TECHNICAL PAPER

Assessment of nitrous oxide emission from cement plants: Real data measured with both Fourier transform infrared and nondispersive infrared techniques

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Nitrous oxide (N_2O) is the third most important greenhouse gas after carbon dioxide and methane, and contributes about 6% to the greenhouse effect. Nitrous oxide is a minor component of the atmosphere, and it is a thousand times less than carbon dioxide (CO_2). Nevertheless, it is much more potent than CO_2 and methane, owing to its long stay in the atmosphere of approximately 120 yr and the high global warming potential (GWP) of 298 times that of CO_2. Although greenhouse gases are natural in the atmosphere, human activities have changed the atmospheric concentrations. Most of the values of emission of nitrous oxide are still obtained by means of emission factors and not actually measured; the lack of real data may result in an underestimation of current emissions. The emission factors used for the calculation of N_2O can be obtained from the "Guidelines for the implementation of the national inventory of emissions" of the Intergovernmental Panel on Climate Change, which refer to all nations for the realization of their inventory. This study will present real data, measured in several Italian cement plants with different characteristics. The work also shows a comparison between N_2O concentration measured with in situ Fourier transform IR (FTIR) and the reference method EN ISO 21258 based on nondispersive IR (NDIR), in order to investigate the interfering compounds in the measurement with NDIR.

Implications: N_2O may arise as an unwanted by-product of nitrogen oxide (NO_x) abatement systems, in particular selective noncatalytic reduction (SNCR). Since it is applied in the cement plants, N_2O emission from cement industry is evaluated, with both FTIR and NDIR instrument. Several considerations emerged from the results. First of all, the emission from this industrial sector is not negligible, and for that reason N_2O concentration should be regulated; another observation is that the reference method based on the NDIR technique is not as selective as FTIR could be.

Introduction

The major greenhouse gases (GHGs) emitted into the atmosphere through human activities are carbon dioxide (CO_2), methane, nitrous oxide (N_2O), and fluorinated gases. Some of these gases are produced almost entirely by human activities; others come from a combination of natural sources and human activities. The industrial sector is an important direct and indirect source of GHG emissions; GHGs are produced from a variety of industrial activities that are related not only to energy. The main emission sources are industrial production processes that are involved in chemical or physical transformation of materials. Many of the major greenhouse gases can remain in the atmosphere for tens to hundreds of years after being released. They become globally mixed in the lower atmosphere, reflecting contributions from emission sources worldwide. Several factors determine how strongly a particular greenhouse gas will affect the earth's climate. One factor is the length of time that the gas remains in the atmosphere. A second factor is each gas' unique ability to absorb energy. To compare GHG emissions from different sources, they are indexed according to their global warming potential (GWP), i.e., the ability of a GHG to trap heat in the atmosphere relative to an equal amount of carbon dioxide. According to the Intergovernmental Panel on Climate Change (IPCC) (2007), over a 100-yr time span carbon dioxide (CO_2) assumes the value of 1. The two other GHGs of importance in this analysis are methane (CH_4) and nitrous oxide (N_2O), which, according to a reevaluation of the IPCC in 2001, take a value of 25 and 298, respectively. From a legislative point of view, the first regulations on non-CO_2 GHGs are emerging in Europe. During the review of permits for large emitters under the European Union's (EU's) Integrated Pollution Prevention and Control (IPPC) Directive (96/61/EC), a number of facilities have been required to implement the best available control technologies for N_2O and fluorinated gases (Wartmann et al., 2006). The European Pollutant Emission Register (EPER) includes 50 pollutants, and for each of them threshold values are defined (i.e., 10,000 kg yr^{-1} in air for N_2O). If emissions exceed threshold values at specific facilities, such emissions must be reported. Facilities with lower emissions are not included (EU, 2000). The European Pollutant

Release and Transfer Register (E-PRTR) is the successor to EPER. It is a Web-based register established by Regulation 2006/166/EC, which implements the United Nations Economic Commission for Europe (UNECE) PRTR Protocol, signed in May 2003 in Kiev.

Nitrous oxide (N_2O)

