환경영향평가 제13권 제4호(2004) pp.187~196

연구논문

Methane Oxidizing Capacity of Landfill Cover Soils to Reduce Atmospheric Methane Emissions

Soyoung Park

OIKOS Co., Ltd.,

(Manuscript received 2 June 2004; accepted 5 August 2004)

메탄의 대기 배출량을 저감시키는 매립지 복토층의 메탄 산화능력에 관한 연구

박소영

(주)오이코스

(2004년 6월 2일 접수, 2004년 8월 5일 승인)

요 약

매립지에서 배출되는 메탄가스는 이산화탄소에 이어 두 번째로 많이 배출되는 지구온난화 가스이지만 열을 흡수하는 능력에 있어서는 이산화탄소 보다 25에서 35배 정도 더 크기 때문에 지구 온난화 현상에 대한 메탄가스의 영향은 중요하다고 할 수 있다. 매립지로부터 배출되는 메탄가스는 호기성 상태의 매립지 복토층을 통과 할 때 산화될 수 있으므로 매립지 복토층은 메탄가스의 배출을 저감시키는 바이오필터의 역할을 할 수 있다. 본 연구에서는 batch 실험을 통하여 매립지 복토층에서의 메탄산화속도에 대한 토양수분과 온도의 영향을 연구하였다. 최대 산화속도는 토양수분 15%(w/w), 배양온도 35°C의 환경조건에서 1.03 μmol CH_4 g^{-1}soil h^{-1}으로 나타났다. 이러한 실험결과를 이용하여 토양수분과 온도를 함수로 하는 회귀모형을 개발하였다. 또한 전국에 4 군데 지역을 선발하여 각 지역의 토양수분과 온도 데이타를 수집하고 개발된 모형을 이용하여 각 지역에 위치하고 있는 매립장에서의 월 평균 메탄산화량을 예측하였다. 예측결과 환경조건이 양호한 지역의 매립지 복토는 메탄의 배출량을 저감시킬 수 있는 효율적인 바이오필터의 효과를 가지지만 환경조건이 불리한 지역의 매립지 복토에서는 바이오필터의 효과가 크지 않는다고 할 수 있다.

주요어 : 매립지 가스, 온실가스, 지구온난화, 메탄산화, 바이오필터

Corresponding Author: Soyoung Park, OIKOS Co., Ltd. #1007 Daeryung Techno Town 8-cha, 481-11 Gasan-dong, Geum cheon-gu, Seoul, 153-775, Korea Tel: 82-2-855-5166 Fax: 82-2-855-6451 E-mail: s0p0623@hotmail.com

I. Introduction

The earth's climate is undergoing a gradual warming trend due to the accumulation of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone (O_3) in the atmosphere (IPCC, 1995). The emission of greenhouse gases resulting from anthropogenic activities is increasing the atmospheric concentration of greenhouse gases, which can influence the earth's absorption of radiation (U.S. EPA, 1999a). When these gases accumulate in the earth's atmosphere, they absorb excessive amounts of infrared energy causing the earth's surface to become warmer than normal. Since many greenhouse gases are long-lived, they can affect our climate for a long time (IPCC, 1995). This increase in the concentration of greenhouse gases can alter the climatic system by changing the temperature, precipitation, wind and other climate factors. These changes will in turn cause global changes in soil moisture and will result in a slow rise of sea level (U.S. EPA, 1999a; IPCC, 1995).

Methane (CH_4) is a very potent greenhouse gas and is approximately 20-35 times more damaging than CO_2 (Boeckx *et al.*, 1996; Parsons, 1995; U.S. EPA, 1999a; Yashushi *et al.*, 1993). Global releases of CH_4 to the atmosphere have been estimated to be in the range of 500-700 Tg/yr (Visscher *et al.*, 1999; U.S. EPA, 1999a; Bogner *et al.*, 1995). Atmospheric CH_4 is increasing faster than any of the other greenhouse gases (U.S. EPA, 1999a). While the concentrations of CO_2 and N_2O have increased by 30 and 15%, respectively, the CH_4 concentration has increased by 147%, from 700 parts per billion by volume (ppbv) in pre-industrial time to 1,730 ppbv in 1997 (U.S. EPA, 1999a; ICCP, 1995). It is postulated that this increase of CH_4 may be largely due to increasing emissions from antropogenic sources (U.S. EPA, 1999b). CH_4 emissions from anthropogenic sources account for 70% of all CH_4 emissions, while the natural CH_4 emission is about 30% (U.S. EPA, 1999a). Landfills are very important antropogenic sources in the CH_4 emissions (U.S. EPA, 1999a).

