



## Changes in Soil Nitrous Oxide and Carbon Dioxide Dynamics after the Application of Digested Liquid Cattle Manure

**TOMONORI FUJIKAWA\***

*Faculty of Regional Environment Science, Tokyo University of Agriculture, Tokyo, Japan*

*Email: t3fujika@nodai.ac.jp*

**MASATO NAKAMURA**

*National Institute for Rural Engineering, National Agriculture and Food Research Organization (NARO), Tsukuba, Japan*

Received 13 December 2012 Accepted 10 June 2013 (\* Corresponding Author)

**Abstract** The aim of this study was to clarify the changes in N<sub>2</sub>O and CO<sub>2</sub> emission from the soil surface, their concentrations in soil gases, and gas diffusion fluxes after application of digested liquid manure (DL) produced by anaerobic digestion of cattle manure slurry. N<sub>2</sub>O emission increased more and faster after application of DL compared to after the application of conventional inorganic fertilizer. The N<sub>2</sub>O emission rate from the DL was 0.25% of the applied nitrogen. CO<sub>2</sub> emission after the DL application also increased, and the CO<sub>2</sub> emission ratio from the DL was 33% of the applied C. Soil N<sub>2</sub>O concentration increased after DL application. The highest soil N<sub>2</sub>O concentration occurred earlier than the largest N<sub>2</sub>O emission. The increase in CO<sub>2</sub> concentrations near the surface was small. The largest N<sub>2</sub>O diffusion flux was observed near the surface, and a negative flux was observed in deeper layers 14 days after DL application. The difference in the CO<sub>2</sub> flux between deeper and surface layers flux was smaller than that in the N<sub>2</sub>O flux, which suggests that the contribution of CO<sub>2</sub> generation in deeper layers is larger than that of N<sub>2</sub>O.

**Keywords** Methane fermentation, soil gas concentrations, gas diffusion, greenhouse gases

### INTRODUCTION

Anaerobic digestion of livestock slurry can potentially reduce greenhouse gas (GHG) emission and sustainably generate electrical and heating energy (Rico et al., 2011). However, digested liquid manure, which is a by-product of anaerobic digestion, contains a large quantity of organic matters. Treatment of wastewater containing the digested liquid manure is expensive in terms of energy and chemicals (Massé et al., 2007). The digested liquid manure contains high levels of carbon and nitrogen compounds and other nutrients that can promote plant growth. Application of this liquid to agricultural fields as liquid fertilizer would therefore be an efficient use of the digested liquid manure, but the environmental effects of this application, and especially the emission of GHGs need to be better understood.

In a farmland soil, GHGs such as N<sub>2</sub>O and CO<sub>2</sub> are generated by the decomposition of the applied nitrogen or carbon compounds by soil microorganisms, and the generated gases diffuse through the soil profile following concentration gradients until the gas is emitted from the soil surface into the atmosphere. This scenario indicates that the emission of the gases from the soil surface depends on not only the total amount of generated gases in the soil but also the location (i.e. depth) of the generation and gas diffusion fluxes.

The aim of this study were to clarify the changes in N<sub>2</sub>O and CO<sub>2</sub> emission from the soil surface, the corresponding changes in their concentrations and gas diffusion fluxes in the soil after the application of digested liquid manure produced by digestion of cattle manure slurry.

## METHODOLOGY

### Site description and experimental setup

Samples of digested liquid manure produced by anaerobic digestion mixture of dairy cattle manure slurry and vegetable scraps at the Yamada Biomass Plant in Katori City, Chiba Prefecture, Japan (Nakamura et al., 2007) was obtained. The digested liquid manure used in the present study was collected in September 2007. Approximately half of the nitrogen in the digested liquid manure is organic nitrogen, and the remainder is  $\text{NH}_4\text{-N}$ , with a very small  $\text{NO}_3\text{-N}$  content. In this study, the digested liquid manure without any dehydration or filtration was used. The field experiments were conducted in an experimental field at the National Institute for Rural Engineering in Tsukuba City, Ibaraki Prefecture. This field was classified as Andosol soil, and the surface soil was light clay (LiC). This field had not been cultivated for more than 3 years prior this experiment.