At present, non-CO_2 GHGs make up for around 18% of total GHG emissions in the EU-25; among these, CH_4 and N_2O clearly dominate, with 92% of total emissions (Wartmann et al., 2006). Nitrous oxide (N_2O) plays an important role as a GHG and is involved in the depletion of the ozone layer in the atmosphere (Pearman et al., 1986; Ravishankara et al., 2009). In the last century, the anthropogenic sources of N_2O increased by a factor 2, and, consequently, the concentration in the atmosphere increased from 285 in 1900 to 330 ppb_v in 2010, at a rate of 0.2–0.3% per year. The fourth assessment report of the IPCC (IPCC, 2007) estimated N_2O emissions from both natural and anthropogenic sources at 8.5–27.7 Tg N_2O-N yr^{-1}. In this regard, there are several studies on methods and models for the estimation of the emission of N_2O from different sources (Osada et al., 1995; Olivier et al., 1998; Seitginzer et al., 2000; Brown et al., 2002; Tsai et al., 2006; Wang et al., 2011; Nol et al., 2012; Desloover et al., 2012). The worldwide increase is generally considered to be caused solely by the anthropogenic sources. Agricultural soils, manure management, and fuel combustion activities are difficult to monitor due to their high uncertainty in emission determination, or their large numbers of small emitters. Wastewater handling also are difficult to monitor, as emissions from the various sources (digester, lagoon, reactor, etc.) varying also in size can be monitored and verified only with difficulty due to a lack of data and high uncertainty. Only the production of adipic and nitric acid are easy to monitor and shows a high enforcement and relevance. Another minor (but not negligible) source is vehicular traffic: it is well established that vehicle exhaust contains N_2O. Furthermore, it is widely accepted that new vehicles equipped with three-way catalysts generally emit more N_2O than older vehicles without catalysts (Becker et al., 1999). With regard to climate change, the emissions of N_2O from light-duty vehicles have impacts that are approximately 1–3% of that of CO_2 emissions from vehicles (Lipman and Delucchi, 2002; Wallington et al., 2008). The numerous sources and sinks are categorized and grouped into major sectors (IPCC, 2006). The sector "Energy" comprises total emission of all greenhouse gases from stationary and mobile energy activities (fuel combustion as well as fugitive fuel emissions). The Emissions Database for Global Atmospheric Research (EDGAR) provides global past and present-day anthropogenic GHG emissions and air pollutants by country and on spatial grid (Joint Research Centre/Netherlands Environmental Assessment Agency [JRC/PBL], 2012). Table 1 shows an overview of contributions of each IPCC sector, referring to USA, Organisation for Economic Co-operation and Development (OECD) Europe, and China, expressed in Gg yr^{-1}. Detailed data are presented in Supplementary Material. USA and EU countries show a relevant decrease in almost all sectors; on the contrary, China shows a great increment in the emission of N_2O.

Another not negligible indirect source of anthropogenic N_2O from emissive systems is the uncontrolled reduction of nitrogen oxides (NO_x) by applying abatement systems listed by the legislation in order to have the emission of a nonpollutant gas such as N_2. There are various ways to control and reduce NO_x emissions from anthropogenic sources in order to meet the legislation; the two broad categories are (i) combustion modifications (i.e., temperature reduction, reduction of nitrogen in fuels, creation of a combustion environment that restrains NO_x formation) (Pershing and Wendt, 1977; Siddiqi and Tenini, 1981; Benitez, 1992; Perry and Green, 1997); and (ii) flue gas treatment. Although a significant reduction of NO_x can be achieved by means of combustion modifications, generally up to 50% as the sum of different measures, this alone is often insufficient to comply with the stringent emission standards and/or cannot be applied in existing combustors. Additional abatement is required and is therefore achieved by the use of end-of-pipe flue gas treatment technologies.

Selective catalytic reduction (SCR).

It is the most advanced and effective method for reducing NO_x emissions and can do so by up to 80–90%. SCR entails the reaction of NO_x with NH_3 within a heterogeneous catalytic bed in the

Table 1. Contribution of IPCC sectors anthropogenic emissions of N_2O in Gg yr^{-1} in USA, OECD Europe, and China, subdivided by IPCC sectors (from EDGAR database, JRC/PBL, 2012)

Sector	USA		OECD Europe[a]		China[b]	
	1990	2008	1990	2008	1990	2008
Energy	221.5	212.0	2069.0	2091.3	2058.7	2184.0
Industrial processes	209.6	137.1	374.4	153.2	107.1	189.9
Solvent and other product use	15.4	17.2	19.0	15.8	6.3	5.8
Agriculture	493.8	562.2	542.7	463.2	835.7	1228.4
Land use and forestry	13.1	1.2	6.2	0.4	12.4	1.8
Waste	23.1	34.3	35.0	48.2	47.4	68.6
Other	94.0	72.0	62.0	45.5	51.8	124.0
Total	1070	1036	3108	2818	3119	3803

