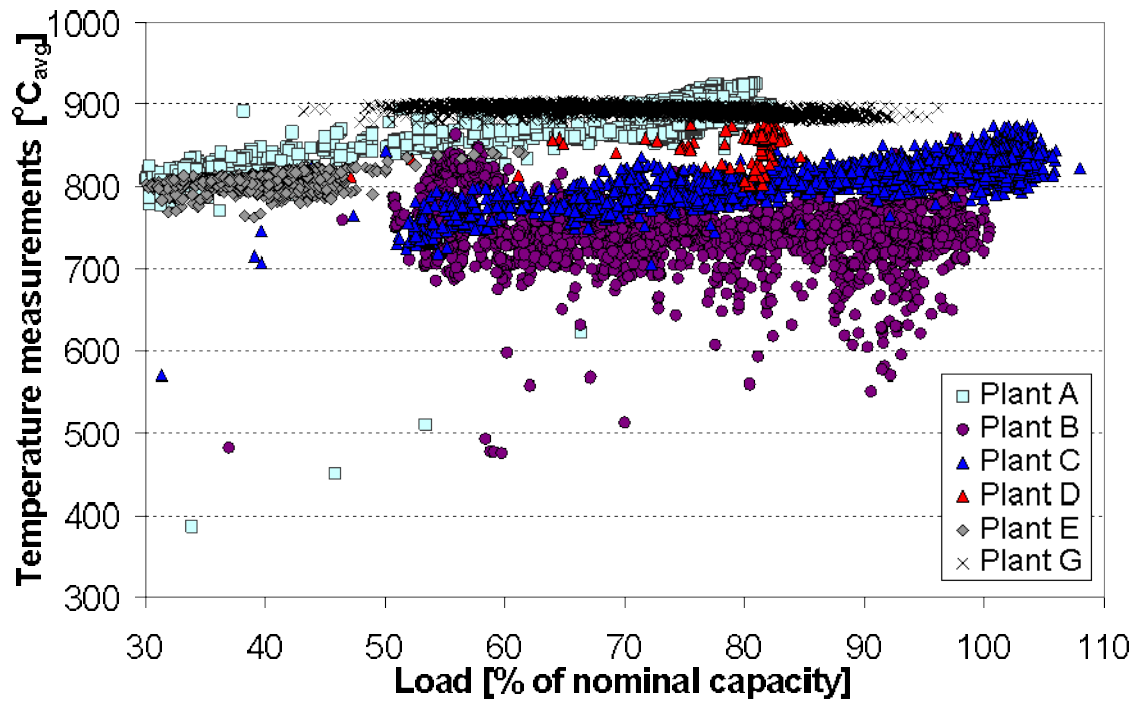

Figure 1. Average temperatures in measured FBC boilers as function of load (% of nominal capacity).

Table 2. Overview on the measurements carried out in this study.

Plant	Size [MW$_{fuel}$]	Type	Fuels [a]	Emission control [b]	Purpose [c]	Duration of measurements [days]
A	50 – 100	CFB	coal	ESP, limestone	DH	15
B	> 100	BFB	peat, biomass	ESP	CHP (DH)	1
C	> 100	CFB	peat, biomass	ESP	CHP (DH)	50
D	> 100	CFB	peat, biomass, coal, REF	ESP	CHP (industry and DH)	4

E	> 100	BFB	biofuels, peat, REF	ESP	CHP (industry and DH)	5
F	< 50	BFB	peat, biomass, REF	ESP	CHP (industry and DH)	6
G	> 100	BFB	biofuels, peat	ESP	CHP (industry and DH)	3

[a] In this study biomass stands for solid biofuels (e.g. bark) and biofuels for all biofuels (e.g. bark and sludge).

