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The Estimation of Emission Factor of N_2O and CH_4 by Measurement from Stacks in the Waste Incinerators and Cement Production Plants

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Abstract: The purpose of this study is to estimate the emission factor of non-CO_2 global warming gases such as N_2O and CH_4 by measuring concentrations from stacks of waste incinerators and cement production plants. Based on the established monitoring methods, N_2O concentration measured from stacks in incinerator were between 0.62 and 40.60 ppm_v (ave. 11.50 ppm_v). The concentration of N_2O was dependent on the incinerator types. However, the concentrations of CH_4 gas were between 2.65 and 5.68 ppm_v (ave. 4.22 ppm_v), and did not show the dependency on the incinerator types. In the cement production plant, the concentration ranges of N_2O from the stack were from 6.90 to 10.80 ppm_v (ave. 8.60 ppm_v), and CH_4 were between 1.80 and 2.20 ppm_v (ave. 2.60 ppm_v). Using measured concentrations, the emission amounts of N_2O and CH_4 from stacks per year were calculated. The results were is 4.2 ton N_2O/yr in the incinerators, and 53.7 ton N_2O/yr in the cement facilities. The big difference is from the flow rate of flue gas in the cement facilities compared to the incinerators. By the same reason, the CH_4 emission amounts in cement plant and incinerator was found to be 339 ton CO_2/yr and 34.1 ton CO_2/yr, respectively. Finally, the emission factor of N_2O in the incinerators were calculated using the measured concentration and the amount of incinerated wastes, and was 42.5~799.1 g/ton in kiln and stoker type, 11.9~79.9 g/ton in stoker type, 90.1 ton/g in rotary kiln type, 174.9 g/ton in fluidized bed type, and 63.8 g/ton in grate type, respectively. Also, the emission factors of CH_4 were found to 65.2-91.3 g/ton in kiln/stoker type, 73.9-122 g/ton in stoker type, 109.5 g/ton rotary kiln, and 26.1 g/ton in fluidized bed type. This result indicates that the emission factor in incinerators is strongly dependent on the incinerator types, and matched with result of IPCC (International Panel on Climate Change) guideline.

Keywords: global warming gases, N_2O, CH_4, emission factor, incinerator, cement production plant, IPCC

Introduction

The concentration of global warming gases such as CO_2, CH_4, N_2O, CFCs, and SF_6 are continuously increasing since 1750. The report published by US EPA in 2000 showed that the percentage of CO_2, CH_4, N_2O were 83%, 9%, 6%, respectively.[1] If these concentrations are keep increasing, the negative effect will be happened in ecosystem and health in the global scale.[2]

Among the greenhouse gases (GHGs), nitrous oxide (N_2O) is usually produced by the usage of fertilizer, and produced by industrial activity, especially produced by nitrate (NO_3^-) denitirfication under anoxic condition. Also, during incineration process, N_2O can be produced by the collision between oxygen atom and nitrogen molecule by collision with third body molecule called M.[3] The life time of N_2O in the atmosphere is approximately 120 years, and the global warming potential (GWP) is 310 times of carbon dioxide. Therefore, even though the amount of N_2O produced from natural and anthropogenic sources are small compared to CO_2, the global warming effect can not be ignored.[4,5] The natural sources of N_2O constitute approximately 60% of total N_2O production, however, the production from industrial sources such incinerators have the large portion.[6,7]

Methane is also one of the greenhouse gases, and is produced by anaerobic degradation by microorganisms in the natural and environmental facilities such as landfill site, sludge treatment process in the wastewater treatment facilities, and from the stacks of the plants by incomplete combustion.[8-11] The global warming potential of CH_4 is 21 times of CO_2 gas, however, the global

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production of CH_4 is the second largest among the greenhouse gases. The global production of CH_4 is approximately 500± 100 Tg per year, and approximately 70% of CH_4 is anthropogenic source.[12,13] The lifetime of CH_4 is approximately 12 year.[14]

The production of non-CO_2 greenhouse gases such as N_2O and CH_4 is the second and third largest GHGs, therefore cannot be ignored. One of the large sources of these non CO_2 gases are from by incomplete combustion from the plant stacks such as incinerators and cement plant facilities. The common method for estimating CO_2 emissions from incineration is based on the estimation of the fossil carbon content in the waste, multiplied by the oxidation factor, and converting the product to CO_2. This approach is called Tier 1 approach suggested by IPCC (International Panel on Climate Change) guideline in 1996.[15] In Tier 1 process, the emission factors of greenhouse gases can be estimated by default values (Tier 1). Presently, the estimation of GHGs in Korea follows Tier 1 method suggested by IPCC guideline (1996). However, in 2001 IPCC (2001) good practice guidance suggested the country-specific (Tier 2) emission factor instead of simple emission factor calculation,[16] therefore, the study of estimation of GHGs is being conducted in many countries.