CH_4 can be degraded by methanotrophic bacteria in aerated soil and thus, soil can serve as an important biological sink of atmospheric CH_4 (King and Adamsen, 1992). The CH_4 oxidizing capacity in landfill cover soil has been reported to be in the range of 3,796 to 5,475 moles m^{-2} yr^{-1} (Kightley *et al.*, 1995; Visscher *et al.*, 1999). Therefore microbially mediated CH_4 oxidation plays an important role in reducing the atmospheric CH_4 emissions from landfills constructed with conventional soil covers (Ahn *et al.*, 2002; Boeckx *et al.*, 1996; Jones and Nedwell, 1993; Kightley *et al.*, 1995; Seo *et al.*, 1997; Visscher *et al.*, 1999; Whalen *et al.*, 1990). According to the study of Kightley *et al.* (1995), which evaluated the effect of soil texture on CH_4 oxidation, the fine sand and clay soils had similar CH_4 oxidation rates while porous, coarse sand had a higher CH_4 oxidation rate. It was due to soil textures that affect the air filled porosity which controls O_2 and CH_4 penetration. The studies of Seo *et al.* (2001) and Lee *et al.* (2002) indicated other materials such as compost, rice hull and expanded rice hull had the higher CH_4 oxidation rates than landfill cover soil because they have high gas permeability, and can maintain moisture content, temperature, and microorganisms.

In this study the combined effect of soil moisture content and temperature on CH_4 oxidation in landfill cover soil exposed to landfill gas in temperate climate was investigated using batch incubation experiment. Based on the experimental results of this study, a regression model of CH_4 oxidation rate as a function of environmental variables was developed. Using developed CH_4 oxidation rate model, the CH_4 oxidation capacity of landfill cover soil as a biofilter under various environmental conditions was then calculated.

II. Materials and Methods

1. Soil characteristics

The soil used in these experiments was collected from a municipal solid waste landfill in Gyeonggi. The physicochemical properties of the soil was the following: pH of 6.88, organic matter content of 5%, NH_4^+-N of 0.455 mg $kg^{-1}{}_{soil}$ and NO_3^--N of 0.987 mg $kg^{-1}{}_{soil}$. In the laboratory the soil was air dried and passed through a 2 mm sieve prior to use. According to the USDA textural classification, the soil was sandy clay loam.

2. Incubation procedure

Air tight 60-mL vials sealed with rubber septa for gas sampling were used. To evaluate the influence of the moisture content, 13 grams of dry soil were put into the vials and water was added to obtain soil moisture content of 5, 10, 15, 25, 30% w/w (30% = WHC). To study the combined effect soil moisture content and temperature, the vials were incubated at 5, 15, 25, 30 and 35°C in water bath or incubator to keep constant temperature. Each treatment was duplicated. After the vials were closed, 15 mL of the atmospheric air in the vials were replaced by 15mL synthetic LFGs ($CH_4 : CO_2 = 50\% : 50\%$). Zero time gas samples were taken 20 min after gas addition to allow uniform diffusion of the added gas. The initial CH_4 concentration in the vials was about 10%. Before incubation, the vials filled with soil were pre-incubated under same CH_4 concentration of 10% for 5 days to restore the methanotrophic activity and remove lag time.