Notes: [a]OECD Europe comprises Austria, Belgium, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway, Poland, Portugal, Slovak Republic, Slovenia, Spain, Sweden, Switzerland, Turkey, and United Kingdom. [b]China comprises China, Hong Kong, Macao, Mongolia, and Taiwan Province of China.
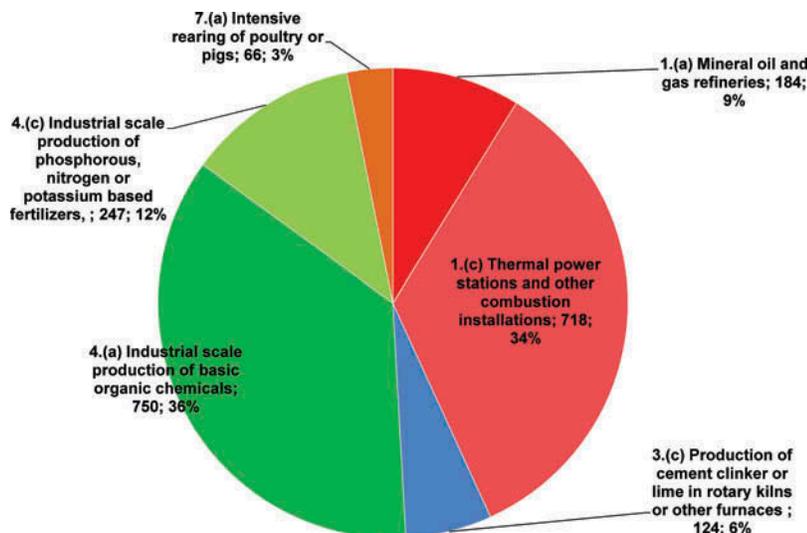
Figure 1. N_2O releases in air (t yr^{-1}) in 2011 in Italy, and contribution (%) of each subactivity of IPCC sectors: 1 = Energy sector; 3 = Mineral industry; 4 = Chemical industry; 7 = Intensive livestock production and aquaculture. Data from E-PRTR.

presence of O_2 at temperatures normally in the range of 250–400 °C (Radojevic, 1998). The formation of N_2O on precious-metal catalysts has been well documented in previous studies of NO_x reduction technologies. Madia et al. (2002) observed that in urea SCR systems, N_2O production is likely if the NO_2/NO ratio is too high. In this case, the standard SCR reaction thermodynamically favors production of N_2O from NO_2 over the complete reduction to N_2.

Selective noncatalytic reduction (SNCR). It is a simple process, referred to as "thermal DeNO$_x$," and involves the reduction of NO_x to N_2 in the presence of oxygen by reaction with amine-based reagents (NH_2-X) (Lucas and Brown, 1982; Lyon, 1987; Bowman, 1992; Rother, 1996; Muzio and Quartucy, 1997). The most common NH_2-X agent is ammonia water of about 25% NH_3 (Cembureau Working Group, 1999). The reaction has an optimum in a temperature window of about 800–1000 °C, and sufficient retention time must be provided for the injected agents to react with NO. Hwang et al. (2009) underlined the importance of maintaining the temperature range: below this level, unconverted ammonia is emitted (so-called "NH_3 slip") and at significant higher temperatures the ammonia is oxidized to NO_x. Emissions of carbon monoxide (CO) and nitrous oxide (N_2O) may also occur (Kupper and Brentrup, 1992). There are opposing studies in the literature about the roles of these last two gases in the N_2O formation/reduction: some laboratory studies show how at low temperature they could be the cause of N_2O emissions (de Soete, 1993; Kramlich and Linak, 1994), but other field studies demonstrated their efficiency as reduction system (Takeshita et al., 1993). SNCR is better suited for applications with high levels of particulate matter in the waste gas stream than SCR, and it is applied in the cement industry.

Case study: The cement industry

Emission inventories and release contribution estimates for the cement industry are usually based on two types of information, earlier literature data or real measurements, providing considerably different results. Atmospheric emissions from an industry could be evaluated only through the in situ verify of the limits listed in the specific legislation or, with a more integrated method, considering also the functional relations with the principal productive, management, and process aspects. E-PRTR (2011) reports the N_2O releases in air, expressed in tons in 2011 in Italy, from 38 facilities, belonging to different IPCC sectors, as shown in Figure 1. Among these, the most important releases are from Sector 4—Chemical industry and Sector 1—Energy: 48% and 43%, respectively. Production of cement (subactivity of Sector 3—Mineral industry) is not a negligible sector, as it contributes 6% of the total releases with seven facilities, and it is comparable to mineral oil and gas refineries (9% with five facilities).

The cement industry is today distributed throughout the world, and global 2012 cement production is estimated at 3.6 billion tonnes, translating into a +3% increase compared with 2011 (Boston Consulting Group [BCG], 2012). On average, approximately 1 ton of concrete is produced each year for every human being in the world. Therefore, concrete (i.e., cement) is one of the world's most significant manufactured materials. Because of its abundance in the world market, understanding the environmental implications of concrete and cement manufacturing is becoming increasingly important (van Oss and Padovani, 2002, 2003; Lippiat and Ahmad, 2004). The clinker burning process is the most important part of the process in terms of the key environmental issues for cement manufacture: energy use and emissions to air (NO_x, SO_2, and dust). The best available techniques (BAT) for reducing NO_x emissions are a combination of general primary measures, staged combustion, and selective noncatalytic reduction (SNCR).

