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Fossil Carbon Fraction and Measuring Cycle for Sewage Sludge Waste Incineration

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Abstract: In this study, the fossil carbon contents of the two facilities were analyzed using 10 or more samples for each facility from June 2013 to March 2015. In addition, the optimal measurement period was calculated from the analyzed fossil carbon contents using a statistical method. As a result of the analysis, the fossil carbon contents were found to be less than 35%, indicating that the biomass content of sewage sludge was not 100%. The fossil carbon content could be representative of using yearly period measurements value. When calculating Green house gas (GHG) emissions from waste incineration, South Korea has been calculating only Non-CO_2 emissions because it regarded the CO_2 emitted in GHGs from sewage sludge (SS) incineration facilities as originating from biomass. However, biomass of the sewage sludge incineration facility is not 100%, so it is necessary to estimate the greenhouse gas emissions considering the fossil carbon content. Therefore, there is a need to increase the reliability of the greenhouse gas inventory by conducting further studies (such as CO_2 concentration analysis) related to the calculation of CO_2 emissions for the relevant facilities (sewage sludge incinerator).

Keywords: fossil carbon fraction; sewage sludge waste incinerator; waste inventory; climate change

1. Introduction

South Korea generated 3,531,250 tons of sewage sludge (SS) in 2014, which is approximately double the amount of 1,902,410 tons generated in 2001, and the number of SS treatment plants increased more than three times between 2000 and 2014 (from 172 to 597) [1]. South Korea disposed of more than 30% of its SS in the ocean until 2011, but since ocean disposal was prohibited by the "Convention on the Prevention of Marine Pollution by the Disposal of Wastes and Other Substances" in 2012, the country has relied on other methods to treat SS, such as recycling, incineration, landfill, and fuel conversion. Incineration is the second most-commonly used method after recycling, which accounts for 55% of the total amount of SS treated, and as both incineration and landfill produce major green house gas (GHG) emissions from treating waste, they require appropriate management.

The IPCC (Intergovernmental Panel on Climate Change) guidelines stipulate that CO_2 emissions from biomass should be excluded from the total amount of CO_2 emissions reported and that they should be reported separately in accordance with carbon neutrality [2]. SS is a representative biomass fuel that can be mixed with fossil fuels or used on its own [3–6].

When calculating GHG emissions from SS incineration facilities, many countries (including South Korea and Japan, German, Austria) have excluded CO_2 emissions from their national GHG emissions and reported them separately [7–10]. However, Giger (1984) and McEvoy (1985) reported that the biomass content of SS may not be 100%, and components including surfactants such as Linear Alkylbenzene Sulphonate (LAS) and 4-Nonylphenol cannot be completely disposed of during sewage treatment [11,12]. Kang et al. (2017) also declared the need to calculate CO_2 emissions from SS incineration facilities because the biomass content of SS measurements was shown to be less than 100% [13].

To improve the reliability of GHG emission measurements from SS incineration facilities, it is therefore necessary to consider the fossil carbon content of SS and reflect this in GHG emission calculations. However, as the fossil carbon content requires a complicated sampling and analytical process, in addition to considerable costs, it would be beneficial to conduct research to determine the optimal measurement period that can be used to secure statistical reliability. This study therefore aims to calculate the fossil carbon content of SS incineration facilities and determine the optimal measurement period that should be used when calculating the fossil carbon content.

2. Methods

In this study, the fossil carbon content was analyzed at two SS incineration facilities within South Korea. The optimal measurement period is defined as the period in which the minimal number of samples are required to provide a useful result, and this period was determined using a statistical method by classifying measurement data into monthly, semi-quarterly, quarterly, and yearly units.

2.1. Selection of Objective Facilities

The target facilities were two SS incineration facilities that incinerate more than 100 tons a day (on average). They were selected from the Gyeonggi region, which treated the largest amount of SS in 2015. The selected target facilities incinerate waste using fluidized beds and a selective non-catalytic reduction method, and also contain a nitrogen oxide prevention facility, a filter dust collector facility, a semi-dry reactor, and a wet scrubber. To calculate the fossil carbon content, more than 10 samples were analyzed for each facility from 2013 to 2015, and Table 1 shows the status of these target facilities.

Table 1. Characteristics of the investigated SS incineration.