The processes of sorption, volatilization, and leakage could occur within the vials resulting in the loss of CH_4. Therefore, to determine the importance of these processes relative to biodegradation, blank vials at 25 and 35°C with different moisture contents were prepared using sterilized soil. Sterilization was achieved by autoclaving the soil at 122°C and 0.138 MPa for 30 min on three successive times.

3. Gas analysis

Gas samples of 300μL were taken from the headspace using gas-tight syringe with time intervals. The gas samples were analyzed for CH_4, CO_2 and O_2 concentration using a Younglin, model 600D, Gas Chromatograph equipped with a Thermal Conductivity Detector (TCD) and CTR1 column. The carrier gas was He at a flow rate of 30 mL min^{-1}. The injector temperature was 120°C, the oven temperature was 35°C, and the detector temperature was 120°C.

III. Results and Discussion

1. Blank test

Methane concentration did not decrease in the blank vials with sterilized soil during the incubation. These results indicate that the processes of a sorption, volatilization, and leakage were not occurring to any significant extent within soil vials. Therefore, the loss of CH_4 from soil vials in other treatments was attributed to oxidation by methanotrophic bacteria.

2. Gas concentration versus time

Figure 1 shows an example of the gas concentration versus time in the vial. The concentration of CH_4 and O_2 decreased with time, while the CO_2 concentration increased. The O_2 concentration in all vials were above 7%. It might be enough to ensure CH_4 oxidation due to CH_4 oxidation in incubation study was insensitive to O_2 mixing ratio above 3% (Czepiel *et al*., 1996) The carbon dioxide concentration did not increase as much as the CH_4 concentration decreased in the vial. It might be due to assimilation of carbon in the biomass dissolution of CO_2 in the soil water (Christohpersen *et al*., 2000; Whalen *et al*., 1990).

3. Effect of soil moisture content and temperature

Figure 2 shows the effect of soil moisture content and soil temperature on the CH_4 oxidation rates. The optimum moisture contents were 10% or 15% on different soil temperature except 5°C. The lower oxidation rate at the 5% moisture content might be due to the lower moisture content as physical stress to methanotrophs. The lower oxidation rate at the 30% moisture content might be due to the higher moisture content which can reduce methanotrophic activity by restricting O_2 diffusion in soil. However, the optimum moisture content in the soil can allow both rapid gas diffusion and a sufficient methanotrophic activity to oxidize CH_4 (Boeckx *et al*., 1996).

The optimum temperatures were between 30

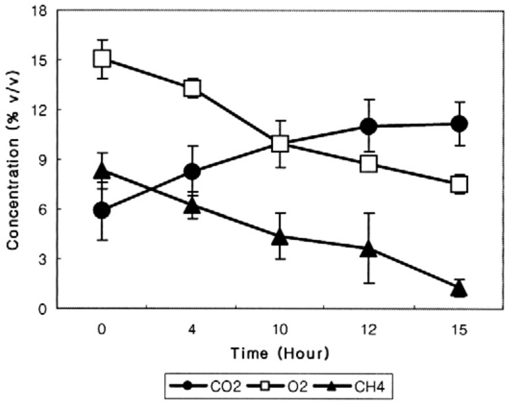

Figure 1. Gas concentration as a function of time in batch test with soil moisture content of 15% (w/w) and soil temperature of 30°C

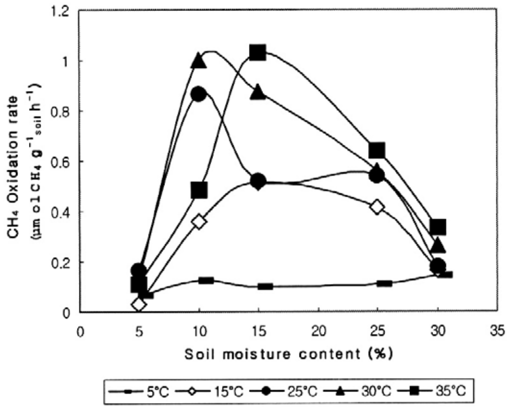

Figure 2. Methane oxidation rates as a function of soil moisture content and temperature

and 35°C under various soil moistures except 5% (w/w). This result was coincident with that of studies of Whalen *et al.* (1990) and Czepiel *et al.* (1996). Methane oxidation rates at 5°C were significantly lower than rates at other temperatures. At the temperature of 5°C and moisture content of 5%, no optimum moisture content or temperature condition was found. The highest CH_4 oxidation rate was 1.03 μmol g^{-1} h^{-1} at soil moisture content of 15% (w/w) and temperature of 35°C. This amounted to a total oxidation of 73% of the applied CH_4.