Recently, IPCC guideline published in 2006 suggested the plant-specific estimation of GHG based on the plant-specific values (Tier 3 method).[17] In Tier 3 method, the most accurate emission estimates can be developed by determining the emissions on a plant-by-plant basis and/or differentiated for each types of waste (e.g. municipal solid waste, industrial waste, sewage sludge, clinical waste, and hazardous waste). However, only a few study of the estimation of global warming gases through plant-specific on-site measurement are conducted.[2,6]

Korea also should prepare the Kyoto Protocol, however, only a few measurement researches have been done in the plant facility. Therefore, the estimation based on the monitoring and measurement is required. In order to do this, the measurement protocol for measuring GHGs such QA (Quality Assurance)/QC(Quality Control) are first needed to get the accurate emission amount estimation.

The estimation of emission factor (ton of CO_2 equivalent/ton waste incinerated) by accurate measurement is very important since only a few difference in the concentration of GHG can result in the big difference in the emission inventory of GHG in the country bases. In this study, the estimation of non CO_2 greenhouse gases (N_2O and CH_4) by the measurement from the stacks of incinerators and the cement production plants in Korea were conducted in order to estimate CH_4 and N_2O emission by Tier 3 method (plant-specific

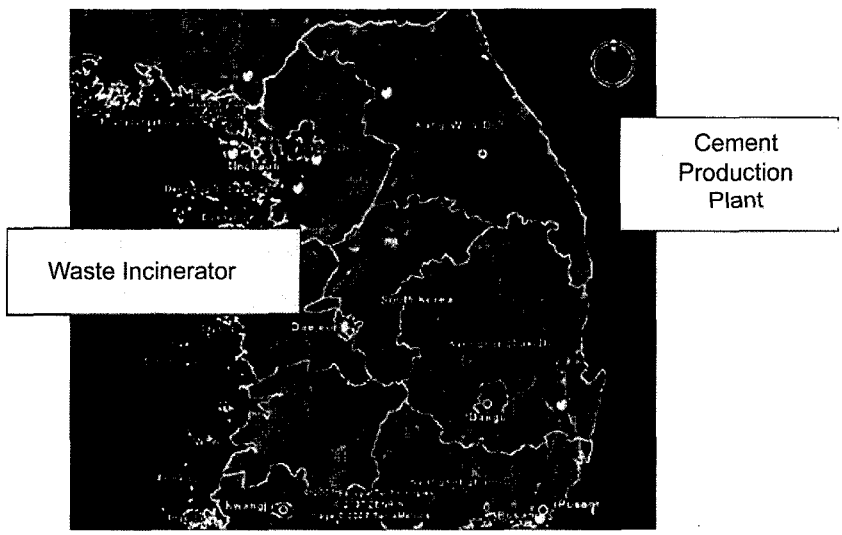

Fig. 1. Location of sampling sites.

estimation). The measurement was performed in seven municipal and hazardous wastes incinerators and five cement production plants. The monitoring was conducted by the sampling of flue gases from the stacks, and the analysis using gas chromatography was conducted. Using the measurement data, the emission factors of N_2O and CH_4 were estimated.

Materials and Methods

Sampling Methods

The sampling were conducted at seven waste incinerators, which is located in the Banwol-Sihwa Industrial Complex in the Kyonggi Province, and at five cement production plants located in the south side of Kangwon Province in Korea. Fig. 1 shows the map of sampling site in the incinerators and cement production plant in this study.

The sampling procedure is as follows; The sampling pipe was connected to the stack, connected to cooling device, and connected to the pump measuring flow rate (SIBATA, Σ100), as well as, the sampling was performed with constant flow rate. Sample air is transported from the intakes to the Tedlar bags (SKC Ltd., USA) through TYGON® tubing using portable pump (SIBATA, Σ100) at flow rates of 0.5 *l*/min, and the cooling system required by this sampling is based on water.[18]

The flue gases in the stacks are produced with over 10 m/sec of flow rate and over 80°C of temperature from the stack. The pipe used in this study was made of the stainless type, and the size of the pipe is around 1.5 m. The sampling bag was used with Tedlar bag (SKC Ltd., USA). The temperature of flue gas was so high, therefore, in order to protect the sampling bag from high temperature gas, the water based cooling system between the sapling pipe and the sampling device was installed. The sampling of flue gases was performed with the portable pump with the flow rate of 0.5 *l*/min for 40 min, and the impinger was used to cool down the flue gas from the stack.