Classification	Facility	A Sewage Sludge Incinerator	B Sewage Sludge Incinerator
Incineration facility	Incinerator capacity	150 ton/day	100 ton/day
Air pollution prevention facility	SNCR	673 Nm^3/min	700 Nm^3/min
	Bag filter dust collector	427 Nm^3/min	300 Nm^3/min
	SDR	427 Nm^3/min	350 Nm^3/min
	Wet scrubber	427 Nm^3/min	300 Nm^3/min

2.2. Sampling of Flue Gas from Industrial Waste Incinerator

Some studies have found that although the method of collecting incineration gas from incineration facilities may be simple in terms of the procedure used, calculating the fossil carbon content from solid wastes is less straight forward [14]. The Mandatory GHG Reporting Act of the United States (US) suggests that the biomass content should be measured continuously over 24-h, or an adequate number of samples should be obtained to meet ASTM D 6866-08 [15]. Therefore, in this study, emission gases were collected continuously over a 24-h period in accordance with the above guidelines to obtain an adequate number of samples to calculate the fossil carbon content.

In South Korea, air pollutants are monitored in real time using a Continuous Emission Monitoring System (CEMS). The sampling point was set at the end of CEMS, and emission gases were collected using an emission gas collection device developed in this study. Figure 1 shows a schematic diagram of the experimental procedure. The emission gas collection device includes a moisture removal device, a pump, and an electronic mass flow meter, and it operates in a stable manner to collect samples over a 24-h period.

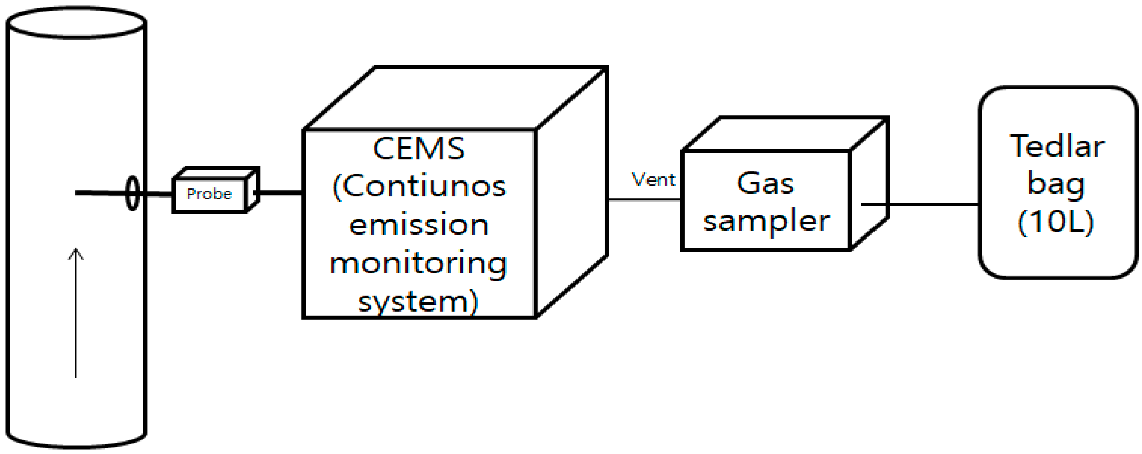

Figure 1. Schematic of the field setup for flue gas sampling.

2.3. Analysis of Fossil Carbon Fraction

Various standard test methods are used in fossil carbon content analysis, such as CEN/TR 15591, DS/CEN/TS 15440, and ASTM D6866 [16–18]. These methods suggest the use of the selective dissolution method, balance method, and ^{14}C method to measure the fossil carbon content. Current studies are researching the fossil carbon content using standard test methods, and the European Union (EU) recommends using the selective dissolution method or the ^{14}C method with their Emission Trading Scheme [19]. Therefore, the ^{14}C method was used in this study.