4. Regression model on CH_4 oxidation rate

The CH_4 oxidation capacity of soil is a function of environmental conditions. Therefore, a mathematical model of CH_4 oxidation rate as a function of soil moisture content and temperature was developed based on the above experimental results. To explain the relationships between the variables, a polynomial regression analysis was used which yielded the following quadratic equation with an R^2 value of 0.71.

$$OR_{CH4} = 0.0284(Ts) - 0.0003(Ts)^2 + 11.3282(\theta s) - 31.8907(\theta s)^2 - 0.7618 \qquad [1]$$

Where:
OR_{CH4} = CH_4 oxidation rate (μmol CH_4 $g^{-1}{}_{soil}$ h^{-1})
Ts = incubation temperature (°C)
θs = soil moisture content (percent by weight)

The CH_4 oxidation capacity of soil under various environmental conditions was then calculated using equation [1] and the monthly soil moisture content and temperature conditions.

To test the model sensitivity to soil moisture content, the soil moisture content was varied in one percent increments from 0 to 30% (w/w) while soil temperature was held at their optimum levels, 35°C. The results indicate that the CH_4 oxidation rate is fairly stable over the moisture content range of 15-20%. However, at moisture contents below 15% or above 20%, the CH_4 oxidation rate changed nearly linearly with a steep slope (Figure 3a) indicating that the model was quite sensitive to changes in soil moisture content within these ranges. This indicates that maintaining the soil moisture content in the optimum range will be critical to increase the methane oxidation rate in the landfill cover soil.

To evaluate the model sensitivity to soil temperature, the soil temperature was varied from 0

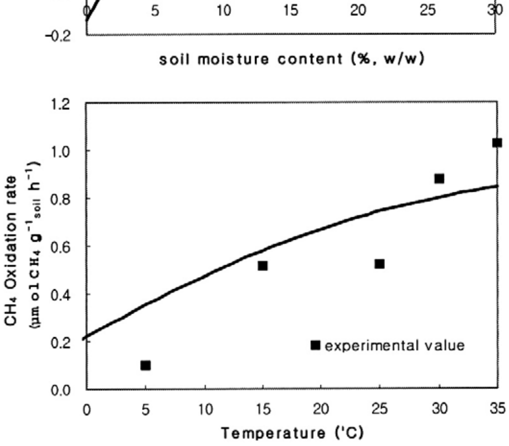

Figure 3. Sensitivity test of the regression model of CH_4 oxidation rate a) Sensitivity test on soil moisture content; b) Sensitivity test on soil temperature

to 35°C while soil moisture content was fixed at optimum value of 15% moisture. The results showed that oxidation rates increased with increasing temperature within these ranges (Figure 3b).

5. Soil moisture content and soil temperature

Rural Development Administration (RDA) in Korea operates agricultural weather observation and service system (AWS). From this service, the data of soil moisture content and soil (subterranean) temperature from January to December in 2004 of the 4 selected sites were collected. Most of the AWS are located in agricultural areas.

The monthly soil temperature data were used without further modification. The soil moisture contents collected from RDA service system were in units of percent by volume. The volumetric moisture contents were converted to gravimetric moisture contents by divided by an assumed bulk density of 1.45 g cm^{-3} which is typical of many agricultural soils. Figure 4 shows the average soil moisture content and temperature of the 4 selected sites.