The Method of Making N_2O and CH_4 Standard Gases

The standard gas of N_2O (499.5 ppm_v) was obtained from Institute of Korean Chemical Engineering certified internationally and CH_4 standard gas are obtained from (99.99%, QUADREN CRYOGENIC PROCESSING, Ltd., USA). From this gas the lower concentration of gas are prepared by the dilution using Tedlar bag.

The method using a Tedlar bag dilution is as follows: the standard 499.4 ppm_v N_2O and CH_4 gases were captured in 1 *l* Tedlar bag (SKC Ltd., USA), and in another Tedlar bag, pure nitrogen gas (99.9999%) were retained. Then, using portable pump (SIBATA, Σ100) with the flow rate of 25 m*l*/min, the known amounts of standard 499.4 ppm_v N_2O and CH_4 gases were added, then using 400 m*l*/min of flow rate, these gases were diluted to make each concentration of standard gases. The trace known amount of standard gases were injected into the Tedlar bag using 500 μ*l* micro syringes for the dilution. Using prepared standard concentration of N_2O and CH_4 gases in the Tedlar bags, the standard calibration curves were constructed by daily analysis of the standard gases with different concentrations. Two of the standard gases are analyzed every six hours. These data are used for the purpose of quality control.

QA/QC of Analysis Method

The analysis of N_2O and CH_4 gases are performed by gas chromatography (HP 6890) using μ-electron capture detector (μ-ECD) and flame ionization detector (FID) as the detector with the capillary chromatographic columns. The detailed analysis conditions are shown in Table 1. The samples from incinerator stack were taken with Tedlar bag (SKC Ltd., USA) through tygon tube (2075 Ultra Chemical Resistant Tubing) using portable air sampling pump (SIBATA, Σ100) at flow rates of 0.5 *l*/min. Next, the samples were brought into the laboratory, and measured with gas chromatography.

The protocol scheme of N_2O and CH_4 measurement and QA/QC is shown in Fig. 2. The reproducibility and linearity of N_2O and CH_4 standard gases analysis were assessed by checking the retention time and peak area of different concentration according to at least three times injections. The relative standard deviation (RSD) was compared, and the relationship between standard gas concentration and peak area were examined. The detection limit was obtained using the procedure of Occupational Safety & Health Administration (OSHA).[19]

Table 1. Temperature program and operating condition of gas chromatography for measuring CH_4 and N_2O gases

	Conditions	
Gas type	N_2O	CH_4
Detector type	μ-ECD	FID
Inlet	Split 10:1 Injector : gas-tight syringe Injection volume: 250 μl Temperature: 80°C	Split 10:1 Injector : gas-tight syringe Injection volume: 250 μl Temperature: 120°C
Column	HP-PLOT Q capillary (30.0 m × 0.53 μm × 40 μm)	HP-1 capillary (30.0 m × 530 μm × 2.65 μm)
Oven temperature programming	Temperature : 80°C at 1 min-5°C/min to 150°C	Temperature : 100°C at 2 min-15°C/min to 250°C
Detector temperature	Temperature: 250°C Make up gas: N_2 gas	Temperature: 250°C Make up gas: N_2 gas
Carrier gas	N_2 gas	N_2 gas

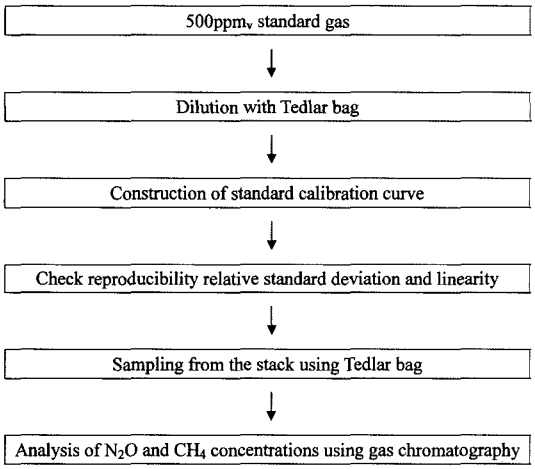

Fig. 2. The protocol scheme of N_2O and CH_4 measurement and QA/QC.

In order to investigate the uncertainties associated with sampling and analysis of N_2O and CH_4 gases, the adsorptive loss due to the contact with the container wall (such as Tedlar bag and vial) was examined, but it was found that the loss was minimal (within 5%).