[b] ESP indicates electrostatic precipitator, limestone indicates limestone addition to fluidised bed

[c] DH indicates district heating

Figures 2 and 3 present examples of the measurement results from plants C, D and E. Figures show how the emissions (hourly averages) varied during measurement periods. Methane emissions were small in most investigated boilers due to good mixing in the fluidised bed.
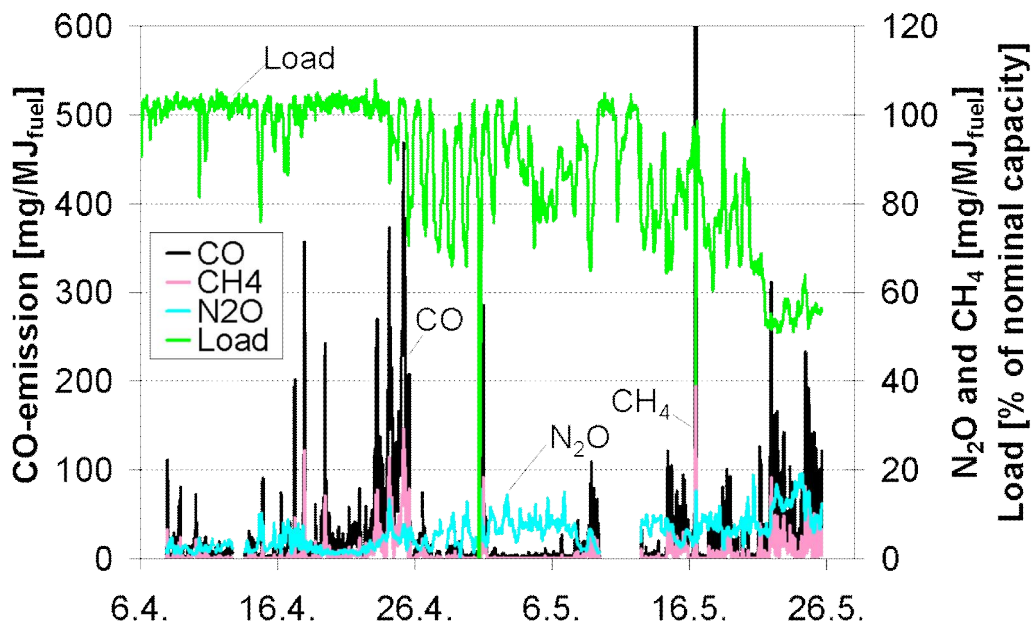

Figure 2. CO, N_2O and CH_4 emissions [mg/MJ$_{fuel}$] and boiler loading from plant C (> 100 MW peat and biomass firing CFB).
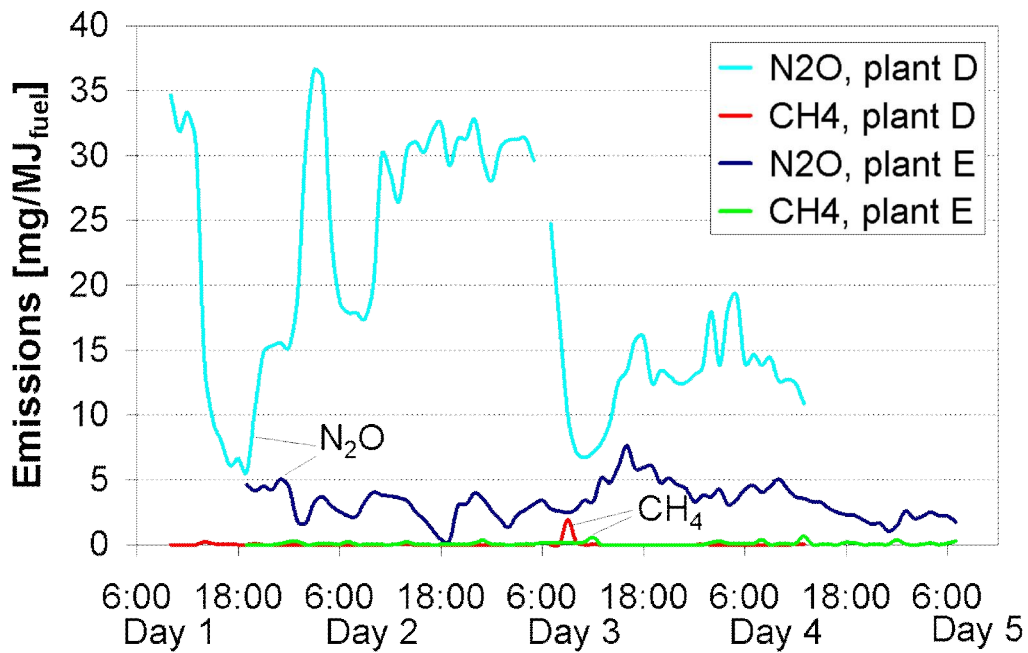
Figure 3. N_2O and CH_4 emissions [mg/MJ$_{fuel}$] from plants D and E (> 100 MW mixed fuels firing CFB and BFB, respectively).

