Oxygen and methane depletion in soil affected by leakage of natural gas

Steven, M.D[*‡], Smith, K.L[†], Colls, J.J[†] and Beardsley, M[†]

* School of Geography, University Park, University of Nottingham, NG7 2RD, UK.
†Division of Agricultural and Environmental Sciences, School of Biosciences, University of Nottingham, NG7 2RD, UK.

‡ corresponding author: **Michael.Steven@nottingham.ac.uk**

Phone +44 (0)115 9515442, Fax +44 (0)115 9515249

Abstract

To simulate effects of leaks of natural gas from pipelines, natural gas was injected into the soil at a depth of 1 metre in plots of grass, wheat and bean. Measurements of oxygen and methane made in gas-exposed soils show that oxygen is depleted significantly below the level predicted for simple displacement by natural gas, indicating consumption within the soil by methanotrophic bacteria. The gas distribution tends to be bimodal: 18% of the oxygen values are below 1% and 52% of the methane values are below 5% indicating a tendency towards either oxygen-limiting or methane-limiting conditions. Measured levels of oxygen depletion were significantly greater in summer. Depletion rates were greatest under grass, and least under wheat. In the grass plots, 36% of the variation in depletion is explained by soil temperature at 10 cm with a Q_{10} over the 0 – 20C range of 2.0. A model was developed that accounts for three gas exchange mechanisms in the soil atmosphere: soil-air displacement by the injected gas; methane and oxygen consumption by methanotrophic bacteria; and reinfusion of the soil atmosphere to account for a net loss of gas volume in the consumption process. On the basis of this model, the average fraction of methane consumed throughout the study was estimated as 37%. However this fraction depends strongly on the initial methane concentration. At initial methane concentrations below 10%, as much as 100% of the gas can be consumed, but consumption efficiency drops rapidly thereafter. These findings indicate that the soil sink for methane is dynamic

and adaptive, acting as a significant constraint on underground methane sources, limited only by the availability of oxygen.

Introduction

Methane is the most important gas after carbon dioxide in terms of climatic forcing and per molecule, has a global warming potential more than 20 times that of carbon dioxide (IPCC, 2001). The current atmospheric burden of methane, 4850 Tg is the highest in the past 420,000 years and is increasing at a rate of about 22 Tg year^{-1} (IPCC, 2001). Total methane emissions amount to about 600 Tg year^{-1}, of which anthropogenic sources account for about 60%. Agriculture, waste disposal, leakage from the gas distribution system and coal mining are all major contributors. Fossil fuel-related emissions amount to about 100 Tg year^{-1} (IPCC, 1996). Emission of methane from the UK gas distribution system in 2001 was estimated as 0.34 Tg, amounting to 16% of the total UK methane emissions, (Baggott *et al.* 2003).

The main sink for methane is reaction with OH radicals in the troposphere, but microbial oxidation in aerobic soils is estimated as contributing 3-9% of the total annual removal of methane from the atmosphere (IPCC 2001). Methanotrophic bacteria in soils are unique in their ability to utilize methane as a sole carbon and energy source (Conrad 1996; Hanson and Hanson 1996). Hűtsch (2001) suggests that if this sink were absent, the rate of atmospheric increase would be 1.5 times greater. In most situations where sub-surface methane diffuses into aerobic environments, large populations of aerobic methanotrophs can be found. Their activity depends on the presence of sufficiently high concentrations of both methane and oxygen and so tends to be confined to narrow soil horizons, typically in the top 30 cm of soil, limited in their distribution by the downward diffusion of atmospheric oxygen and the upward diffusion of methane, (Jones and Nedwell 1993; Lamb *et al.* 1996; Bogner *et al.*1997; Börjesson and Svensson 1997; Hűtsch 2001). Methane oxidation rates are affected by environmental factors such as temperature, water content, nutrients, soil-type and oxygen concentration (Hanson and Hanson 1996; Smith *et al.* 2003). Ammonia or ammonium-based fertilisers have a strong inhibiting effect on methane oxidation (Kightley *et al.*, 1995; Bender and Conrad, 1995; Boeckx and van Cleemput, 1996; Hanson and Hanson, 1996), Hütsch (2001) stating that the methane monooxygenase enzyme has a low substrate specificity and that methane oxidising bacteria metabolise ammonia in preference to methane.