A total of 4 plots ( $1 \text{ m} \times 2 \text{ m}$ ) in the field were established. Based on previous standard fertilizer application rate that has been used around this site, we applied  $24 \text{ g N m}^{-2}$  ( $7800 \text{ cm}^3 \text{ m}^{-2}$ ) of the digested liquid manure to the surface soil in the first plot (hereafter, the DL treatment). In the second plot,  $(\text{NH}_4)_2\text{SO}_4$ , which included the same total amount of nitrogen as in the DL treatment, was applied (hereafter, the conventional fertilizer [CF] treatment). In the third plot, we added the same amount of  $(\text{NH}_4)_2\text{SO}_4$  used in the CF treatment, but added water equal to the amount included in the digested liquid manure; hereafter, we refer to this as the conventional fertilizer plus water (CW) treatment. We also included a non-fertilized plot (hereafter, the NF treatment) as the control. All three treatments were applied in October 2007. In the DL, CF, and CW treatments,  $\text{Mg}_3(\text{PO}_4)_2$  and KCl were also applied to prevent P or K deficiency from affecting the results. Japanese mustard spinach (Komatsuna: *Brassica rapa* var. *perviridis*) was sown 7 days after the fertilizer application. The komatsuna plants were harvested after 57 days. The field was not irrigated, and rainfall during the growth period totaled 169 mm which is normal for the study area; thus, the soils were neither excessively dry nor flooded. The yield of komatsuna was highest in the DL treatment, at  $1900 \text{ g m}^{-2}$  ( $9.1 \text{ g N m}^{-2}$ ). The plants absorbed 37% of the applied nitrogen in this treatment. The yield in the CF treatment ( $890 \text{ g m}^{-2}$ ) was smaller than that in the CW treatment ( $1800 \text{ g m}^{-2}$ ). These differences appear to have resulted from a water shortage during the early growth stages suggested by Fujikawa and Nakamura (2010).

### Measurements

Emissions of  $\text{N}_2\text{O}$  and  $\text{CO}_2$  from the soil were measured surface using the closed-chamber method (Rolston and Moldrup, 2002). Daily measurements were completed between 09:00 to 11:00 h. Three collars were installed in each plot.  $\text{N}_2\text{O}$  and  $\text{CO}_2$  concentrations in the sampled gas were analyzed using a GC-8A gas chromatograph (Shimadzu, Kyoto, Japan) with an electron capture detector and a GC-14A gas chromatograph (Shimadzu) with a thermal conductivity detector, respectively. Hutchinson and Livingstone (2002) estimated the gas emission flux ( $q$ ;  $\text{g N m}^{-2} \text{ h}^{-1}$  for  $\text{N}_2\text{O}$ ;  $\text{g C m}^{-2} \text{ h}^{-1}$  for  $\text{CO}_2$ ) using the slope of the change in gas concentration in the chamber ( $a$ ;  $\text{m}^3 \text{ m}^{-3} \text{ h}^{-1}$ ), the height of the gas chamber ( $h$ ; 0.20 m), the ratio of nitrogen mass to  $\text{N}_2\text{O}$  mass or carbon mass to  $\text{CO}_2$  mass ( $s$ ; 28/44 for  $\text{N}_2\text{O}$ ; 12/44 for  $\text{CO}_2$ ), the density of each gas at 273.15 K ( $\rho$ ;  $\text{g m}^{-3}$ ), and the temperature ( $T$ ; K):

$$q = \left( \rho \cdot \frac{273.15}{T} \right) \cdot a \cdot h \cdot s \quad (1)$$

Cumulative gas emission ( $Q$ ;  $\text{g N m}^{-2}$  for  $\text{N}_2\text{O}$ ;  $\text{g C m}^{-2}$  for  $\text{CO}_2$ ) in the DL, CF, and NF treatments were calculated based on the assumption of linear changes between consecutive measurements:

$$Q = \sum_{i=1}^n \left( \frac{1}{2} \times \Delta t_i \times (q_{i-1} + q_i) \right) \quad (2)$$

where  $q_i$  is the  $i$ th measurement flux,  $\Delta t_i$  is the time interval between measurements  $i$  and  $i - 1$ , and  $n$  is the total sampling time. The increase in emission of each gas as a result of fertilizer application ( $Q'$ ) was calculated by subtracting  $Q$  in the NF treatment from  $Q$  in the DL and CF treatments, and the nitrogen and carbon emission rates were estimated by dividing  $Q'$  by the amount of nitrogen or carbon (respectively) in the applied fertilizer.