The ^{14}C method uses carbon isotopes to measure the age of a sample and the ratio of CO_2 generated by fossil fuels in the atmosphere through the ^{14}C content. Methods of ^{14}C analysis include Isotope Ratio Mass Spectrometer (IRMS), Liquid Scintillation Counter (LSC), and Accelerator Mass Spectrometry (AMS) methods [20–22]. Of these, the AMS method was selected for use in this study, because it requires approximately 1 g of substance to conduct an analysis and is 105 times more precise than general mass spectrometers [23]. It precisely measures the amount of carbon isotopes ^{12}C and ^{13}C (which are both stable isotopes) and ^{14}C (unstable and radioactive) that are present in nature by performing ionization acceleration of sample atoms, analyzing the energy, momentum, and electric charge states, and quantitatively analyzing ^{14}C, which is the isotope of the final atomic nucleus. Using these measurements, the method provides the age and ratio of CO_2 generated by fossil fuels.

2.4. Statistical Analysis Method for Optimal Sampling Cycle Estimate

To calculate the optimal measurement period for determining the fossil carbon content in SS incineration facilities, the monthly, semi-quarterly, and quarterly average distributions were compared with the yearly average distribution. SPSS (Statistical Package for the Social Sciences) software ver. 21 (IBM, Armonk, NY, USA) was used for statistical analysis, and the normality test was employed to identify the distribution of measured data.

The average distribution comparative analysis method can be performed in different ways depending on the results of the normality test. When the fossil carbon content analysis data have a normal distribution, the one-way ANOVA analysis is conducted, and of nonparametric methods, the Kruskal-Wallis test is used, which is capable of comparing the group distributions of more than three groups. Therefore, in this study, the method selected to compare monthly, semi-quarterly, and quarterly data was determined according to the results of the normality test. Figure 2 shows the procedure used in the statistical approach for analyzing the optimal measurement period used to determine the fossil carbon content.

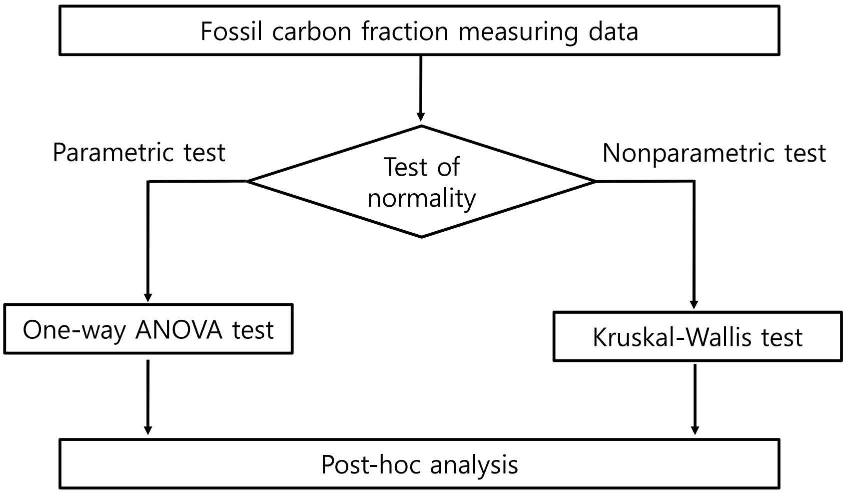

Figure 2. Schematic of statistics analysis.

3. Result and Discussion

3.1. Fossil Carbon Fraction at Sewage Sludge Incinerator

The fossil carbon contents of SS incineration facilities in South Korea were found to be in the range of 19.00–25.55% for A facility and in the range of 14.00–34.24% for B facility (Show Table 2). For A and B facilities, the monthly average was 21.44% and 19.52%, respectively; the quarterly average was 21.23% and 20.24%, respectively; the semi-quarterly average was 21.47% and 19.94%, respectively; and the yearly average was 21.52% and 20.48%, respectively, resulting in differences of less than 3% for facility A and less than 5% for facility B. Analysis showed that the fossil carbon contents of the target facilities were less than approximately 35%, and the biomass content of SS was not 100%. This can be supported the case where the biomass content of Kang et al. (2017) study is 77% rather than 100%.

Kang et al. (2017), explained. The reason why sewage sludge incineration biomass is not 100% is because sewage sludge as a raw material when incinerating sewage sludge contains substances of fossil carbon content origin such as surfactant [13].