Aim of the work

The aim of the work was to evaluate the contribution of cement plant to air emission of N_2O. In particular, data from

eight Italian facilities were analyzed, in respect to each plant's characteristic and installed abatement systems. The knowledge of real concentrations and flow rate of each plant made also possible an estimate of N_2O emission to the Greenhouse effect.

In addition, the effect of the different measuring principles of the N_2O analyzer concerning the results will be found with comparison measurements. In spot measurements, the reference nondispersive infrared (NDIR) technique will be measured in parallel with the in situ Fourier transform infrared (FTIR) technique.

Experimental Section

Cement plants

Air emission data from eight Italian cement plants were investigated. Data were gathered from the automatic flue gas monitoring system of each plant, installed both at the stack and at the boiler exit. Since the production of clinker (pyroprocessing step) is the most energy- and emission-intensive process in the manufacturing of cement, accounting for more than 80–85% of the overall environmental impact score (Hutzinger and Eatmon, 2009), data refer to the clinker burning emission point. The lines of the clinker burning adopt the latest best available techniques (BAT) for the sector. In particular, they consist of dry process rotary kilns with preheaters and multistage precalcinators. Within the preheater and kiln systems, particulate control devices are used to capture fine particulates of unburned and partially burned raw material that become entrained in the combustion gases (i.e., baghouse filters [BH], electrostatic precipitators [ESPs], and hybrid filters, in which ESP is combined in series to a BH). The lines of the clinker burning are also equipped with abatement systems for NO_x, using the technique of SNCR with ammonia or urea as a reducing agent, and multistage combustion. In addition, in some plants the use of conventional fuels (petroleum coke) is combined with the use of the refuse-derived fuel (RDF). Table 2 shows the characteristics of the facilities analyzed in this work.

Flue gas analysis

The concentration of gaseous pollutants in the flue gas as well as plant characteristics were continuously measured by online instruments and data were provided by the manager of each plant. Concentration of NO_x, N_2O, CO, CO_2, H_2O, and NH_3 were measured by a multicomponent analyzer using Fourier transform infrared (FTIR) spectrometer (measuring range: 0–100 mg Nm^{-3} and limit of detection [LOD]: 0.25 mg Nm^{-3} for N_2O); O_2 was measured by a zirconium oxide detector. Data (measured every minute by FTIR) were collected in 24 hr for each week of the year and presented as annual arithmetic average. The reference standard method for the measurement of N_2O, ISO 21258 (2010), is based on nondispersive infrared (NDIR) instrument. A dual-beam-type NDIR analyzer (measuring range: 0–150 mg Nm^{-3} and LOD: 0.20 mg Nm^{-3} for N_2O) was used in parallel spot measurements versus FTIR. All measured values related to dry gas under standard conditions: temperature 273 K, pressure 101.3 kPa, and oxygen content of 10%.

Results and Discussions

N_2O emissions

Table 3 shows the average concentration of punctual measurements of N_2O, NO_x, CO (expressed in mg Nm^{-3}) and of CO_2 (expressed in % *v/v*) on a monthly basis, collected by inline instruments installed on plants. In addition, NO_x/N_2O ratio is calculated (expressed in %).

It is interesting to observe that plants A and B emit the higher concentrations of NO_x among all the facilities concerned. They have the same abatement systems (ESP for dust and SNCR with ammonia solution for NO_x), and they both use RDF as an additional fuel. The replacement of the traditional fuel (petcoke) with RDF could be the cause of the higher emissions of NO_x and, as a consequence, of N_2O. From a detailed analysis of fuel data and N_2O concentrations of the plants, however, no correlation has been found.

The concentration of N_2O is around 1% of the emission of NO_x (Table 3) for the investigated plants. Since N_2O is an unwanted by-product of de-NO_x technology, unreacted ammonia could be found at stack emissions (Kupper and Brentrup, 1992). Concentrations of both gases (N_2O and NH_3) were analyzed for each plant. Figure 2 shows the profiles of N_2O and NH_3 for plants with the highest N_2O/NO_x ratios.

Table 2. Characteristics of the cement plants analyzed

Characteristic	Plant A	Plant B	Plant C	Plant D	Plant E	Plant F	Plant G	Plant H
Fuel rate (t hr^{-1})	8	7	6	8	12	9	10	10
Fuel type	Petcoke + RDF (70:30)	Petcoke + RDF (60:40)	Petcoke	Petcoke	Petcoke	Petcoke	Petcoke	Petcoke
Installed abatement systems	ESP	ESP	BH Urea-SNCR	ESP + BH	ESP	ESP Urea-SNCR	BH Urea-SNCR	BH
Stack temperature (°C)	122	112	120	154	111	108	103	100
Flow rate (Nm^3 hr^{-1})	350,000	240,000	240,000	320,000	470,000	380,000	340,000	230,000
O_2 (%)	15	15	13	12	13	13	13	8
H_2O (%)	7	7	7	8	12	8	11	16

Notes: RDF = refuse-derived fuel; ESP = electrostatic precipitator; BH = baghouse filter; SNCR = selective noncatalytic reduction.