Most changes in the N_2O emissions presented in the figures can be explained by the changes of load or fuel mix as the figure 4 shows. In figure 4 the measured N_2O emissions are given as a function of load but also divided into different fuel categories if data of temporal fuel use were available. From figure 4 also the example of the effect of oil firing in boiler start up can be seen. Correlation between N_2O emission and load was notable in all the cases, but changes in the fuel mix results variation to emissions of some plants.
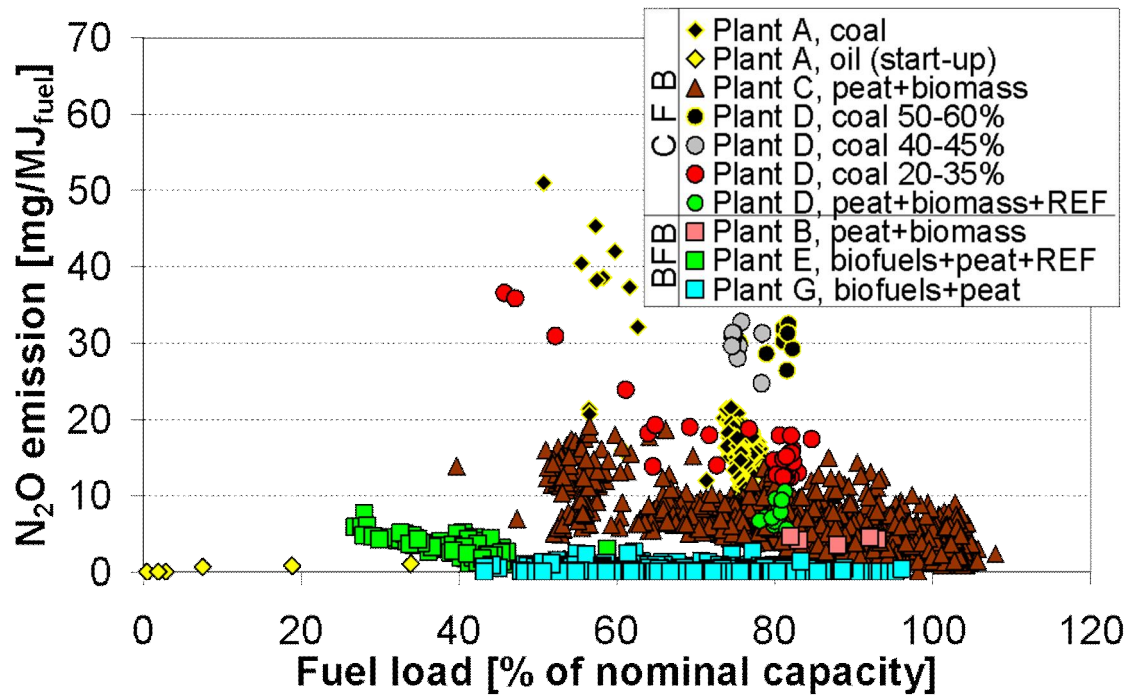
Figure 4. Correlation between boiler load and N_2O emissions [mg/MJ$_{fuel}$] in boilers A, B, C, D, E and G with different fuel mixes.

By using the measurement data and methods described in the section 3.2, Table 3 can be compiled. Plant F is not presented in the table because the plant could not supply the process data needed for calculations. Unit conversions for measurement data in the case of this plant had to be done by the Equation [5].

$$EF = 0.4 * \rho * c / (1 - c_{H2O} / 100) * (20.9 - 6) / (20.9 - c_{O2}) \qquad [5]$$

where *0.4* is a typical flue gas flow [m^{3}n/MJ] as dry gases reduced to 6 % oxygen content in the case of peat combustion (Jalovaara et al., 2003), ρ is the density of CH_4 or N_2O [kg/m^{3}n], *c* is a measured CH_4 or N_2O concentration [ppm$_{vol, wet}$] and c_{H2O} and c_{O2} are the concentrations of H_2O [%$_{vol, wet}$] and O_2 [%$_{vol, dry}$], respectively.

