Nitrous oxide and methane emissions and nitrous oxide isotopic composition from waste incineration in Switzerland

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ABSTRACT

Solid waste incineration accounts for a growing proportion of waste disposal in both developed and developing countries, therefore it is important to constrain emissions of greenhouse gases from these facilities. At five Swiss waste incineration facilities with grate firing, emission factors for N_2O and CH_4 were determined based on measurements of representative flue gas samples, which were collected in Tedlar bags over a one year period (September 2010–August 2011) and analysed with FTIR spectroscopy. All five plants burn a mixture of household and industrial waste, and two of the plants employ NO_x removal through selective non-catalytic reduction (SNCR) while three plants use selective catalytic reduction (SCR) for NO_x removal.

N_2O emissions from incineration plants with NO_x removal through selective catalytic reduction were 4.3 ± 4.0 g N_2O tonne^{-1} waste (wet) (hereafter abbreviated as t^{-1}) (0.4 ± 0.4 N_2O GJ^{-1}), ten times lower than from plants with selective non-catalytic reduction (51.5 ± 10.6 g N_2O t^{-1}; 4.5 ± 0.9 g N_2O GJ^{-1}). These emission factors, which are much lower than the value of 120 g N_2O t^{-1} (10.4 g N_2O GJ^{-1}) used in the 2013 Swiss national greenhouse gas emission inventory, have been implemented in the most recent Swiss emission inventory. In addition, the isotopic composition of N_2O emitted from the two plants with SNCR, which had considerable N_2O emissions, was measured using quantum cascade laser spectroscopy. The isotopic site preference of N_2O – the enrichment of $^{14}N^{15}NO$ relative to $^{15}N^{14}NO$ – was found to be 17.6 ± 0.8‰, with no significant difference between the two plants. Comparison to previous studies suggests SP of 17–19‰ may be characteristic for N_2O produced from SNCR. Methane emissions were found to be insignificant, with a maximum emission factor of 2.5 ± 5.6 g CH_4 t^{-1} (0.2 ± 0.5 g CH_4 GJ^{-1}), which is expected due to high incinerator temperatures and efficient combustion.

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1. Introduction

Incineration of municipal solid waste (MSW) and solid recovered fuels (SRF) in waste-to-energy (WTE) plants is the most important waste disposal method employed in Switzerland, accounting for the disposal of >3.7 million tonnes of waste in 29 WTE plants annually (FOEN, 2014). The use of waste incineration as a waste disposal method is increasing worldwide due to concerns about the space requirements and the potential for soil and water pollution associated with landfilling, and because of the added benefit of energy recovery from incineration (Astrup et al., 2009; Hoornweg and Bhada-Tata, 2012). In Europe, approximately 22% of waste is currently incinerated; this amount is increasing due to the EU Landfill Directive (Bogner et al., 2007; Bogner et al., 2008).

Significant amounts of CO_2 and N_2O are emitted during waste incineration, as well as minor amounts of CH_4. Emissions of these important greenhouse gases (GHGs) must be reported under the United Nations Framework Convention of Climate Change (UNFCCC; UN (1992)). Although WTE is not a key category for GHG emissions, its increasing use in both developed and developing nations makes monitoring of emissions important (Bogner et al., 2008). Tier III reporting is good practice for WTE emissions, which requires the use of plant- and management-specific emission factors (IPCC, 2006).

The type of incineration facility (e.g. stoker or fluidized bed), waste type (e.g. sewage sludge or MSW) and flue gas cleaning all have a significant impact on greenhouse gas emissions. This study focuses on flue gas cleaning technologies, as the other factors are very similar throughout all WTE plants in Switzerland. NO_x removal is important for air quality and a wide range of environmental issues, such as photochemical smog, acid rain, and tropospheric ozone formation (Skalska et al., 2010). However, NO_x

removal can result in the conversion of a significant amount of NO_x to N_2O. The most common NO_x abatement methods are selective non-catalytic and selective catalytic reduction (SNCR and SCR, respectively).

SNCR involves the reduction of NO_x by a reducing agent such as ammonia (Zandaryaa et al., 2001; Svoboda et al., 2006). It is advantageous due to simplicity, retrofittability, and low operating costs. However, the NO_x reduction efficiency with SNCR is limited to 60–90%. Under optimal conditions with ammonia as a reducing agent, NO_x to N_2O conversion can be as low as 2%, however with urea or cyanuric acid as a reducing agent NO_x to N_2O is >10% (Svoboda et al., 2006; Grosso et al., 2009).

NO_x removal with SCR achieves a more efficient reduction of NO_x, on the order of 80–90%, using a catalyst operated at 200–350 °C. The three major types of catalysts are currently: (i) supported noble metal catalysts e.g. Pt/Al_2O_3, (ii) base metal oxide catalysis e.g. those containing vanadium, such as TiO_2–V_2O_5–WO_3, and (iii) metal ion exchanged zeolites-crystalline silicate e.g. Cu-ZSM-5 (Skalska et al., 2010). Recently, base metal-oxide catalysts are being replaced by the more modern zeolite catalysis. N_2O emissions from SCR are typically <1% of reduced NO_x, however, the use of a catalyst makes operation more expensive and complicated (Skalska et al., 2010). N_2O emissions can increase due to catalyst aging, process temperature and water vapour concentration (Svoboda et al., 2006).