Table 3. Average concentration of punctual measurements of N_2O, NO_x, CO, and CO_2 on a monthly basis, collected by inline instruments installed on plants, and NO_x/N_2O ratio

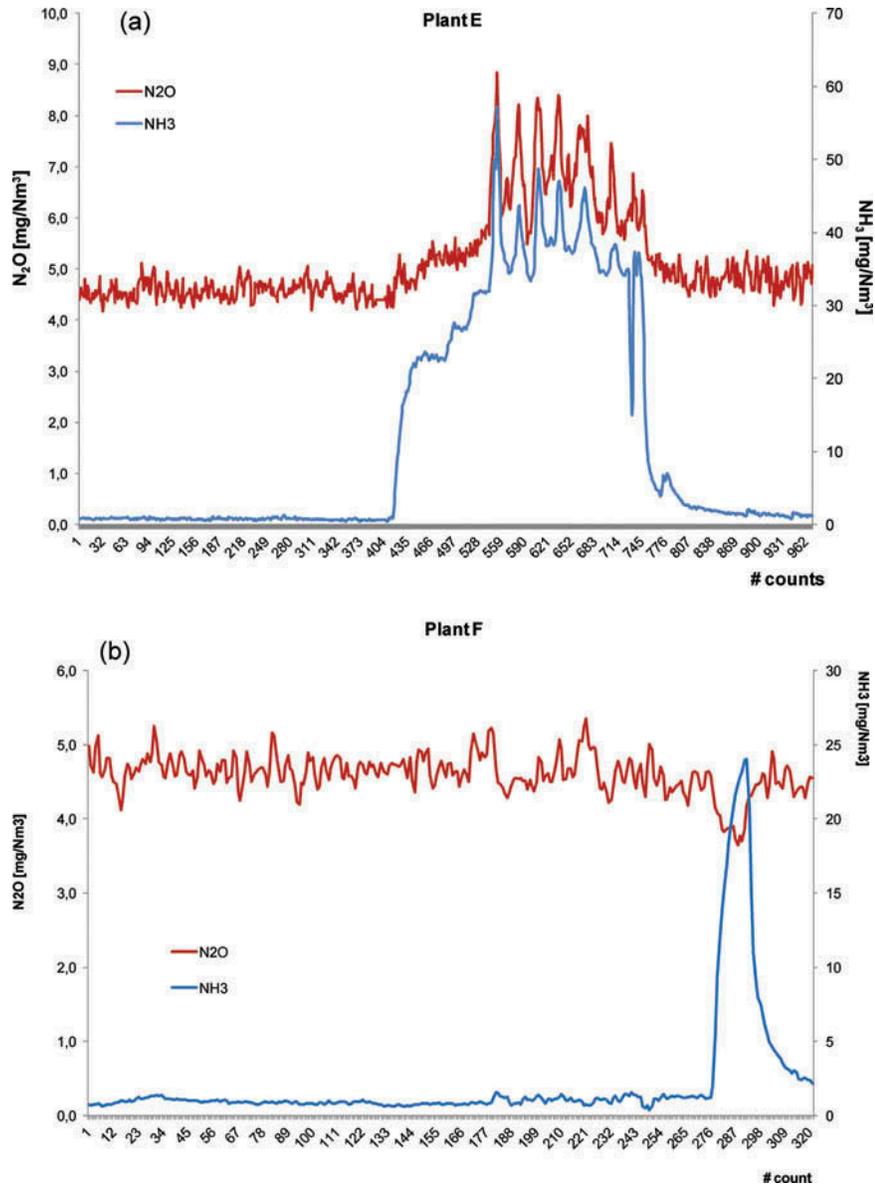| Plant	N_2O (mg Nm^{-3})	NO_x (mg Nm^{-3})	NO_x/N_2O (%)	CO (mg Nm^{-3})	CO_2 (% v/v)
Plant A	6.8	665	1.03	449	10.2
Plant B	7.6	777	0.98	232	10.3
Plant C	4.9	583	0.84	206	9.8
Plant D	4.5	501	0.91	162	11.7
Plant E	4.8	318	1.52	233	8.9
Plant F	4.8	430	1.11	108	11.2
Plant G	3.7	559	0.59	149	13.9
Plant H	4.1	694	0.66	518	24.4

Figure 2. Profiles of N_2O and NH_3 (mg Nm^{-3}) for plants with highest N_2O/NO_x ratio. (a) profile of plant E; (b) profile of plant F.

The difference in the trend stands out from Figure 2. In both cases, there is a high "ammonia slip," but in the first case (plant E) there is a simultaneous increase of N_2O concentration. It could be explained considering that plant E is equipped with ammonia-based SNCR and plant F with urea-based SNCR, and the peak of NH_3 at the stack can be explained as unreacted ammonia, added as a surplus.