Table 3. Average CH_4 and N_2O emission factors for four loading levels of measured plants.

Plant	CH_4 [mg/MJ_fuel]				N_2O [mg/MJ_fuel]			
	EF_{80+}	EF_{60-80}	EF_{40-60}	EF_{0-40}	EF_{80+}	EF_{60-80}	EF_{40-60}	EF_{0-40}
A (CFB: coal)	<0.5	<0.5	<0.5	<0.5	13.9	26.7	27.7	0.9 [a]
B (BFB: peat, biomass)	1.8	-	-	-	4.3	-	-	-
C (CFB: peat, biomass)	1.6	1.4	3.6	42.7 [b]	4.0	7.7	11.8	12.6
D (CFB: biomass 60%, peat 40%) [c]	<0.5	0	-	-	9.3	7.0	-	-
D (CFB: peat 75%, biomass 24%, REF 1%) [c]	0	<0.5	-	-	8.1	6.9	-	-
E (BFB: biofuels, peat, REF) [d]	-	-	<0.5	<0.5	-	-	2.5	4.2
G (BFB: biofuels, peat) [d]	<0.5	<0.5	0.7	-	0	<0.5	<0.5	-

- Indicates that there are no measurement data at that load level. Notation '<0.5' is used in cases where emission factor was between 0.05 and 0.5 (this is due to uncertainties in measurement data in case of small emissions). Notation '0' is used when emission factor is <0.05.

[a] Oil combustion during boiler start-up.

[b] High value is due to disorder. Disorders, however, should be included in emission factors and therefore this value is used as others.

[c] The main purpose of measurements in plant D was to find out the effect of different fuel mixes on N_2O emissions. N_2O emission increased significantly when share of coal in fuel mix was increased (figure 4). Methane emission was low (<0.5 mg/MJ) with all fuel mixes.

[d] In this study biomass stands for solid biofuels (e.g. bark) and biofuels includes also sludge.

By using the data in Tables 1 and 3 the emission factors of Table 4 can be calculated by Equation 4. For plant E we made a very conservative assumption that EF_n does not decrease with increasing load further than measured. Thus, emission factors of highest measured load level (50-60 %) were used also for higher load levels. For plant G emission factors can be calculated for the case where share of 0-40% load is 0% (>50 MW district heating or CHP plants). For the other cases estimation of load-dependent emission factors is more difficult, because the effect of partial load on emissions of these boilers is unclear. However, some conservative approximations for annual emission factors can be made. These approximations are presented in Table 5.

Table 4. CH$_4$ and N$_2$O emission factors [mg/MJ$_{fuel}$] calculated using measurement data and load distributions.

Category	Capacity	CFB coal (Plant A)		CFB peat (Plant C)		BFB biofuels (Plant E)		BFB biofuels (Plant G)	
		CH$_4$	N$_2$O	CH$_4$	N$_2$O	CH$_4$	N$_2$O	CH$_4$	N$_2$O
Condensing power	5 - 50 MW$_e$	1	18	3	6	1	2		
	> 50 MW$_e$	1	17	3	6	1	2		
Forest industry	All	1	22	6	9	1	3		
District heating and CHP	5 - 50 MW$_{fuel}$	1	20	7	8	1	3		
	> 50 MW$_{fuel}$	1	16	2	5	1	2	1	1

Table 5. Other annual CH$_4$ and N$_2$O emission factors approximated based on the long period measurements.

Plant type and fuel	CH$_4$ [mg/MJ]	N$_2$O [mg/MJ]
CFB, peat (plant D)	< 1	< 10
CFB, biomass (plant D)	< 1	< 10
BFB, peat (plants B, F and G)	< 1..4	< 1..5 [a]

[a] Measurements in plant B were done during full load, but it can be seen from Figure 1 that average temperature in this furnace does not decrease notably with decreasing load. Therefore, measurement from full loading situation is assumed representative for the entire year for this particular plant. This kind of behaviour of boiler temperature is nevertheless uncommon according to this study.