The Paris Convention was adopted at the 21st UN Climate Change Summit Conference of Parties 21 (COP 21), and this stipulates that GHG inventory data must be reported every five years. Therefore, the importance of providing a reliable inventory is gradually increasing. When calculating GHG emissions from waste incineration, South Korea has been calculating only Non-CO_2 emissions because it regarded the CO_2 emitted in GHGs from SS incineration facilities as originating from biomass. However, the results of this study show that fossil carbon contents are also present in SS incineration facilities. Therefore, it is necessary to calculate the fossil carbon contents as well as the CO_2 emissions at SS incineration facilities. As the CO_2 emissions of sewage sludge incineration facilities are not currently calculated in South Korea. However, in order to reduce CO_2 emissions due to climate change problems, it is necessary to estimate the accurate inventory. Therefore it is necessary to estimate CO_2 emissions from sewage sludge incineration facilities which are not currently being measured. Research on the calculation of CO_2 emissions in sewage sludge incineration facilities is lacking. Therefore, related researches are needed both inside and outside the country.

Table 2. The results of Fossil Carbon Fraction at Sewage sludge incinerators (from June 2013 to March 2015).

Period	Statics Value	A Sewage Sludge Incinerator	B Sewage Sludge Incinerator
Month	Mean	21.44	19.52
	SD *	0.34	1.43
	RSD ** (%)	1.58	7.32
	Max	21.20	21.13
	Min	21.68	18.39
Quarter	Mean	21.23	20.24
	SD	1.12	1.47
	RSD (%)	5.28	7.28
	Max	22.76	21.99
	Min	19.79	18.39
Half-year	Mean	21.47	19.94
	SD	1.11	2.54
	RSD (%)	5.15	12.74
	Max	23.28	23.25
	Min	19.88	14.31
Year	Mean	21.52	20.48
	SD	1.70	4.66
	RSD (%)	7.91	22.74
	Max	25.55	34.24
	Min	19.00	14.00

* SD: Standard Deviation. ** RSD: Relative Standard Deviation. Unit: %.

3.2. Normality Test of Fossil Carbon Fraction at Sewage Sludge Incinerator

To statistically analyze the measured fossil carbon content, the normality of the data must firstly be tested. For the normality test, the chi-square test, Q-Q plot, Shapiro-Wilks test, and Kolmogorov-Smirnov test are mainly used. When using the Shapiro-Wilks test and K-S test, the method is determined through the number of populations: when the number is less than 2000, the Shapiro-Wilks test is used, and the K-S test is used for higher numbers. For all of these tests, normality is tested through the significance probability. In general, the normality test assumes a normal distribution as a null hypothesis. If the significance probability is higher than 0.05, it determines a normal distribution, and if not, it rejects the null hypothesis and determines non-normality. In his study, the normality of the monthly, quarterly, semi-quarterly, and yearly fossil carbon content data was tested using statistical software (SPSS ver. 21) for each incineration facility. As the sample size of the fossil carbon content was less than 2000 for such data, normality was tested using the Shapiro-Wilks method (Show Table 3). However, facility A failed to produce normality results for monthly data, because the number of monthly data was too small, but it showed normal distributions for the other data because the significance probability was higher than 0.05. For B facility, yearly data showed a non-normal distribution with a significance probability of less than 0.05, but the monthly, quarterly, and semi-monthly data exhibited normal distributions with a significance probability higher than 0.05. When average distributions are compared, a nonparametric method must be used if at least one of the target data does not have a normal distribution. Since both A and B facilities contained one group without a normal distribution, they were compared using the Kruskal-Wallis test, which is a nonparametric method.

Table 3. The result of normality test at Fossil carbon fraction data.

Normality Test Result		Shapiro-Wilk		
		Statistic	Degree of Freedom, Df	Sig.
A sewage sludge incinerator	Month	-	-	-
	Quarter	0.94	6.00	0.618
	Half-yealy	0.97	8.00	0.900
	Year	0.94	15.00	0.402
B sewage sludge incinerator	Month	0.92	3.00	0.436
	Quarter	0.88	7.00	0.248
	Half-yealy	0.81	8.00	0.036
	Year	0.79	14.00	0.004