Methanotrophic bacteria have been found to operate in two distinct regimes. Bacteria with a high affinity consume methane at concentrations 2 – 3 orders of magnitude lower than in low affinity systems (Knowles, 1999) and are the sink that accounts for about 5% of atmospheric methane. Conrad (1996) claims that the microbes responsible, which must be capable of metabolising nanomolar concentrations of methane, have never been isolated. Most studies of methane oxidation by methanotrophic bacteria however, have been done on landfill gases with much higher concentrations of methane (Whalen *et al.* 1990, Jones and Nedwell 1990, Jones and Nedwell 1993, Boeckx and van Cleemput 1996, Czepiel et al 1995, Börjesson and Svensson 1997, Haarstad 1997, Christophersen *et al.* 2001,). Several of these studies have found that methane oxidation in the top cover of landfills can be sufficient to prevent methane emission to the atmosphere. Adamse *et al.* (1972) and Hoeks (1972) demonstrated similar methane oxidation activity around leaks in natural-gas pipes. They found that in a normal soil in which there is no leakage of methane the population of methanotrophic bacteria is low, but about two weeks after the start of a gas leak the bacterial population starts to develop and oxidation of methane increases. Lamb *et al.* (1996) also demonstrated methane oxidation from simulated pipeline leaks and extrapolated the results to suggest that 22% of U.S. methane emissions from underground pipeline leaks might be oxidised in this way.

The study reported here was part of an investigation into systems for the remote detection of gas leaks (Smith, Steven and Colls, 2004). Natural gas was injected into the soil to induce stress responses in crop plants at the surface. Because plant responses are believed to be largely due to asphyxiation of the roots rather than toxicity, it was necessary to measure soil oxygen concentrations as well as methane. This paper reports on the characteristics of bacterial activity inferred from the measured concentrations of these gases.

Materials and methods

Study site

The experiments were conducted in a field, previously under permanent pasture, at the Sutton Bonington campus of the University of Nottingham (52.8°N, 1.2°W). Eighteen plots, each 2.5 x 2.5 m, were laid out within the experimental area to enable controlled studies of responses to gas. Natural gas from the UK domestic supply was injected into twelve of these plots at a depth of 80-100 cm below the plot centres. Soil temperature data were obtained from an automatic weather station at a distance of about 600 m. Details of the gas injection facility, control systems and measurement techniques are described in Smith, Colls and Steven, (2004).

Gas measurements

Gas concentration in the soil was sampled at a depth of 35-50 cm by means of vertical plastic sampling tubes installed 15 cm from the centre of each plot. The soil gas concentration was measured using a Gasurveyor 442 (GMI Ltd, Renfrewshire, Scotland), which measures methane in the ranges 0-1000 ppm and 0-5 % volume gas by means of pellister-type catalytic oxidation and in the range 5-100 % volume gas by a thermal conductivity sensor. Oxygen is measured in the range 0-25% using an electrochemical cell. The instrument was attached to an on/off valve on the sampling tube and a sample of soil air extracted; the gas measurement was recorded as the maximum reading attained after the 15-second instrument response time. Measurements of methane and oxygen concentration were taken between 8 and 8.30 am on weekdays from 1st October 2002.

Plants and treatments

Six plots each of grass, winter wheat, and field bean were grown. A perennial rye grass mixture (cv Long Ley) was pre-established at the site and the plots were prepared by mowing. The grass plots were mown at approximately two-weekly intervals throughout the study. Winter wheat (*Hordeum vulgare* cv Claire) was sown at a density of 300 seeds m^{-2} in six plots on 30th October 2002 and germination commenced on 11th November 2002. Bean (*Vicia faba* cv Clipper) was sown at a rate of 30 seeds m^{-2} into the remaining six plots and germination commenced on 28th November 2002. Ammonium nitrate was added to the grass plots at a rate of 50 kg N/ha on 3rd and 28th April 2003 and to the wheat plots at a rate of 40 kg N/ha on the 3rd April 2003 and 80 kg N/ha on the 28th April 2003 and 8th May 2003. No fertiliser was added to the bean plots.