Results and Discussions

QA/QC of N_2O and CH_4 Analysis

First, the monitoring protocol of N_2O and CH_4 was constructed. The standard gases prepared by dilution method, and the standard calibration curves of the standard N_2O and CH_4 gases were constructed. The standard calibration curves are shown in Fig. 3 and Table 2.

Table 2. The calibration curve parameters and limit of detection for N_2O and CH_4

Compounds	Slope	Intercept	LOD (ppm_v)	R^2
N_2O	2.6777	4.6659	0.23	0.99
CH_4	0.6304	0.3226	1.15	0.99

The retention time reproducibility of N_2O was found to be between 0.2 and 0.6%, and overall reproducibility was found to be 0.39%. The retention time reproducibility of CH_4 was in the range of 0% to 0.3%, and the overall reproducibility was 0.18%.

Second, the relative standard deviation (RSD) of peak areas was calculated using measurement data. The RSD values of N_2O gas were between 1.4% and 15.7%, and the overall reproducibility was 5.64%. The RSD values of CH_4 were between 6.1 and 11.3%, and overall reproducibility was 8.2%.

Finally, the linearity was checked by multiple measurement; N_2O (56 times), CH_4 (48 times). The correlation between injected amounts and peak areas, the R^2 values were more than 0.99. The detection limit of N_2O and CH_4 were 0.23 ppm_v and 1.15 ppm_v, respectively. Therefore, the QA/QC analysis showed that the method used for the measurement of N_2O and CH_4 was reliable.

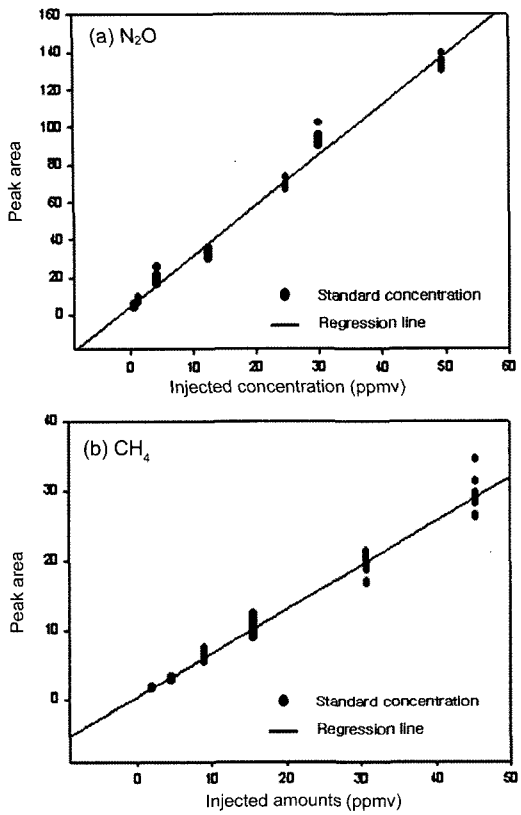

Fig. 3. Regression curve of N_2O and CH_4 gases.

Analysis of Measured Concentration of N_2O and CH_4 in the Incinerator

Presently, few studies are performing in the estimation of N_2O and CH_4 gases in the plants by using measurement data. Especially, 2006 IPCC report showed that the emission factor in the incineration plant was characterized by waste and incinerator type,[17] therefore the comprehensive measurement studies using different waste and incinerator types are needed. In this study, the measurement of N_2O and CH_4 were performed in the incinerator stack using gas probe and impinger, and the results are shown in Table 3 and Table 4.

As shown in Table 3, the concentrations of N_2O gas in the waste incinerators were between 0.6 and 40.6 ppm_v, and the average concentration was 11.5 ppm_v. The minimum concentration in one plant (EC) was 0.6~3.4 ppm_v, the maximum concentration in other plant (HK) was 36.7~40.6 ppm_v, indicating the difference in the concentration is dependent on the incinerator. This indicates that the emission of N_2O is dependent on the incineration types (grate, fluidized bed, rotary kiln) not by the emission capability, the waste amount, and the characteristics of wastes.