Based both on Tables 4 and 5 and to some extent on literature (Fabritius et al., 2002; Harju, 2001) and confidential measurements, recommendations for national emission factors can be given (Table 6). In the Table 6, classification given in Table 4 is simplified because e.g. emission factors of larger condensing power and CHP boilers seem to be close to each other. If forest industry is not taken into account, most FBC boilers in Finland are in "District heating and CHP" sector and therefore national emission factors should be close to the factors presented for this sector in Table 4. For industrial boilers N$_2$O emission factors may be somewhat higher due to the larger share of partial load.

The recommended N_2O emission factor for coal CFB firing in Table 6 differs significantly from the values given in Table 4. The reason for the difference is that in this case also unpublished measurement data were taken into account. The data showed that N_2O emissions of one plant varied between 45 and 12 mg/MJ when the temperature of bed varied between 870 and 920 $^\circ$C, respectively. Because the typical bed temperature for this plant is about 900 $^\circ$C and the average N_2O emission factor of plant A is 15 mg/MJ, emission factor 30 mg/MJ is recommended. This is a conservative estimation for Finnish boilers, because these two plants cover most of the coal combusted in CFB boilers in Finland (excluding co-firing). The emission factor is, however, strongly the dependent on e.g. temperatures in furnaces and the type and age of coal and therefore it should not be generalised to other countries without further research about e.g. furnace temperatures.

Table 6. Recommended emission factors (EF) for Finnish GHG inventory with estimated 95% confidence intervals (CI).

	Size [MW$_{fuel}$]	EF [mg/MJ$_{fuel}$]	CI of EF [mg/MJ$_{fuel}$]
CH$_4$			
CFB, coal	> 50	1	<0.5 – 1.4
CFB, peat, biofuels	> 50	3	0.6 – 4.8
BFB, peat	5 - 50	4	0.8 – 6.4
BFB, peat, biofuels	> 50	2	<0.5 – 3.2
N$_2$O			
CFB, coal	> 5	30	20 – 50
CFB, peat, biofuels	> 5	7	3 – 14
BFB, peat, biofuels	> 5	3	1 – 6

The recommended emission factors presented in Table 6 are for combustion of fuels mentioned or for fuel mixes where only peat and biofuels are co-fired. If even a small share of coal is co-fired, the N_2O emission factors should be increased (figure 4). Small amounts (< 5% of energy input) of REF do not significantly increase the emission factors presented in Table 6 if significant reduction in combustion

temperature is not occurring.

Uncertainties of emission factors arise due to many different reasons. Sources of uncertainty are presented in the list below in decreasing order of importance, i.e. the first point has the largest effect on total uncertainty:

- representativeness of conditions in measured plants with regard to other plants of the same type in Finland
- uncertainties in average load distributions are due to (1) possible errors in data obtained from plants; (2) potential unsuitability of one-year-data to present an average load distribution in any year; and (3) representativeness of plants included in the survey with regard to the total plant fleet in Finland
- uncertainties in measured concentrations [ppm] are around ±10%, but for concentrations <10ppm, uncertainties are around 1 ppm
- uncertainties arising from unit conversion from [ppm] to [mg/MJ], where data from plants is needed, is estimated at ±5%

The uncertainties given in Table 6 refer to uncertainties of the average annual emission factor of all plants in Finland. If the emission factors were used for single plants, uncertainties would be much larger. In addition, if these emission factors were used in other countries, uncertainties would increase due to potential differences in fuel mixes, fuel type and quality or plant design, operation and maintenance. Uncertainties of recommended emission factors are smaller upwards than downwards in most cases. This is due to conservativeness of developed emission factors.

N_2O emission factors presented above contain rather large uncertainties. On the other hand, continuous measurements may be too expensive for the estimation of emissions. Therefore, we present a method which gives more accurate emission estimates than emission factors, but is more cost-efficient than continuous measurements.

Figure 4 presents correlations between N_2O emissions and boiler load. Similarly, we can calculate the correlation between emissions and furnace temperature or load by using measurement data gathered during one day only. In case of plant C, the relationship between load and N_2O emissions can be described using Equation [6]. The equation is obtained by fitting a straight line to measurement data of a

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randomly selected day (where enough different load levels exist).

$$N_2O \ emission = \Sigma_i \ (-0.028 * P_i + 12.12) \ kg \hspace{4cm} [6]$$

where P_i denotes average fuel load [MW$_{fuel}$] during each hour, and Σ_i is the sum over all the hours that are of interest, e.g. all the hours in a year.