Greenhouse effect gases. CO_2 is the most important greenhouse gas emitted from cement industry. N_2O, however, should not be underestimated as a greenhouse effect gas, as its GWP is 298 (IPCC, 2007). An easy way to evaluate the contribution to greenhouse effect is to consider the average emission rate of N_2O from a cement plant. In this work, we analyzed data from eight Italian facilities, about one tenth of the Italian cement industry; by multiplying the average concentration of N_2O (5 mg Nm^{-3}) and the average flow rate (320,000 Nm^3 hr^{-1}), the emission rate of N_2O is about 1.6 kg hr^{-1}.

If we consider that the European Union (EU) cement industry consists of some 250 plants and 86 of these are in Italy (34%) (Wagner and Vassilopoulos, 2000), the importance of the control of the emission of N_2O from cement plant is an issue to be considered by policy makers.

FTIR versus NDIR

Simultaneous measurements were made in three sampling campaigns at the eight cement plants under examination, in order to evaluate data from both in situ system (FTIR) and reference methods (NDIR). Data (measured every minute by each instrument) were collected in 8 hr for each sampling campaign and presented as annual arithmetic average. The international reference method for sampling and determination of N_2O

content in flue gas, ISO 21258 (2000), and the United Nations Framework Convention on Climate Change Clean Development Mechanism (UNFCCC CDM) methodology (2010) specify the use of NDIR technique. However, the literature data suggest that grab samples containing NO, SO_2, and condensed H_2O produce N_2O as an artifact (Muzio and Kramlich, 1988; Montgomery et al., 1989; Muzio et al., 1989). As a result, the N_2O levels reported may be higher than the levels actually produced directly by combustion systems. N_2O has strong infrared absorbances at 4.5, 7.8, and 17.0 μm, from which the main band of 4.5 μm is commonly being used in the NDIR analyzers. In this region, other oxides of nitrogen (NO, NO_2) have no significant cross-interferences, but water vapor, carbon dioxide, and carbon monoxide have an effect on the N_2O measurement. They have infrared absorbances in the same region as N_2O; thus, they have an overlap with the N_2O absorbance, as reported by Bruce (1999).

First of all, in accordance with the Italian Legislative Decree 152 (2006), a "Relative Accuracy Index" (Iar) for N_2O and for the most interfering compounds (CO and CO_2) was calculated. Data are presented in Table 4, together with mean, minimum, and maximum concentrations of these species analyzed with both systems.

In almost all the sampling campaigns, the Iar for CO and CO_2 was >80%, meaning a good accordance between the two systems. As an example, Figure 3 shows these good accordance even with a high variability of the concentration of the gases.

As for N_2O, the Iar gave poor results (<50%), meaning that the two measurement systems cannot be equivalent. In Figures 4 and 5, two particular cases are reported. Figure 4 shows the profiles of N_2O concentrations measured in plant G. It can be seen a good accordance as for the trend, but the concentration measured with NDIR is 7 times higher than that measured with FTIR.

Figure 5 shows the profiles of N_2O concentrations measured in plant B. A different behavior can be observed: NDIR and

Table 4. Mean, minimum, and maximum concentrations of CO, CO_2, and N_2O obtained with NDIR and FTIR techniques and relative accuracy index (Iar)