The first study of measuring GHGs from the plants in Korea was performed by Korean EPA

Table 3. The concentrations and conditions of N_2O gas from stacks in waste incinerators

Stack no. of plants	Incinerator type	N_2O (ppm_v)					T (°C)	Flow rate	N_2O emission	
		Mean	S.D	Min	Max	N	Stack	(Nm^3/hr)	(ton/yr)	(ton CO_2/yr)
SU-1	Kiln & Stoker	9.10	1.41	6.90	10.2	5	168	41,500	3.48	1,080
SU-2	Kiln & Stoker	28.1	0.88	26.8	29.2	5	165	38,000	9.93	3,079
EC-1	Stoker	0.86	0.11	0.70	1.00	5	170	49,200	0.39	120
EC-2	Stoker	0.62	0.08	0.50	0.70	5	168	46,300	0.26	82
EC-3	Stoker	3.44	0.25	3.18	3.74	5	168	55,000	1.75	541
BK-1	Kiln & Stoker	2.31	0.37	1.98	2.94	5	165	42,000	0.90	279
BK-2	Grate	3.62	0.45	2.98	4.12	5	200	43,200	1.35	417
DI-1	Stoker	1.66	0.11	1.50	1.80	5	160	39,600	0.62	191
DI-2	Stoker	4.35	0.61	3.60	5.30	5	170	35,000	1.40	433
DI-3	Rotary Kiln	2.89	0.21	2.80	3.12	5	165	38,000	1.02	316
HK-1	Stoker	36.7	2.82	43.6	38.4	5	168	53,000	17.9	5,560
HK-2	Kiln & Stoker	40.6	2.04	9.85	12.4	5	168	28,000	10.5	3,247
SL-1	Kiln & Stoker	10.8	0.96	11.9	13.2	5	168	45,000	4.50	1,395
SL-2	Stoker	12.5	0.53	13.2	12.9	5	169	50,000	5.76	1,786
YK	fluidized	15.7	0.48	14.9	16.1	5	207	19,000	2.53	783
Average		11.5	0.75	9.6	10.3		171.9	41,520	4.15	1287

Table 4. The concentration and conditions of CH_4 gas from stacks in waste incinerators

Stack no. of plants	Incinerator type	CH_4 (ppm_v)				T (°C)		Flow rate (Nm^3/hr)	CH_4 emission	
		Mean	S.D	Min	Max	N	Stack		(ton/yr)	(ton CO_2/yr)
SU-1	Kiln & Stoker	4.68	0.3	4.2	5.1	5	168	41,500	1.81	38
SU-2	Kiln & Stoker	5.60	0.3	5.3	5.8	5	165	38,000	2.00	42
EC-1	Stoker	5.44	0.3	5.1	5.8	5	170	49,200	2.40	52
EC-2	Stoker	3.82	0.2	3.6	4.1	5	168	46,300	1.62	34
EC-3	Stoker	4.74	0.3	4.3	5.1	5	168	55,000	2.43	51
BK-1	Kiln & Stoker	3.58	0.2	3.3	3.9	5	165	42,000	1.38	29
BK-2	Grate	-	-	-	-	5	200	43,200	-	-
DY-1	Stoker	3.50	0.2	3.2	3.8	5	160	39,600	1.29	27
DY-2	Stoker	3.62	0.2	3.4	3.8	5	170	35,000	1.14	24
DY-3	Rotary Kiln	3.48	0.2	3.4	3.6	5	165	38,000	1.24	26
HK-1	Stoker	3.68	0.1	3.6	3.9	5	168	53,000	1.81	38
HK-2	Stoker	4.82	0.2	4.6	5.3	5	168	28,000	1.24	26
SL-1	Kiln & Stoker	2.65	0.3	2.4	3.1	5	168	45,000	1.10	23
SL-2	Stoker	5.68	0.2	5.4	5.9	5	169	50,000	2.62	55
YK	Fluidized	3.75	0.1	3.6	3.9	5	207	19,000	0.62	13
Average		4.22	0.2	3.9	4.5	5	171.9	41520	1.62	34.14

(KEPA) in 2002.[20] This report showed that the average concentration of N_2O and CH_4 in the incinerator was between 2.44 and 2.32 ppm_v, 0.77~136.87 ppm_v, respectively. This report also showed that the concentration of N_2O was largest in fluidized bed type incinerator, and kiln/stoker type was the second.

Next, the concentration of CH_4 measured from the stack of incinerator is shown in Table 4. As shown in Table 4, the minimum and maximum concentrations of CH_4 were 2.65 ppm_v and 5.68 ppm_v, respectively. The average concentration was 4.22 ppm_v. The measurement result showed that the deviation of CH_4 concentration from the incinerator was small compared to the concentration of N_2O gas. During the sampling, the temperature of flue gas was 165-207°C (ave. 171.9°C), and the flow rate of stack was found to be 19,000-55,000 Nm^3/hr (ave. 41,520 Nm^3/hr). In the CH_4 case, the deviation of CH_4 concentration was small, and the dependency on the waste type and incinerator type was small.