Soil gas was collected using the stainless-steel gas sampling pipes described by Fujikawa et al. (2000). Soil gas samples ( $10 \text{ cm}^3$ ) from around the gas inlets were removed from the pipes using a syringe. The  $\text{N}_2\text{O}$  and  $\text{CO}_2$  concentrations in the soil gases were quantified using the gas chromatographs, as described above.

Undisturbed  $100 \text{ cm}^3$  soil cores were collected to determine the gas diffusion coefficient of each soil layer. The soil gas diffusion coefficient for  $\text{O}_2$  was quantified using the non-steady-state method suggested by Osozawa and Hasegawa (1995). Relative gas diffusivity ( $D/D_0$ ) was calculated by dividing the  $\text{O}_2$  gas diffusion coefficient of the soil ( $D$ ) by that in the atmosphere ( $D_0$ ). The gas diffusion coefficient of each gas ( $D_a$ ) was estimated by multiplying the relative gas diffusivity by the diffusion coefficient in the atmosphere for each gas ( $\text{N}_2\text{O} = 0.0514 \text{ m}^2 \text{ h}^{-1}$ ,  $\text{CO}_2 = 0.0756 \text{ m}^2 \text{ h}^{-1}$ ) as suggested by Rolston and Moldrup (2002).

The gas diffusion flux ( $q_d$ ) in the soil was calculated by multiplying the gas diffusion coefficient ( $D_a$ ;  $\text{m}^2 \text{ h}^{-1}$ ) by the gas concentration gradient, which was obtained by dividing the difference in gas concentrations by the distance between two measurements at adjoining depths:

$$q_d = -\left(\rho \cdot \frac{273.15}{T}\right) \cdot s \cdot \frac{C_u - C_d}{z_u - z_d} \cdot D_a \tag{3}$$

where  $C_u$  and  $C_d$  are the gas concentrations at depths of  $z_u$  and  $z_d$ , respectively, where u and d refer to the upper and deeper soil layers, respectively. The datasets for the calculation of  $q_d$  are shown in Table 1. The values of  $D_a$  of the samples obtained 3 days after the fertilizer application were used for  $q_d$  after 7, 14 and 21 days and those of the samples obtained 36 days after the application were used for  $q_d$  after 36 days.

**Table 1 Datasets of  $z_u$ ,  $z_d$  and  $D_a$  for the calculation of the gas diffusion flux ( $q_d$ ) in the soil**

Depth of $q_d$ (cm)	$z_u$ (cm)	$z_d$ (cm)	Depth of $D_a^*$ (cm) (atmosphere <sup>***</sup> )
-2.5	-5 <sup>**</sup>	0 <sup>**</sup>	
2.5	0 <sup>**</sup>	5	0 to 5
7.5	5	10	5 to 10
12.5	10	15	10 to 15
22.5	20	25	20 to 25
32.5	30	50	30 to 35
42.5	30	50	40 to 45

\*: Depth of the undisturbed samples using for the measurement of  $D_a$

\*\* : The atmosphere above the soil surface was also sampled using a syringe.

\*\*\*:  $D_a$  at -2.5 cm is gas diffusion coefficient in the atmosphere ( $D_0$ )

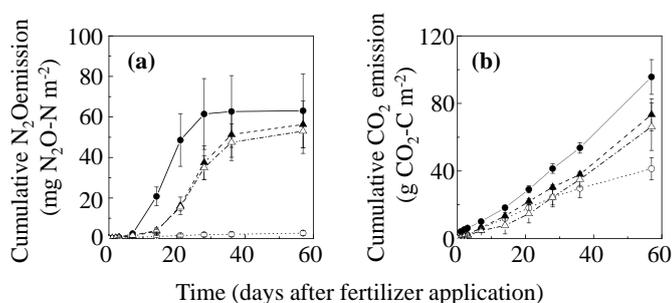
## RESULTS AND DISCUSSION

### Emissions of $\text{N}_2\text{O}$ and $\text{CO}_2$

One week after fertilizer application, a strong increase in  $\text{N}_2\text{O}$  emission was observed in DL. The increase of  $\text{N}_2\text{O}$  emission were also observed in CF and CW but it took about 7 days longer to reach its peak in CF and CW than in DL. The difference in  $\text{N}_2\text{O}$  emission between the CF and CW treatments was negatively small, even though plant growth was much lower in the CF plot. Changes in cumulative  $\text{N}_2\text{O}$  emissions in the DL, CF, CW and NF treatments over time are shown in Fig. 1(a). The cumulative  $\text{N}_2\text{O}$  emission in DL was higher than that in CF or CW for about 30days after the fertilizer application. The difference in  $\text{N}_2\text{O}$  emission rates could have resulted

from activation of microorganisms by the organic compounds in the digested liquid manure. The cumulative  $N_2O$  emission in DL was  $63 \text{ mg N m}^{-2}$  (reached after 57 days) and the  $N_2O$  emission rate was 0.25%. This emission rate was similar to that (0.17%) reported by Wulf et al. (2002).