| Plant	Technique	CO (mg Nm^{-3})				CO_2 (% v/v)				N_2O (mg Nm^{-3})			
		Mean	Min	Max	Iar (%)	Mean	Min	Max	Iar (%)	Mean	Min	Max	Iar (%)
Plant A	NDIR	177.9	125.5	917.3	62.6	8.9	6.9	10.7	95.5	2.8	0.2	7.8	40.5
($n = 1495$)	FTIR	183.6	64.1	1973.6		8.7	2.9	10.4		4.1	2.2	7.0	
Plant B	NDIR	97.9	16.9	266.1	−0.6	10.8	6.8	12.9	97.8	20.5	14.5	28.4	36.2
($n = 885$)	FTIR	194.4	53.7	390.2		10.6	6.9	12.7		7.5	2.9	21.1	
Plant C	NDIR	179.0	0.1	1188.0	60.0	10.7	0.1	18.6	86.6	2.4	0.1	11.0	−36.3
($n = 535$)	FTIR	215.7	81.9	806.2		11.0	4.6	18.9		5.4	2.5	8.2	
Plant D	NDIR	204.4	159.5	621.9	85.6	12.8	10.1	13.5	92.3	23.2	18.3	42.0	20.7
($n = 692$)	FTIR	175.7	36.5	474.5		11.9	2.0	12.8		4.9	1.7	11.8	
Plant E	NDIR	308.6	143.1	1301.6	76.3	10.6	8.8	12.8	81.9	3.6	1.0	10.7	48.0
($n = 971$)	FTIR	302.7	170.9	1247.6		9.3	7.8	11.2		5.2	4.2	8.8	
Plant F	NDIR	116.3	94.7	227.9	85.5	12.3	10.3	13.4	90.7	1.5	0.0	6.4	−278.5
($n = 321$)	FTIR	101.7	84.3	156.1		11.2	9.3	12.2		7.2	5.4	8.2	
Plant G	NDIR	112.3	4.1	1080.9	60.3	13.4	2.0	18.0	88.4	27.2	56.7	−3.3	12.9
($n = 1407$)	FTIR	137.9	2.3	1430.9		14.8	2.2	19.7		3.7	36.7	0.2	
Plant H	NDIR	418.8	6.7	1177.1	91.4	23.2	0.4	24.2	97.3	1.3	0.1	2.9	−99.6
($n = 1190$)	FTIR	431.2	59.5	328.9		23.7	0.4	21.6		3.8	0.3	2.3	
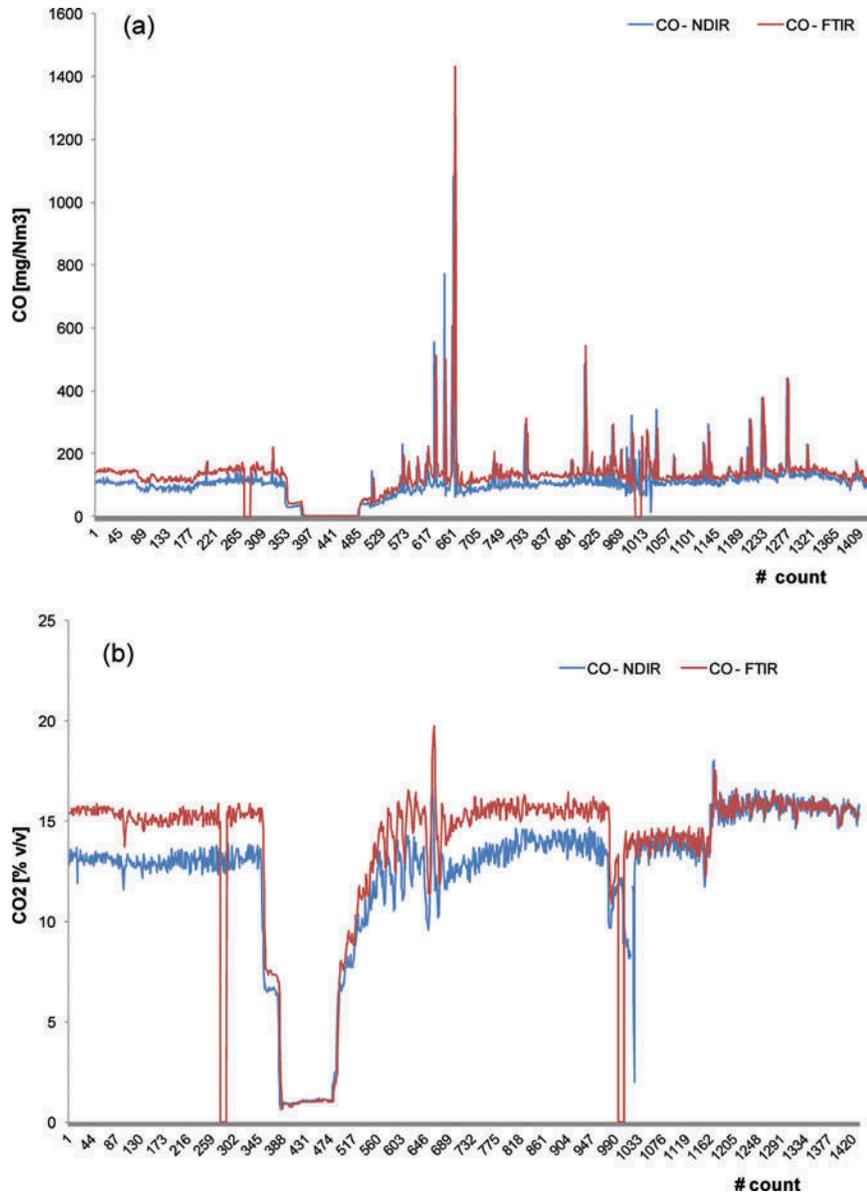
Figure 3. Profiles of (a) CO (mg Nm^{-3}) and (b) CO$_2$ (% *v/v*) obtained in a simultaneous sampling campaign with FTIR- and NDIR-based instruments in plant G.
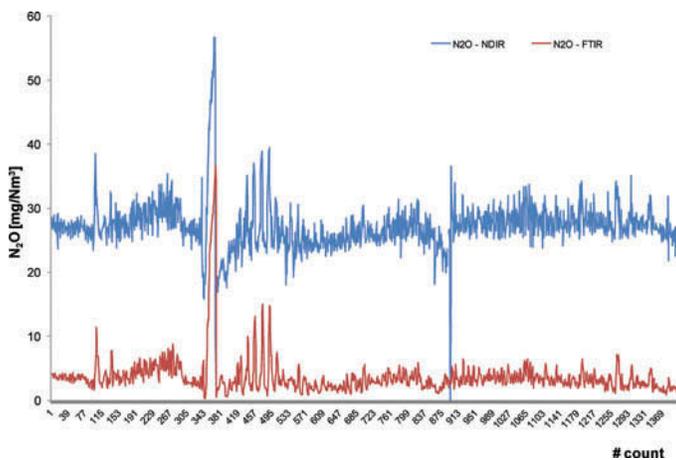