The emission amounts of N_2O and CH_4 from the stacks in the waste incinerators were calculated using measured concentration and the flow rate of flue gas. The results are also shown in Table 3 and 4. The emission amount of N_2O from the stack of incinerator was in the range of 0.26 to 9.93 ton/day (ave. 4.15 ton/day) and the emission of CH_4 was from 0.62 to 2.62 ton/day (ave. 1.62 ton/day).

Next, the emission amounts of N_2O and CH_4 expressed as CO_2 equivalent were calculated using global warming potential (GWP) values, and the results are also shown in Table 3 and Table 4. The values are 279~5,560 ton CO_2/yr (ave. 1287 ton CO_2/yr) in N_2O, 13-55 ton CO_2/yr (ave. 34.14 ton CO_2/yr) in CH_4.

Analysis of N_2O and CH_4 Concentration and Emission Amount in the Cement Production Plant

The cement production plants in Korea have been used the coals as the main fuel and the waste as the minor fuel in order to save the money. The typical characteristics of cement plant is the large production of greenhouse gases such as CO_2 gas compared to other plants. However, due to the usage of the waste as a minor fuel, N_2O and CH_4 can be produced from the stack of cement production plants.

Table 5 and 6 show the results of N_2O and CH_4 measurement from the cement production plants. The results show that N_2O concentration is in the range of between 6.9 and 10.8 ppm_v (ave. 8.6 ppm_v),

Table 5. The concentrations and conditions of N_2O gas from stacks in cement production plants

Stack no. of plants	N_2O (ppm_v)					T (°C)	Flow rate (Nm^3/hr)	N_2O emission	
	Mean	S.D	Min	Max	N	Stack		(ton/yr)	(ton CO_2/yr)
AS-3	6.9	0.2	6.8	7.1	3	147	510,000	34.1	10,567
AS-4	10.4	0.1	10.3	10.5	3	148	492,000	49.4	15,328
HD-1	7.6	0.6	7.3	8.4	5	100	637,545	52.8	16,383
HD-2	7.6	0.1	7.5	7.7	3	170	746,064	52.1	16,142
DY-10	8.2	0.3	7.8	8.4	4	128	934,296	77.7	24,095
DY-11	10.8	0.2	10.7	10.9	3	132	846,846	91.8	28,481
SS-6	8.8	0.1	8.5	8.9	3	146	210,469	17.9	5,575
Average	8.61	0.23	8.41	8.84	3.43	138.71	625317.14	53.7	16,653

Table 6. The concentrations and conditions of CH_4 gas from stacks in cement production plants

Stack # of plants	CH_4 (ppm_v)					T (°C)	Flow rate (Nm^3/hr)	CH_4 emission	
	Mean	S.D	Min	Max	N	Stack		(ton/yr)	(ton CO_2/yr)
AS-1	2.2	0.1	2.1	2.3	4	147	510,000	10.86	228
AS-3	1.8	0.2	1.6	1.9	4	148	492,000	8.57	180
HD-1	-	-	-	-	5	100	637,545	-	-
HD-2	-	-	-	-	5	170	746,064	-	-
DY-1	2.9	0.4	2.8	3.3	5	128	934,296	27.48	577
DY-2	3.3	0.1	3.2	3.4	3	132	846,846	28.10	590
SS-6	2.8	0.2	2.6	2.9	4	146	210,469	5.71	120
Average	2.6	0.2	2.46	2.76	4.29	138.71	625317.14	16.14	339

and CH_4 concentration is in the range from 1.8 to 2.2 ppm_v (ave. 2.6 ppm_v).

The reason of the small deviation in the concentration range in the cement production plant is that the fuel used in the cement plant was more consistent than the incinerator. The main fuel in the cement plant is fossil fuel, and the waste is used as the minor fuel. However, the composition of waste in the incinerator was not consistent; therefore the deviation could be large due to the incinerator type and the waste type.

The emission amount in the cement production plant was calculated using the measurement concentration, and the results are also shown in Table 5 and 6. N_2O emission amount is 17.9-91.8 ton/day (ave. 53.7 ton/day), and CH_4 emission amount is 5.7-28.1 ton/day (ave. 16.1 ton/day). Similarly, the emission amount of N_2O and CH_4 converted to CO_2 equivalent amount were calculated, and the results ere 16,653 ton CO_2/yr for N_2O gas and 120~590 ton CO_2/yr (average 339 ton CO_2/yr) for CH_4.

The Emission Characteristics of N_2O and CH_4 in Each Plant

As shown in Table 3 and Table 4, the concentrations of N_2O and CH_4 from the incinerator were 11.5 ppm_v and 4.2 ppm_v, respectively. The emission concentration of N_2O and CH_4 from the cement production plants in Table 5 and Table 6 were 8.6 ppm_v and 2.6 ppm_v, respectively. The interesting result is that the concentrations of N_2O and CH_4 measured in the cement production plant were lower than in the waste incinerators. However, the annual emission amounts of N_2O and CH_4 calculated based on the concentration and the flow rate in the cement plant were much higher than in the incinerators.