In the DL treatment, the peak  $CO_2$  emission was observed just after the fertilizer application. The  $CO_2$  emission decreased with time after 2 days from the application and remained relatively constant or increased slightly until about 57 days after fertilizer application. No significant difference between that in CF and CW and that in NF during the first 20 days after the fertilizer application. This suggests that the effect of the application of inorganic nitrogen and water on the  $CO_2$  emission rate was small and that the increase in  $CO_2$  emission after application of the digested liquid manure was caused by 1) the decomposition of the organic matter in the digested liquid manure and/or by 2) the activation of soil microorganisms by the organic nitrogen. By 30 days after the fertilizer application,  $CO_2$  emission in CF and CW became larger than that in NF. The reason for this increased  $CO_2$  emission was probably that promotion of plant growth by the fertilizer increased root respiration. The cumulative  $CO_2$  emission by the application of digested liquid manure during the first 28 days, during that time the effect of plant root respiration would be small, was  $41 \text{ g CO}_2\text{-C m}^{-2}$  (Fig. 1(b)). The  $CO_2$  emission rate was 33% in the DL plot. Part of the carbon applied to the soil was emitted as a gas and the remainder moved downward into the groundwater after dissolving in the soil water or accumulated in the soil.



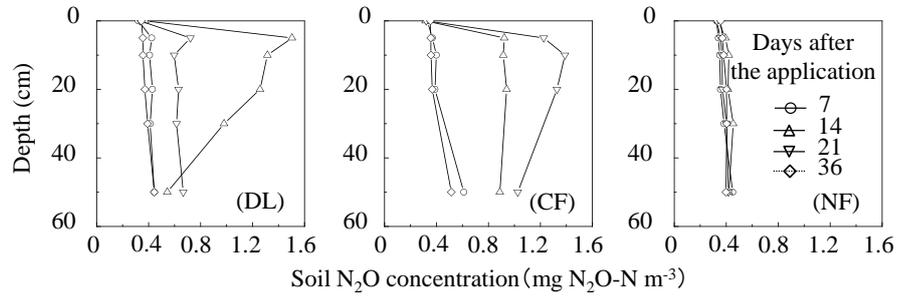
**Fig. 1 Changes in cumulative (a)  $N_2O$  and (b)  $CO_2$  emission in DL and CF, and NF plot.**

### Concentrations of $N_2O$ and $CO_2$ in the soil

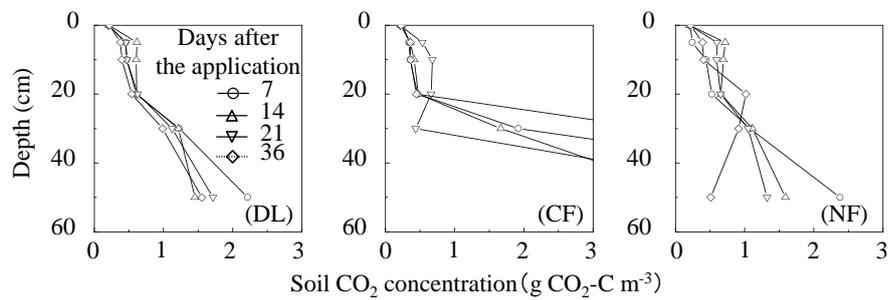
The soil  $N_2O$  concentration increased after the fertilizer application in both the DL and CF treatments (Fig. 2). Soil  $N_2O$  concentrations remain unchanged throughout the study period in the NF treatment. Throughout the first 7 days of the study, the  $N_2O$  concentration increased with increasing depth in the DL and CF treatments; in contrast, at 14 days, the  $N_2O$  concentration in both treatments increased to a depth of 5 cm, then decreased thereafter with increasing depth. The decrease in the  $N_2O$  concentration in DL was faster than that in CF, which agrees with the changes in  $N_2O$  emission. The highest  $N_2O$  concentration occurred between 7 and 14 days (DL) and between 14 and 21 days (CF), which were earlier than the largest  $N_2O$  emissions observed in these plots. This suggests that the increase in  $N_2O$  emission is delayed compared with the increase in the  $N_2O$  concentration in the surface soil layers.