Figure 4. Profiles of N$_2$O (mg Nm^{-3}) obtained in a simultaneous sampling campaign in plant G with FTIR- and NDIR-based instruments: good accordance in trend.
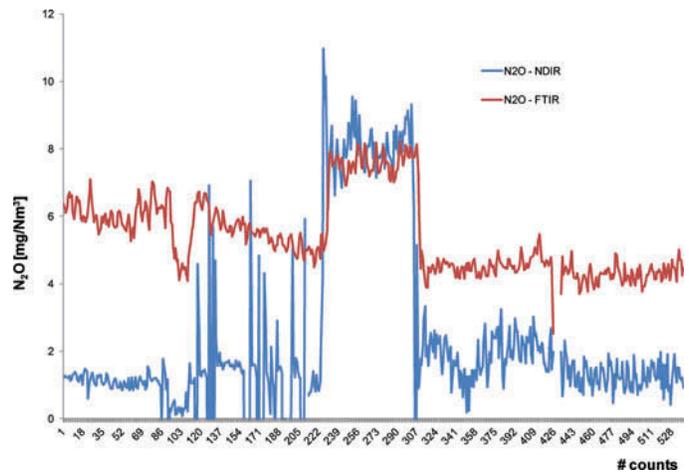
Figure 5. Profiles of N$_2$O (mg Nm^{-3}) obtained in a simultaneous sampling campaign in plant C with FTIR- and NDIR-based instruments.

FTIR are in good accordance as for the measured concentration when it is higher. It could be due to a reduced selectivity at low concentrations.

The two different analyzers are designed to avoid the interference problem on the N_2O measurement due to the overlap or the IR absorption spectra of the other gases. The NDIR system introduces an additive and multiplicative compensation on the result of the measure of the single gas, eliminating the contribution associated with the presence of other interfering component such as CO, CO_2, and H_2O, in the case of N_2O. The FTIR system, on the other hand, create an integrated combination of all the IR absorption spectra of the gases in the emission and, after that, eliminates the contribution of the interfering components, using the IR reference spectrum obtained during the calibration of the instrument. The NDIR analyzer seems to be more affected by the presence of interferences than the FTIR analyzer. This could be due to the lack of a very selective optic and detecting system.

Conclusion

The limited number of results available at present supports almost a preliminary evaluation of the importance of accurate N_2O measurements in flue gas. In this regard, the Technical Committee ISO/TC 146, Air quality, Subcommittee SC 1, Stationary source emissions, is preparing a standard about quality assurance procedures for calibration and ongoing quality control needed to assure that automated measurement systems (AMS), installed to measure emissions of greenhouse gases to air. It means that measurement of greenhouse gas emissions (carbon dioxide, nitrous oxide, methane) in a framework of emission trading is important and requires an equal and known quality of data. Some significant results emerged from this preliminary work. First of all, the contribution of cement plant to global N_2O emission (and to greenhouse gas effect) should not be neglected, in consideration of the number of cement industries present and their flow rate. Another important aspect that emerged from the analysis of data is the different unwanted production of N_2O from urea- and NH_3-based SNCR systems. Lastly, the reference method based on NDIR is highly affected by interfering compounds. It is important to underline that the reference method ISO 20258 has been tested on an industrial plant where the N_2O concentration in the flue gas was up to about 200 mg Nm^{-3}. In the cement plants investigated, however, the average concentration was 5 mg Nm^{-3}. This strengthen previous considerations on lack of selectivity in NDIR techniques. The further reduction of NO_x to values below 100 mg Nm^{-3}, if done with the described technique (SNCR), can lead to significant levels of N_2O. Apart from highlighting the presence of N_2O from industrial sources (i.e., E-PRTR), there should be the need to understand if, at international level, a specific emission limit for N_2O, or the inclusion of this gas to the total NO_x (= NO + NO_2 + N_2O), should be established. In light of the above considerations, NO_x and N_2O should be put onto the scale: what is more advisable? The continuous reduction of NO_x, a pollutant that has local implications, from industrial plants; with the improvement of abatement systems, which can cause the formation of N_2O; or the control (even in a legal aspect) of N_2O emissions, a pollutant that undergoes climate changing, sacrificing the reduction of NO_x?

Supplemental Material

Supplemental data for this article can be accessed on the publisher's website.

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