The annual emission amount of N_2O in the cement plant was average of 53.7 ton N_2O/yr, the amount of N_2O in the incinerator was 4.2 ton N_2O/yr, and therefore, the approximately twelve times higher in the cement plant. This is mainly due to the higher flow rate in the cement plant than the cement production facilities. Therefore, the higher production of flue gases such as cement production plant has

the higher potentiality of GHGs emission.

The emission amounts of CH_4 in both facilities were also calculated. Comparing Table 4 and 6, the emission amount of CH_4 in the cement facilities was 339.0 ton CH_4/yr and the amount of CH_4 in the incinerator was 34.1 ton CH_4/yr. The same reason can be applied for the higher emission amount of CH_4 in the cement production plants.

Estimation of N_2O and CH_4 Gas Emission Factor

The estimation method of emission factor of GHG in US EPA Report[21] and 2006 IPCC Guidelines.[17] Therefore, using the flow rate and the area of stack, the emission amounts of greenhouse gases were calculated according to 2006 IPCC guidelines as shown in Eq. (1);

$$E = M \times V \times 10^{-9} \qquad EF = E/A \qquad (1)$$

Where E is the GHGs emission amount (ton/day), M is the concentration of N_2O and CH_4 (mg/m^3), V is the flow rate (N m^3/day), EF is the emission factor (ton CO_2/ton waste), and A is the activity (ton waste/day).

By using Eq. (1), the emission factor of N_2O and CH_4 was calculated and is shown in Table 7. As shown in Table 7, the emission factor of N_2O was as follows: kiln & stoker type 42.5~799.1 g/ton, stoker type 11.9~79.9 g/ton, rotary kiln 90.1 ton/g, fluidized bed type 174.9 g/ton, grate type 63.8 g/ton. This result indicates that the emission factor is strongly dependent on the incineration type.

The average value of N_2O emission factor is found to be 200.1 g/ton. This value is higher than the value (149 g/ton) measured first in Korean EPA (KEPA) report in 2002.[20] In 2002 KEPA report, the emission factor of nitrous oxide was 454 g of CO_2/ton waste in waste plant, 65 g of CO_2/ton waste in vinyl type waste, 43 g of CO_2/ton waste in dry type wastes, 36 g of CO_2/ton waste in rotary kiln type waste.

Next, the estimation of CH_4 emission factor was also performed, and the result is also shown in Table 7. As shown in Table 7, emission factor in rotary kiln and stoker type was 65.2-91.3 g/ton, 73.9-122.0 g/ton in stoker type, 109.5 g/ton in rotary kiln type, and 26.1 g/ton in fluidized bed type. This is first reported values of methane emission factors based on the measurement data. The result indicates that the concentration of CH_4

Table 7. N_2O and CH_4 emission factors from incineration of waste in this study

Country	Type of incinerator	g N_2O/ton waste	g CH_4/ton waste
Korea	Kiln & Stoker	42.5-799.1	65.2-91.3
	Stoker	11.9-79.9	73.9-122
	Rotary kiln	90.1	109.5
	Fluidized bed	174.9	26.1
	Grate	63.8	

Table 8. N_2O emission factors for incineration of waste depending on the incineration types by 2006 IPCC guidelines[21]

Country	Type of Incineration/Technology		Municipal solid waste	Industrial waste
Japan	Continuous incineration	Stoker	47 g N_2O/ton wet weight incinerated	
		Fluidized bed	67 g N_2O/ton wet weight incinerated	
	Semi-continuous incineration	Stoker	41 g N_2O/ton wet weight incinerated	
		Fluidized bed	68 g N_2O/ton wet weight incinerated	
	Batch type incineration	Stoker	56 g N_2O/ton wet weight incinerated	
		Fluidized bed	221 g N_2O/ton wet weight incinerated	
			900 g N_2O/ton dehydrated sewage sludge	450 g N_2O/ton dehydrated sludge (except sewage sludge)
Netherlands			20 g N_2O/ton	
Austria			12 g N_2O/ton wet weight	
Germany			8 g N_2O/ton wet weight	420 g N_2O/ton solid waste wet weight
			990 g N_2O/ton sewage sludge dry weight	

is similar to the incineration type, however, the emission factor is different with the incinerator type.