6. Oxidation rate calculation

The monthly CH_4 oxidation rate for each city was calculated (Figure 5) using the soil moisture content and temperature data plus the CH_4 oxidation model (equation 1) and assuming soil tex-

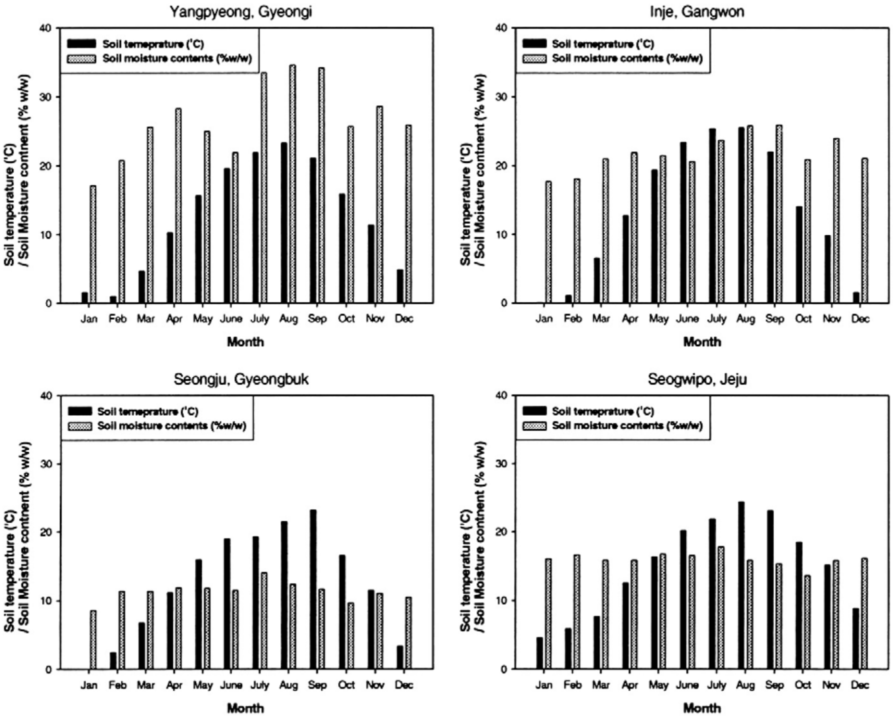

Figure 4. Soil moisture content and temperature of the 4 selected sites

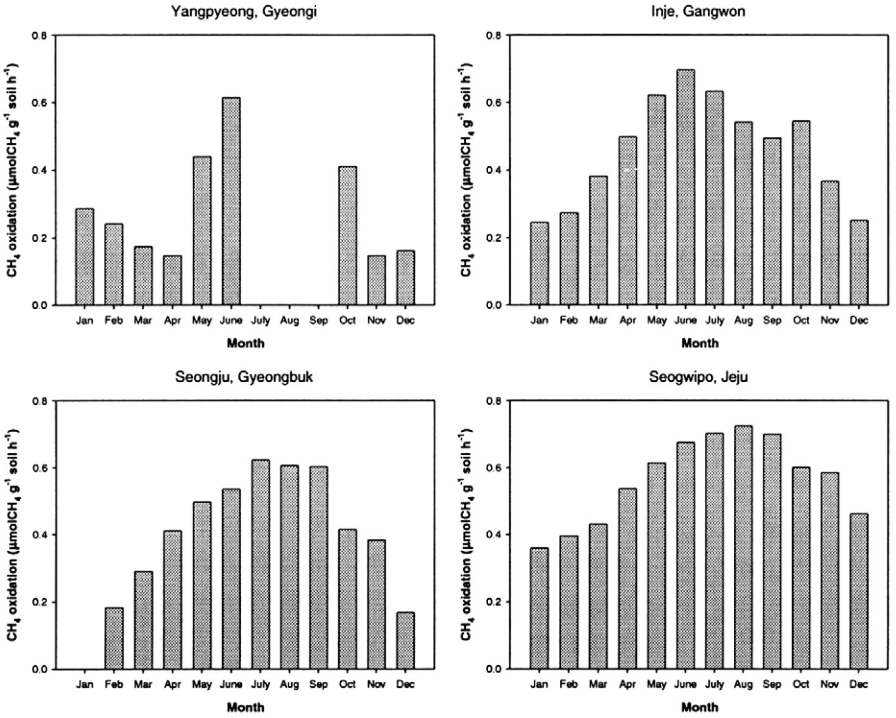

Figure 5. Calculated CH_4 oxidation rate of the 4 selected sites

tures of the selected 4 sites were sandy clay loam. At most sites, the oxidation rates during the winter months of December, January, and February were lower than those of the remainder of the year. The lower oxidation rates were due to lower soil temperatures that reduce methanotrophic activity.