Gas was delivered at a nominal rate of 100 l hr^{-1} to two plots of grass from 1st October 2002 and to two plots of wheat and bean from the time of sowing. On the 12th May 2003 gas was also switched on to two additional plots each of grass, bean and winter wheat to determine the effect of a new gas leak on an established crop. The early-gassed wheat and bean were harvested on 15 May 2003. In the late-gassing experiment, the gas supply was terminated and the crops harvested on 28th July 2003.

Results

Relationships between oxygen and methane levels

A typical trace of methane and oxygen concentrations is shown in figure 1 for one of the grass plots subjected to long-term gassing. In general, high values of methane are associated with low values of oxygen and *vice versa*. Over the period of study, there was a general increase in methane level and a decrease in oxygen, a pattern that occurred in most of the experimental plots but not universally. Daily values were at times quite erratic with a series of sharp excursions. Single day excursions seem to be associated with a change in just one of the gases, suggesting occasional measurement error. However longer excursions of a few days to three weeks occurred in which methane and oxygen tended in opposite directions. Although such excursions occurred in all the plots studied, their timing was largely independent. No relationships were found between soil-gas levels and weather variables (Smith, Colls and Steven, 2004).

Over the whole study, soil oxygen was found to be related to methane concentration as shown in figure 2. The oxygen concentration expected by direct displacement is indicated by the straight line, where the oxygen intercept is 21% corresponding to the atmospheric (and undisturbed soil) value, and consistent with soil gas measurements made in the control plots. Because the displacement of soil air is by natural gas, which is only 80 to

95% methane, the methane intercept is estimated as 87.5%. The measured data in the gassed plots lie almost entirely below the displacement line, which is strongly indicative of methane oxidation by methanotrophic bacteria. The distribution of data has two peaks: 18% of the oxygen values are below 1% and 52% of the methane values are below 5%, suggesting a bi-stable process where either oxygen or methane is limiting. In spite of the individual scatter, the data show clear relationships when averaged across 5% bands of methane concentration, both for the full data set and by season. Quadratic functions fitted through the averaged data sets (figure 2) account for 93 – 97% of the variance in these averages. Depletion of oxygen, measured as the difference between the measured oxygen and the level expected after displacement, is about one third greater in summer than in winter.

Oxygen depletion with crop cover type and season

The fitted curves in figure 2 conceal a great deal of variation and do not account for a data distribution that tends to be biased towards either low oxygen or low methane. To test the significance of differences between seasons and treatments, oxygen depletion was calculated separately for each data point and a series of t-tests applied. Mean values of oxygen depletion and standard deviations are shown in Table 1. Differences between summer and winter; grass and bean; grass and wheat; and bean and wheat were all highly significant ($P<0.001$). Differences between land cover types have been noted in earlier studies and are attributed not to plant growth *per se*., but to the effects of cultivation, pesticide application, pH and the inhibiting effect of ammonia (Hütsch, 2001). Crop residues with low C/N ratios have also been found to have an inhibiting effect on methane oxidation (Boeckx, and van Cleemput, 1996). In our study bean and wheat had been cultivated whereas the grass was relatively undisturbed favouring a higher methane oxidation rate.

Table 1: Means and standard deviations of oxygen depletion (as percentage of total soil air), for different treatments

Data set	**Mean O_2 depletion (%)**	**Standard deviation**
All crops, all year	3.6	3.3
All crops, winter	3.1	2.9
All crops, Summer	4.2	3.6
Grass, all year	4.7	3.4
Wheat, all year	1.8	1.5
Bean, all year	3.4	3.5