Finally, we compared our data with the values of emission factors which have been published recently on 2006 IPCC guideline. The values in 2006 IPCC guideline are shown in Table 8. As shown Table 8, in Japan, the emission factor in the continuous incineration type, 47 g/ton in stoker type, and 67 g/ton in fluidized bed type. In the semi-continuous type, the emission factor in stoker type was 41 g/ton, 68 g/ton in fluidized bed. In the batch type, 56 g/ton in stoker type, 221 g/ton in fluidized bed type. This result indicated that the emission factor is dependent on the incinerator type. However, other countries have very low emission factors of N_2O such as 20 g/ton waste in the Netherlands, 12 g/ton waste in Austria, and 8 g/ton waste in Germany. Therefore, the emission factor in this study (200 g/ton waste) seems larger than the values of other countries. The similar patterns of higher emission factor of N_2O in the fluidized bed incinerator were obtained. This is maybe due to the lower incineration temperature in the fluidized bed incinerator.

Conclusions

This study investigated the concentration of non CO_2 gases (N_2O and CH_4) in the incinerator and cement production plant stacks in order to estimate the emission factor of N_2O and CH_4. The monitoring protocol of N_2O and CH_4 was constructed, and using this method the measurement of N_2O and CH_4 was performed. The results are as follows:

1) The analysis of N_2O and CH_4 gases in the waste incineration and cement production plants were performed by capturing flue gases from the stack using Tedlar bag, and using gas chromatography. In order to assess QA/QC of this method, the standard gases of N_2O and CH_4 was diluted and made the standard calibration curves. The retention time reproducibility was checked by relative standard deviation. The RSD of N_2O and CH_4 was 0.39% and 0.18%, respectively, the R^2 values was more than 99.99%, and the linearity was reliable, Detection limits of this methods were 0.23-0.33 ppm_v, for N_2O and 1.15-1.58 ppm_v for CH_4, respectively.

2) The concentrations of N_2O gas in the waste incinerators were between 0.62~40.6 ppm_v, the minimum concentration was 0.62~3.44 ppm_v, the maximum concentration in other plant was 36.7~40.6 ppm_v, indicating the difference in the incinerator. The average concentration of N_2O was 11.5 ppm. The emission amount of N_2O was not dependent on the emission capability, the waste amount, the characteristics of wastes, but dependent on the incineration types (grate, fluidized bed, or rotary kiln type). The CH_4 concentration from stacks was ave. 4.22 ppm_v (2.65~5.68 ppm_v), and the deviation depending on the incineration type was small.

3) The emission factor of N_2O were shown to be 42.5~799.1 g-CO_2/ton waste (kiln and stoker type), 11.9~79.9 g-CO_2 eq/ton of waste (stoker type), 90.1 g-CO_2 eq/ton of waste (rotary kiln type), 174.9 g CO_2/ton of waste (fluidized bed), 63.8 g-CO_2/ton of waste (grate type). In a year bases, the emission amount of N_2O and CH_4 from the incinerator was found to be 279-5,560 ton CO_2/yr and CH_4 was 13-55 ton CO_2/yr, respectively.

4) The emission amount of N_2O (53.7 ton/yr) in the cement plant was more than ten times higher than in incinerator (4.1 ton/yr). This is due to the higher flow rate of flue gas in the cement plant compared to incinerator. The emission amount of CH_4 gas in cement plant (339.0 ton CO_2/yr) is also much higher than in incinerator (34.1 ton CO_2/yr) due to the same reason.

5) The emission factor of N_2O from the plants calculated by the measurement data showed that it was dependent on the incineration type: 42.5~799.1 g/ton in kiln and stoker, 11.9~79.9 g/ton in stoker, 90.1 ton/g in rotary kiln, 174.9 g/ton in fluidized bed, 63.8 g/ton in stoker type. The average amount of emission factor of N_2O gases was 200.1 g/ton and this value was higher than the 149 g/ton measured in 2002 by KEPA report.[20]

6) The emission factor of CH_4 from measurement data was 65.2-91.3 g/tom in rotary kiln and stoker type, 73.9-122.0 g/ton in stoker type, 109.5 g/ton in rotary kiln type, and 26.1 g/ton in fluidized bed type, and also shown to be dependent on the incineration type.

In the past, the emission factor estimation are mostly conducted in CO_2, and also the estimation was performed by using waste amount incinerated and default value based on the waste incinerated.

However, in this study, the estimation of N_2O and CH_4 production was performed based the measurement from stacks. Even though there is some uncertainty from the measurement and the limited measurement, this process can contribute the plant based estimation of emission factor of GHGs in Korea. The continuous measurement should be performed in order to decrease the uncertainty of the measurement data.

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