The soil  $CO_2$  concentration tended to increase with increasing depth in all plots (Fig. 3). In the DL treatment, there was a small and possible non-significant increase in  $CO_2$  concentration between days 7 and 14 in the surface layers (0 to 20 cm). However, the amount of the increase in DL was smaller than that in CF and NF, which indicates that changes in  $CO_2$  concentration in the surface soil after the application of the digested liquid manure were smaller than those caused by the changes in the temperature, aeration, and water content of the soil. Changes in  $CO_2$  concentrations in deeper layers (> 30 cm) were larger than those in surface layers in each plot. This agrees with the results of Fujikawa et al. (2000) stated that diurnal fluctuations in soil  $CO_2$  concentrations were larger in deeper layers in a field with a hard pan. The large diffusion flux of  $CO_2$  negated the effect of changes in generation of  $CO_2$  by soil microorganisms, although the

respiration rates of roots and microorganisms would be larger in this layer because of the abundant substrate and oxygen availability.



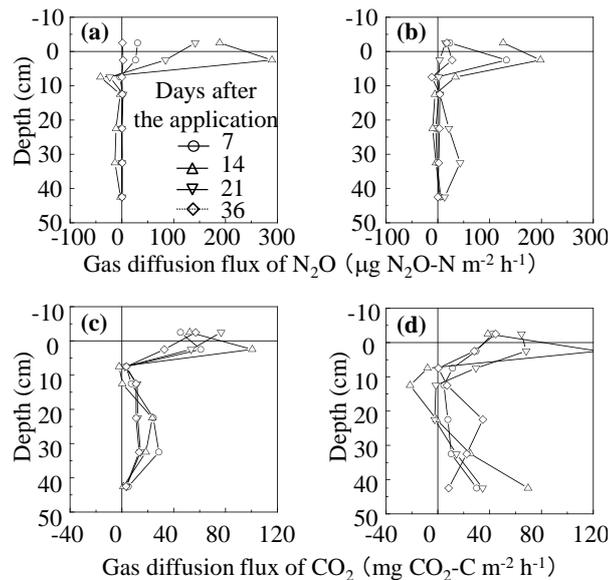
**Fig. 2 Distribution of the concentration of N<sub>2</sub>O as a function of time**



**Fig. 3 Distribution of the concentration of CO<sub>2</sub> as a function of time**

#### Soil gas diffusivity and diffusion flux

In DL, agglutination of the soil particles was observed, and the bulk density of the soil was reduced by these large pores. However in the top layer of the soil (0 to 5 cm) the differences in air-filled porosity and the relative gas diffusivity between treatments were small, whereas in deeper layers, the differences were large because of the large differences in bulk density in these deeper layers.



**Fig. 4 Distributions of the gas diffusion flux of N<sub>2</sub>O in the (a) DL and (b) CF treatments and of the gas diffusion flux of CO<sub>2</sub> in the (c) DL and (d) CF treatments**

The maximum N<sub>2</sub>O gas diffusion flux in the top layers of the soil (Fig. 4(a), (b)) was larger in DL than in CF. A negative flux was observed in DL at 5 to 50 cm in depth 14 days after the fertilizer application. This indicated that downward N<sub>2</sub>O diffusion occurred as a result of the application of digested liquid manure. It must be verified whether the larger downward flux of N<sub>2</sub>O by digested liquid manure than inorganic fertilizer originated from the properties of the digested liquid manure. The CO<sub>2</sub> gas diffusion flux decreased with increasing depth in the DL and CF treatments (Fig. 4(c), (d)). Compared with the N<sub>2</sub>O diffusion flux, the difference in the CO<sub>2</sub> flux between deeper and surface layers was smaller. This supports previous reports that the contribution of the generation of CO<sub>2</sub> in deeper layers is larger than that of N<sub>2</sub>O. The distribution of the CO<sub>2</sub> gas flux in CF varied with time; for this scenario, further research need to be conducted.