According to the calculations, the CH_4 oxidation rate of Seongju, Gyeongbuk in January was negative value, so it was considered to be zero. This was due to a synergistic effect of low soil temperature (0°C) and low soil moisture content (8.6%).

As expected, methane oxidation rates were highest during the summer months of May to September in 3 sites except Yangpyeong, Gyeonggi. The highest oxidation rate among all sites was 0.725 μmol CH_4 g^{-1}soil h^{-1} for Seogwipo, Jeju in August. In Seogwipo, Jeju, the CH_4 oxidation rates were relatively high throughout the entire year, and thus this site had the highest yearly average oxidation rate of 0.566 μmol CH_4 g^{-1}soil h^{-1}. Methane oxidation capacity of a landfill cover soil located in this site with favorable environmental conditions might be higher than that in the other sites, and thus a landfill cover soil in this site should act as a biofilter effectively.

Yangpyeong, Gyeonggi had lowest average oxidation rate of 0.182 μmol CH_4 g^{-1}soil h^{-1}, caused by higher soil moisture content than that of the other sites. The maximum oxidation rate for this site was 0.615 μmol CH_4 g^{-1}soil h^{-1} in June. The CH_4 oxidation rate from July to September in this site was calculated as the negative value and considered to be zero. This was due to the high moisture content (above 30%), which was nearly saturated condition. The methane oxidation capacity of a landfill cover soil in this site was lower than other sites, and thus a landfill cover soil should not act as a biofilter effectively.

However, the efficiency of a landfill cover soil as biofilter may be increased by designing and managing the landfill cover soil to optimize the soil moisture content. During dry seasons, moisture may be added by irrigation to maintain optimal soil moisture contents to promote the maximum methane oxidation rate. To prepare wet seasons, well-drained sandy soils can be used as the landfill cover soil medium. This will minimize times of saturation when methane oxidation is inhibited.

IV. Conclusions

The results of this study clearly show the potential of a landfill cover soil to biodegrade CH_4 to CO_2 and water. This study also showed that the CH_4 oxidation rate in landfill cover soil was significantly influenced by environmental factors of soil moisture content and temperature. The optimum range of soil moisture content and temperature for CH_4 oxidation in a sandy clay loam textured soil were between 10 and 15% (w/w) and between 30 and 35°C, respectively. The maximum CH_4 oxidation rate was 1.03 μmol CH_4 g^{-1}soil h^{-1} under optimum conditions (15% moisture content and 35°C temperature). This amounted to a total oxidation of 73% of the applied CH_4. However, this value was gotten from short term laboratory studies and exact percent reductions in the amount of methane emitted cannot be predicted since it will vary on a case-by-case basis.

A quadratic regression equation was developed to describe the dependence of CH_4 oxidation rate in a sandy clay loam soil as a function of soil moisture content and temperature. Using this equation and the average monthly soil moisture contents and temperatures for 4 different sites, the monthly CH_4 oxidation rate at each location was calculated. Considering the CH_4 oxidation rates calculated by the regression equation, the landfill cover soils located in the sites with favorable environmental conditions may be expected to be effective as biofilters to reduce the atmospheric CH_4 emissions. In contrast, the calculations indicate that landfill cover soils in the sites with unfavorable soil moisture content and temperature ranges will have much lower efficiencies as biofilters.