3.3. Kruskal-Wallis Test of Fossil Carbon Fraction at Swage Sludge Incinerator

As the measured fossil carbon content data of the sewage sludge incineration facilities were not normal distributions, the Kruskal-Wallis test was used among nonparametric methods. Using this method, the average distributions of the monthly, quarterly, semi-quarterly, and yearly fossil carbon content data of the SS incineration facilities were compared, and results are shown in Table 4. The Kruskal-Wallis test showed that the significance probability was higher than 0.05 and that the averages of the monthly, quarterly, semi-quarterly, and yearly data were the same for the fossil carbon contents of the two facilities. It was thus determined that the fossil carbon contents of the facilities could be calculated using measurements from the yearly period, which thus requires use of the smallest number of samples. In this study, only the measurement period of fossil carbon content required to estimate CO_2 emissions was examined. It is necessary to carry out a study on CO_2 concentration measurement and cycle, which is an additional factor necessary for calculating CO_2 emissions.

Table 4. The result of normality test by Fossil carbon fraction data.

Hypothesis Test	Null Hypothesis	Test	Sig.	Decision
A Sewage sludge incinerator	The distribution of biomass fraction is the same across categories of term	Independent-Samples Kruskal-Wallis Test	0.996	Retain the null hypoyhesis
B Sewage sludge incinerator	The distribution of biomass fraction is the same across categories of term	Independent-Samples Kruskal-Wallis Test	0.841	Retain the null hypoyhesis

4. Conclusions

In this study, the optimal measurement period was calculated from the analyzed fossil carbon contents using a statistical method.

Two sewage sludge incineration facilities were selected as target facilities. For the calculation of the fossil carbon content, the emission gas was collected for 24 h using a self-developed collection device. The collected samples were analyzed using the AMS method.

As a result of the analysis, the fossil carbon contents were found to be less than 35%, indicating that the biomass content of sewage sludge was not 100%.

To statistically analyze the optimal measurement period based on the analyzed sewage sludge fossil carbon content data, normality was tested first. The normality test used the Shapiro-Wilks method because all of the monthly, quarterly, semi-quarterly, and yearly data of the fossil carbon content had sample sizes less than 2000. As a result of the normality test, at least one of the monthly, quarterly, semi-quarterly, and yearly biomass content data did not form a normal distribution for both A and B facilities. Therefore, average distributions were compared using the Kruskal-Wallis test, which is the nonparametric statistical method.

The results of the Kruskal-Wallis test showed that the average distributions of the monthly, quarterly, semi-quarterly, and yearly data were the same for the two facilities, indicating that the biomass contents of the facilities can be measured from the yearly period, which is the largest range.

Currently, Korea and other countries do not estimate CO_2 emissions by considering the biomass content of sewage sludge incineration facilities as 100%. However, in order to reduce GHG emissions, it is necessary to accurately estimate the GHG inventories. Therefore, various studies related to the biomass content in sewage sludge incineration facilities are needed. According to this study, it is considered that some carbon fossil content exists, so it is necessary to estimate CO_2 emissions. If the same fossil carbon content exists in sewage sludge incineration facilities in other countries, the reliability of this study is expected to be even higher.

The fossil carbon content measurements of the sewage sludge incineration facilities, and those relating to the calculated measurement period in this study, are expected to be used as basic data for calculating coefficients reflecting national characteristics. However, since the optimal measurement period was calculated using less than 20 samples per incineration facility in this study, further studies are required. The acquisition of larger amounts of data in related studies would extend GHG inventory reliability related to SS incineration.