## **CONCLUSION**

We cultivated komatsuna in the field under three fertilization treatments, inclusive of digested liquid manure and an unfertilized control, to clarify the changes in N<sub>2</sub>O and CO<sub>2</sub> dynamics in the soil and at the soil surface. N<sub>2</sub>O emission increased more rapidly and substantially after the application of the digested liquid manure compared to inorganic fertilizer. Based on the cumulative N<sub>2</sub>O emission, the N<sub>2</sub>O emission rate was 0.25% for the digested liquid manure. CO<sub>2</sub> emission increased drastically after the application of the digested liquid manure, and then decreased with time from 2 days after the fertilizer application, but remained higher than the initial value. The CO<sub>2</sub> emission ratio for the digested liquid manure was 33%. The soil N<sub>2</sub>O concentration increased after the application of digested liquid manure and inorganic fertilizer. The increase in N<sub>2</sub>O emission is delayed compared with that in the N<sub>2</sub>O concentration in the surface soil. The changes in the CO<sub>2</sub> concentration in the surface soil caused by the application of digested liquid manure were smaller than those caused by changes in the temperature, aeration, and water content of the soil. The largest N<sub>2</sub>O gas diffusion flux was observed in the surface layer and negative flux was observed in deeper layers 14 days after the application of digested liquid manure. The difference in the CO<sub>2</sub> flux between deeper and surface layers was smaller than that for N<sub>2</sub>O. This suggests that the contribution of CO<sub>2</sub> generation in deeper layers is larger than that of N<sub>2</sub>O after the application of digested liquid manure.

## **ACKNOWLEDGEMENTS**

The present study was supported by grant from Ministry of Agriculture, Forestry and Fisheries of Japan (Rural Biomass Research Project, BUM-Cm3200). And for soil carbon analysis, it was also supported a Grant-in-Aid for Young Scientists (B), No. 22780222, provided by the Ministry of Education, Culture, Sports, Science and Technology, the Government of Japan.

## **REFERENCES**

- Fujikawa, T. and Nakamura, M. 2010. Influence of application method and rate of digested liquid from methane fermentation on N<sub>2</sub>O gas emission and plant growth. (In Japanese with English abstract.) *Jpn. J. Soil Sci. Plant Nutr.*, 81(3), 240-243.
- Fujikawa, T., Miyazaki, T., Seki, K. and Imoto, H. 2000. Correlation between the distribution of microorganisms and CO<sub>2</sub> and O<sub>2</sub> gas concentrations in a field under rotating use. (In Japanese with English abstract.) *Trans. Jpn. Soc. Irrig. Drain. Reclam. Eng.*, 68(4), 443-452.
- Hutchinson, G.L. and Livingstone, G.P. 2002. Chap 4.5. Soil-atmosphere exchange; In: Dane, J.H. and Topp, G.C. (eds.), *Methods of Soil Analysis Part 4*, Soil Sci. Soc. Am., Madison, U.S.A., 1159-1182.
- Massé, D.I., Croteau, F. and Masse, L. 2007. The fate of crop nutrients during digestion of swine manure in phydrophilic anaerobic sequencing batch reactors. *Bioresour. Technol.*, 98, 2819-2823.
- Nakamura, M., Yuyama, Y., Yamaoka, M. and Fujikawa, T. 2007. Material balance in biogas plant and fertilizer characteristics of digested liquid and digested liquid supplement. (In Japanese with English abstract.) *Trans. Jpn. Soc. Irrig. Drain. Reclam. Eng.*, 75(3), 337-343.

- Osozawa, S. and Hasegawa, S. 1995. Diel and seasonal changes of carbon dioxide concentration and flux in an andisol. *Soil Sci.*, 55, 55-62.
- Rico, C., Rico, J.L., Tejero, I., Muñoz, N. and Gómez, B. 2011. Anaerobic digestion of the liquid fraction of dairy manure in pilot plant for biogas production: Residual methane yield of digestate. *Waste Manage.*, 31, 2167-2173.
- Rolston, D.E. and Moldrup, P. 2002. Chap 4.5. Gas Diffusivity; In: Dane, J.H. and Topp, G.C. (eds.), *Methods of Soil Analysis Part 4*, Soil Sci. Soc. Am., Madison, U.S.A., 1113-1139.
- Wulf, S., Maeting, M. and Clemens, J. 2002. Application technique and slurry co-fermentation effects on ammonia, nitrous oxide, and methane emission after spreading: II. Greenhouse gas emissions. *J. Environ. Qual.*, 31, 1795-1801.