If we use Equation [6] (which was derived based on measurements carried out during one day only) to estimate the emissions during the whole measurement period in plant C (50 days), we get an emission estimate of 4.70 t N_2O, whereas continuous measurements during the same period gave an emission estimate of 5.38 t N_2O. The error made when using Equation [6] is thus 13%. This is notably less than the uncertainties in emission factors.

5   Discussion and conclusions

The results reveal that boiler load has a notable effect on annual N_2O emissions from FBC, especially in the case of boilers that are used to adjust the heat supply to the demand. Currently, FBC as a combustion technology is increasing its share in many countries due to its advantages. Moist fuels like biomass, wastes and sludge can be efficiently combusted by FBC. Technology is suitable especially for REF (recycled fuel) co-firing with other fuels. In-process capture of SO_2 and relatively low NO_x emissions are important advantages regarding air pollution. It is to be expected that with the increasingly stringent future GHG requirements, increasing electrification of developing countries and the growing utilisation of various-grade biomasses and wastes, FBC will continue to increase its global market share considerably.

In Europe, due to CO_2 emissions trading (Official Journal of the European Union, 2003) and increasing MSW landfilling fees, landfilling prohibition and prices of recycled materials, combined steam and electricity production in industry is moving from natural gas use towards the utilisation of bark and REF fuels. Compared to direct MSW combustion, in the co-combustion of REF variation in the fuel quality is minor. This contributes to better control of emissions but also corrosion problems remain minor, which allows higher steam temperatures and increased electric efficiency and power to heat ratio. Both the

increasing energy prices and the recent EU directive on the promotion of cogeneration (EU, 2004) will increase the share of CHP. This may increase also the occurrence of partial load among power plants and due to the fuel flexibility and experiences in CHP production FBC may be one of the key technologies to be used.

These trends emphasise the need for local studies of N_2O emissions of the FBC plants in operation taking into account furnace temperatures in different conditions (e.g. typical loading levels and fuel mixes) in order to have accurate estimates of the actual GHG emission levels and the GHG emission reductions to be achieved if e.g. old coal-fired combustion plants are replaced with new FBC plants operating with various fuel mixes.

The emission factors recommended for FBC boilers based on this study varied from 1 to 4 mg CH_4/MJ and from 3 to 30 mg N_2O/MJ depending of fuel, size class and technology of the boilers. The results show that N_2O emissions from peat and biofuels co-combustion are more dependent on other conditions than on the share of these components in fuel mix. This is an important result for Finland and presumably also for other countries where these fuels are co-fired. The share of coal has a major effect on N_2O emissions but the level of emissions is boiler specific mainly because of combustion temperatures and properties of coal. Co-combustion of coal and biomass reduces N_2O emissions compared to 100 % coal combustion also according to the studies by e.g. Shen et al. (2003) and Leckner et al. (2004), when furnace temperatures are the same. In practice, temperatures in 100% coal combustion are often higher than in biomass or co-combustion, where lower temperatures are used due to the behaviour of alkali compounds of biomass. For example in our study, N_2O emissions [mg/MJ_{fuel}] from CFB, where 100 % of fuel was coal (plant A), were smaller than N_2O emissions from CFB where 40 % of the fuel mix was coal (plant D). This was due to differences in combustion temperatures (Figure 1). However, emissions of plant D increased when share of coal was increased and N_2O emissions from both boiler A and D increased with decreasing load. Figure 4 also presented N_2O emissions from oil combustion during the boiler start-up. The reason for low emissions in this case was high combustion temperature of oil burner, which was used at its maximum load. At partial load also emissions of some oil burners increase according to measurements.

According to this study, N_2O emissions from BFB boilers were smaller than those of CFB boilers, but varied notably between different plants mainly due to combustion temperatures. For example, N_2O emissions of > 4 mg/MJ were measured from plant B in peat combustion whereas emissions of plant G were small (<0.5 mg/MJ) for all fuel mixes considered (peat 20 - 100% of energy). In Finland, there are no pressurised FBC boilers (CFB boilers with high pressure in furnace with a gas turbine after the boiler increasing power to heat ratio) in commercial use. Globally there are few PFBC boilers and according to e.g. VTT Chemical Technology (2000) N_2O emissions [mg/MJ$_{fuel}$] in coal firing at high load are near to emission factors presented in this paper for plant A (coal firing CFB). In literature (e.g. König et al., 1994; Hayhurst & Lawrence, 1992) it is estimated that limestone addition to fluidised bed for SO_x reduction may have a small effect also on N_2O emissions. According to measurements of this study, the correlation between limestone addition and N_2O emissions could not be found and it was estimated insignificant compared effect of fuel mix and temperatures.