In addition to direct emissions of N_2O and CO_2, the energy balance and the environmental and climatic impact of WTE in waste-to-energy plants is strongly affected by various upstream and downstream factors. The diversion of waste from landfilling provides a GHG benefit by reducing CH_4 emissions, which accounts for the majority of GHG emissions from the waste sector (e.g. 67% in Korea, 49% in Taiwan – Bogner et al. (2007), Park et al. (2011a), Fukushima et al. (2008)). Energy generation from waste incineration in WTE plants also provides a major GHG benefit (Fukushima et al., 2008). Ammonia slip (loss of ammonia) from NO_x reduction can result in significant downstream GHG emissions following waste incineration, which can be more detrimental than the NO_x being removed if the process is not operated efficiently (Moller et al., 2011). High NO_x removal efficiency in SNCR operations requires high ammonia:NO_x ratios, resulting in lower ammonia use efficiency and potentially higher ammonia slip – thus waste gas is usually washed with scrubbers (Zandaryaa et al., 2001; Moller et al., 2011).

Emission factors can be used to make a 'bottom-up' estimate of N_2O source contributions. Monitoring of isotopic composition provides an independent means to characterize sources through atmospheric measurements to compare with bottom-up estimates (Mohn et al., 2010, 2012b; Toyoda et al., 2011; Harris et al., 2014). N_2O has four major isotopocules: $^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$ ($\delta^{15}N^\alpha$), $^{15}N^{14}N^{16}O$ ($\delta^{15}N^\beta$), and $^{14}N^{14}N^{18}O$; the oxygen isotopic composition was not measured in this study, therefore only the first three isotopocules are considered. 'Site preference' (SP) refers to the difference in ^{15}N isotopic composition of the central (α) position N compared to the terminal (β) position N:

$$SP = \delta^{15}N^\alpha - \delta^{15}N^\beta \qquad (1)$$

Site preference, unlike $\delta^{15}N$, is independent of the isotopic composition of the reactant forming N_2O, and is therefore particularly useful to trace reactions and sources (Park et al., 2011b).

This study presents measurements of greenhouse gas (N_2O, CH_4 and CO_2) mixing ratios in flue gas from five Swiss waste incineration plants with grate firing. N_2O and CH_4 emission factors are calculated and compared to expectations based on NO_x removal technologies and IPCC recommendations. In addition, the isotopic composition of the N_2O in flue gas is presented as a tool to disentangle sources and processes.

2. Materials and methods

2.1. Sample collection

Representative flue gas samples were collected from five Swiss WTE facilities, labelled A–E, over week-long periods between September 2010 and August 2011 (Table 1). At plants A, C and E, 16–21 flue gas samples were collected, and at plants B and D, 7–9 samples. Facilities A–C employ NO_x abatement with SCR while facilities D–E employ SNCR for NO_x reduction. All incinerators are continuously operated underfeed stoker-type, burning solid recovered fuels without addition of sewage sludge. The shares of household and industrial waste are given in Mohn et al. (2012a). The facilities burn between 92,000 and 233,000 tonnes of waste per year (BAFU, 2012).

Samples were collected in 44 L aluminium-lined gas bags (Ritter GmbH, Germany) at a flow rate of 3 mL min^{-1}, as described in detail in Mohn et al. (2012a). Most samples were collected for an entire week, except for the 4–5 July 2011 sample at plant E, which was collected over just two days. One sample each from plants A and D was not used due to interruptions in plant operation, and one sample from plant E was not used due to a power outage within the sampling setup. The bag sampling method was validated and found to produce equivalent results for N_2O and CH_4 mixing ratios compared to standard monitoring procedures (Zeyer and Mohn, 2013; VDI, 2005; VDI, 2008).

2.2. FTIR analysis

The mixing ratios of N_2O, CH_4 and CO_2 in the bag samples were measured with a Nicolet Avatar 370 MCT FTIR spectrometer (Thermo Fisher Scientific Inc., USA) using a 50 mL heated (40 °C) flow-through gas cell with a 1 m pathlength (LFT-210, Axiom Analytical Inc., USA), as described in Mohn et al. (2012a). Quantitative results were obtained based on a Classical Least Square algorithm (TQ Analyst, Thermo Fisher Scientific, Inc.). Calibration spectra for CO_2, N_2O and CH_4 as well as interferent spectra for CO and H_2O were obtained over the relevant mixing ratio range for the bag samples.

The uncertainty and limit of detection were estimated by comparing the absorption area of the reference spectra with the residuals of the acquired spectra over the relevant wavelength region for each component, according to NIOSH (2000). The limit of detection (LOD) for both CH_4 and N_2O is 0.3 ppm. Samples with a mixing ratio lower than the LOD are set to the LOD when calculating averages, thus reported values are a 'worst case' scenario. The measurement uncertainty for CH_4 and N_2O is 10% of the measured mixing ratio, minimum 0.3 ppm.

2.3. Calculation of emission factors

The N_2O emission factors (EF) were estimated for each plant based on the ratio of N_2O to CO_2 in the flue gas, considering a CO_2 emission factor of 1271 kg CO_2 t^{-1} (EMIS, 2013):

$$EF_{N_2O} = \frac{[N_2O]}{[CO_2]} \times \frac{MW_{N_2O}}{MW_{CO_2}} \times 1271 \times 1000 \qquad (2)$$

where EF is the emission factor for N_2O, $[N_2O]$ and $[CO_2]$ are the concentrations of CO_2 and N_2O measured in the flue gas, and MW is the molecular weight. The methane emission factors were calculated analogously. This approach is different from IPCC Tier 3, where emission factors are calculated based on emission concentrations, the amount of combusted waste and the flue gas volume by amount of incinerated waste IPCC (2006). The applied Swiss CO_2 emission factor was calculated based on analyses of the waste carbon content of