The CH_4 oxidation rates calculated by the regression equation developed in this study may have some limitation because this equation was developed from short term laboratory studies and the factors affecting on CH_4 oxidation rate of landfill cover soil in specific field will also include soil texture, soil depth and landfill gas composition as well as soil moisture content and temperature. However, the result of this study suggested that a properly designed and managed cover soil should be capable of achieving a significant reduction in atmospheric CH_4 emission, and thus a landfill cover soil can act as an effective biofilter to reduce the accumulation of greenhouse gases in the earth's atmosphere.

Acknowledgement

This work was supported by grant No. (R03-2002-000-20014-0) from the Basic Research Program of the Korea Science and Engineering Foundation.

References

Ahn, Y.M., Kim, J.Y., Nam, K., and Yoon, S.P., 2002, Enhanced methane oxidation technology by methanotrophs in solid waste landfills, The 2nd Asian Pacific Landfill Symposium Proceedings, 482-488.

Boeckx, P., Cleemput, O.V., and Villaravo, I., 1996, Methane emission from a landfill and the methane oxidizing capacity of its covering soil, Soil Biology & Biochemistry, 28, 1397-1405.

Bogner, J., Spoakas, K., Burton, E., Sweeney, R., and Corona, V., 1995, Landfills as atmospheric methane sources and sinks, Chemosphere, 31, 4119-4130.

Czepiel, P.M., Mosher, B., Crill, P.M., and Harriss, R.C., 1996, Quantifying the effect of oxidation on landfill methane emissions, Journal of Geophysical Research, 101, 16721-16729.

Christophersen, M., Linderod, L., Jensen, P.E., and Kjeldsen, P., 2000, Methane oxidation at low temperatures in soil exposed to landfill gas, Journal of Environmental Quality, 29, 1989-1997.

IPCC, 1995, Second assessment Report: Climate Change.

Jones, H.A. and Nedwell, D.B., 1993, Methane emission and methane oxidation in land-fill cover soil, FEMS Microbiology Ecology, 102, 185-195.

Kightley, D., Nedwell, D.B., and Cooper, M., 1995, Capacity for methane oxidation in landfill cover soils measured in laboratory-scale soil microorganisms, Applied and Environmental Microbiology, 61, 592-601.

King, G.M. and Adamsen, A.P.S., 1992, Effect of temperature on methane consumption in a forest soil and in pure cultures of the methanotroph methylomonas rubra, Appl. Environ. Microbiol, 58, 2758-2763.

Lee, J., Seo, D., and Lee, D., 2002, Methane oxidation capacity in landfill cover soil, sludge compost and rice hull, J. Korea Solid Waste Engineering Society, 19, 699-707.

Parsons, M.L., 1995, Global warming: The truth behind the myth, Insight Books, New York, 159.

Seo, D., Lee, D., and Kim, E.Y., 1997, Experimental study on methane oxidation rates by methane-utilizing bacteria in a landfill cover layer soil, J. Korea Solid Waste Engineering Society, 14, 525-530.

Seo, D., Lee, J., Lee, D., and Kim, E., 2001, Methane oxidation rates in landfill cover soil and other materials, J. Korea Solid Waste Engineering Society, 18, 693-701.

U.S. EPA, 1999a, U.S. methane emissions 1990-2020: Inventories, Projection, and Opportunities for Reductions, EPA/430/R-99-013.

U.S. EPA, 1999b, Inventory of U.S. greenhouse gas emissions and sinks: 1990-1997, EPA-236/R-99/003.

Visshe r, A.D., Thomas, D., Boeckx, P., and Cleemput, O.V., 1999, Methane oxidation in simulated landfill cover soil environments, Environ. Sci. Technol., 33, 1854-1859.

Whalen, S.C., Reeburgh, W.S., and Sandbeck, K.A., 1990, Rapid methane oxidation in a landfill cover soil, Applied and Environmental Microbiology, 56, 3405-3411.

Yasushi, M., Hanashimn, M., Nagano, S., and Tanaka, A., 1993, Generation of greenhouse effect gases from different landfill types, Engineering Geology, 34, 181-187.

최종원고채택 04. 08. 10