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References

1. Ministry of Environment. *2014 Waste Generation and Treatment Status in Korea*; Ministry of Environment: Incheon, Korea, 2015.
2. IPCC. *2006 IPCC Guidelines for National Greenhouse Gas*; Intergovernmental Panel on Climate Change: Incheon, Korea, 2006; Volume 5.
3. Fytili, D.; Zabaniotou, A. Utilization of sewage sludge in EU application of old and new methods—A review. *Renew. Sustain. Energy Rev.* **2008**, *12*, 116–140. [CrossRef]
4. Kargbo, D.M. Biodiesel Production from Municipal Sewage Sludges. *Energy Fuels* **2010**, *24*, 2791–2794. [CrossRef]
5. Kotay, S.M.; Das, D. Biohydrogen as a renewable energy resource—Prospects and potentials. *Int. J. Hydrogen Energy* **2008**, *33*, 258–263. [CrossRef]
6. Zabaniotoua, A.; Theofiloub, C. Green energy at cement kiln in Cyprus—Use of sewage sludge as a conventional fuel substitute. *Renew. Sustain. Energy Rev.* **2008**, *12*, 531–541. [CrossRef]
7. Greenhouse Gas Inventory & Research Center of Korea (GIR). *National Inventory Report in Korea*; Greenhouse Gas Inventory & Research Center of Korea: Seoul, Korea, 2015.
8. Greenhouse Gas Inventory Office of Japan (GIO). *National Greenhouse Gas Inventory Report of Japan*; Greenhouse Gas Inventory Office of Japan: Ibaraki, Japan, 2015.
9. Federal Environment Agency (UBA). *National Inventory Report for the German greenhouse Gas Inventory 1990–2013*; Federal Environment Agency: Dessau, Germany, 2015.
10. Environment Agency Austria Umweltbundesamt. *Austria's National Inventory Report 2015*; Environment Agency Austria Umweltbundesamt: Vienna, Austria, 2015.
11. Giger, W.; Brunner, P.H.; Schaffner, C. 4-Nonylphenol in sewage sludge: Accumulation of toxic metabolites from non-ionic surfactants. *Science* **1984**, *225*, 623–625. [CrossRef] [PubMed]
12. McEvoy, J.; Giger, W. Accumulation of linear alkylbenzenesulphonate surfactants in sewage sludges. *Naturwissenschaften* **1985**, *72*, 429–431. [CrossRef]
13. Kang, S.; Kim, S.; Lee, J.; Jeon, Y.; Kim, K.-H.; Jeon, E.-c. A Study on Applying Biomass Fraction for Greenhouse Gasses Emission Estimation of a Sewage Sludge Incinerator in Korea: A Case Study. *Sustainability* **2017**, *9*, 557. [CrossRef]

14. Kim, S.; Kang, S.; Lee, J.; Lee, S.; Kim, K.H.; Jeon, E.C. The comparison of fossil carbon fraction and greenhouse gas emissions through an analysis of exhaust gases from urban solid waste incineration facilities. *J. Air Waste Manag. Assoc.* **2016**, *66*, 978–987. [CrossRef] [PubMed]
15. Environmental Protection Agency (EPA). *40 CFR Part 98 Mandatory Reporting Rule of Greenhouse Gases*; Federal Register; Environmental Protection Agency (EPA): Washington, DC, USA, 2011.
16. CEN/TR 15591. *Solid Recovered Fuels—Determination of the Biomass Content Based on the ^{14}C Method*; Danish Standards: Brussels, Belgium, 2007.
17. DS/CEN/TS 15440. *Solid Recovered Fuels—Solid Recovered Fuels—Methods for the Determination of Biomass Content*; Danish Standards: Brussels, Belgium, 2011.
18. ASTM D 6866. *Standard Test Methods for Determining the Bio Based Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis*; ASTM International: West Conshohocken, PA, USA, 2007.
19. European Commission. *Biomass Issues in the EU ETS*; MRR Guidance Document; European Commission: Brussels, Belgium, 2012.
20. Muir, G.K.P.; Hayward, S.; Tripney, B.G.; Cook, G.T.; Naysmith, P.; Herbert, B.M.J.; Garnett, M.H.; Wilkinson, M. Determining the biomass fraction of mixed waste fuels: A comparison of existing industry and ^{14}C-based methodologies. *Waste Manag.* **2015**, *35*, 293–300. [CrossRef] [PubMed]
21. Sanne, W.L.P.; Harro, A.J.M. Biogenic Carbon Fraction of Biogas and Natural Gas Fuel Mixtures Determined with ^{14}C. *Radiocarbon* **2016**, *56*, 7–28. [CrossRef]
22. Seongmin, K.; Jaehyung, C.; Yoon-jung, H.; Daekyeom, L.; Ki-Hyun, K.; Eui-Chan, J. Estimation of optimal biomass fraction measuring cycle for municipal solid waste incineration facilities in Korea. *Waste Manag.* **2018**, *71*, 176–180. [CrossRef]
23. Ruff, M. *Radiocarbon Measurement of Micro-Scale Samples—A Carbon Dioxide Inlet System for AMS*; Philosophisch-naturwissenschaftlichen Fakulttp der Universiter Bern: Bern, Germany, 2008.