We presented also an alternative method to estimate N_2O emissions, which was based on measurement and operation data from one day. Using this method, emissions could be estimated much more reliably than by using emission factors. The method would be much more cost-efficient than continuous measurements. Therefore, we recommend using this method, if more accurate data of N_2O-emissions from FBC boilers are of interest, but continuous measurements are considered too expensive.

The effect of load changes on annual emissions was small for largest public boilers, because most of the fuel used was combusted with >80% load. For many other plant types, the occurrence of partial load is nevertheless significant and should be taken into account in annual emission factors. The general assumption that all large boilers are used nearly always at full load seems to be incorrect.

N_2O emissions can be significantly reduced by several measures, including fuel selection. Coal combustion can be reduced by increasing biomass and/or peat co-firing and the share of these fuels in fuel mix of already co-firing boilers. However, possible decrease in furnace temperatures should be taken into account when assessing the achievable N_2O reduction. In addition, the coal type can often be changed. Increase in furnace temperature decreases N_2O emissions but often increases NO_x emissions. However, a stable temperature at all load levels could reduce N_2O emissions without a significant increase in NO_x

emissions. For example, in the measured boiler G, decreased load did not significantly increase N_2O emissions due to the stable bed temperature. The occurrence of partial load in FBC could also be minimised.

CH_4 emissions from large combustion plants are usually small, but larger methane emissions occur during disorders and in some plants due to poor mixing. Peat and biomass combustion often results greater methane emissions than coal or oil combustion. In the case of plant C the peak in methane emissions occurred concurrently with the great and sudden decrease in fuel consumption. Estimation of frequency and the effect of disorders is very difficult, and therefore, emission factors derived in this study contain notable uncertainties. However, these emission factors should include also old and small boilers where combustion is not as complete as in modern boilers and also frequency of disorders may be higher. Therefore the recommended emission factors for methane are conservative to avoid underestimating emissions. CH_4 emissions are well correlated with CO emissions which are often continuously measured by large combustion plants. This correlation could be used to estimate CH_4 emissions more accurately, but the use of this method may be toilsome when compared with the small importance of CH_4.

IPCC recommends the use of national emission factors if data are available. This study presented one method to estimate emission factors and indicated that the national emission factors may be significantly smaller than given by international organisations even when the load changes and disturbances are taken into account. For example, the IPCC (2006) gives a default emission factor of 61 mg N_2O/MJ for coal FBC and emission factor 7 mg N_2O/MJ for wood and wood waste boilers to be used in absence of national data. For peat combustion, IPCC (2006) recommends the emission factor obtained in this study (Finland is the largest fuel peat consumer in the world). In the 1997 guidelines of the IPCC, a default emission factor of 96 mg N_2O/MJ for coal FBC was given (IPCC, 1997). IIASA (Klaassen et al., 2004) uses an emission factor of 80 mg N_2O/MJ in the RAINS model for the combustion of all fuels in FBC. There are many reasons for relatively large differences between our results and international sources. International emission factors may be overestimated due to uncertainties in the estimations of these emissions and the unknown effect of load changes and disorders on emissions globally.

The emission factor presented in this study for coal firing in CFB is relatively low because temperatures

in the measured boilers were high. These boilers cover most of the coal fired in CFB boilers in Finland, and therefore the emission factor is representative for Finland. Low N_2O emissions are presented also e.g. in studies by Kvaerner Power (2004), Orthofer et al. (1996), Rautanen et al. (1997) and VTT Chemical Technology (2000) where N_2O emission factors were smaller than 40 mg/MJ in all presented cases. However, combustion of some coal types in very low furnace temperatures at small load (below 750 ^{o}C, at 30 % boiler load) has resulted in N_2O emission factors above 100 mg/MJ (Hiltunen, 2006).

6   Acknowledgements

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