The seasonality of oxygen depletion suggests an effect of temperature. Several authors have found a positive relationship of methane oxidation with temperature (Hoeks, 1972; Börjesson, and Svensson, 1997; Christopherson *et al.*, 2001) up to a peak at 25-30 C, Boeckx and van Cleemput, (1996), 30C (Whalen et al., 1990) or above 35 C (Czepiel *et al.*, 1996). These authors also found an optimum moisture level for methane oxidation, typically around 15%. In the present study, oxygen depression was calculated for all data points and correlated with soil temperatures at the soil surface, 10 cm, 30 cm and 100 cm depth. With the full data set, a very weak relationship with temperature was found. To increase the sensitivity of the analysis, the data set was restricted to the measured methane range 10-60%. This corresponds to the range with greater oxygen depletions (figure 2), but excludes values for which either oxygen or methane were limiting. By removing the large number of data points with no recorded methane, it also excludes any data where the injected methane had failed to reach the measurement point. With this restriction, the temperature at 10 cm depth explained about 20% of the variance in oxygen depletion. Finally, to remove the effect of crop cover type noted earlier, the analysis was restricted to grass data in the 10-60% range of measured methane. Grass had the longest run of data and showed the most consistent behaviour. The result of this analysis is the correlation shown in figure 3, in which 36% of the variance is explained by the temperature at 10 cm depth. This depth gave the strongest correlation and is consistent with previous findings of many of the authors already cited that maximum methane oxidation occurs in the uppermost layers of the soil. Although the relationship in figure 3 is better fitted by a linear relationship than an exponential, the average Q_{10} over the range 0 – 20 C was calculated for comparison with others and is consistent with many of the values cited in the literature for similar elevated methane environments (Table 2).

Table 2: Values of Q_{10} for soil methane oxidation from the literature. (Only studies with forced methane are included).

Source	**Temperature range C**	**Q_{10}**
This study	0-20	2.0
Hoeks (1972)	13.5 – 20.5	~6-8
Whalen, Reeburgh and Sandbeck, (1990)	5 – 26	1.9
Czepiel, Mosher, Crill, and Harriss, (1996)	20-30	2.4
Börjesson and Svensson (1997)	3 – 24	3.4-7.3

Modelling methanotrophic activity

A critical issue is to determine the fraction of methane consumed by bacteria as an estimate of the efficiency of this methane sink. This is not provided directly by the estimate of oxygen depletion, because the measured quantities of methane and oxygen have both been modified by methanotrophic activity. To estimate this efficiency, a model of the modified soil atmosphere was developed to calculate the initial quantity of methane and the amount consumed on the basis of the measured data. The model accounts for three processes: soil-air displacement by the injected gas; methane and oxygen consumption by methanotrophic bacteria; and reinfusion of the soil atmosphere to account for a net loss of gas volume in the consumption process.

Expressed as proportions of total soil air, the key components of our system are: Methane [CH_4] as a proportion μ of natural gas, so that the total volume of natural gas is

$[CH_4]/\mu$; Oxygen $[O_2]$; carbon dioxide $[CO_2]$; and nitrogen, which together with other gases acts as bulk $[N_2]$. By definition:

$$[CH_4]/\mu + [O_2] + [CO_2] + [N_2] = 1 \qquad (1)$$

If we define the natural levels (no methane input) with subscript 0, then $[CH_4]_0 = 0$ and

$$[O_2]_0 + [CO_2]_0 + [N_2]_0 = 1 \qquad (2)$$

With simple displacement only (subscript d), the relative proportions of all gases except $[CH_4]$ remain constant.

$$[O_2]_d/[O_2]_0 \quad = ([O_2]_d + [CO_2]_d + [N_2]_d)/([O_2]_0 + [CO_2]_0 + [N_2]_0)$$

$$= [O_2] + [CO_2] + [N_2]$$

from (2)

$$= 1 - [CH_4]_i/\mu \qquad (3)$$

from (1), where subscript i denotes the initial amount injected into the system. Equation 3 defines the displacement line in figure 2.

However, if methanotrophic bacteria consume some of the methane, the primary reaction follows the general formula for oxidation (Hoeks, 1972).

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2H_2O \qquad (4)$$

Application of this formula assumes that the amount of carbon taken up in additional bacterial mass can be ignored. Whalen *et al*., (1990) found that this uptake could be up to 69% of the total, but their study used a closed incubation system. As our system involved the continuous throughput of injected methane over several months, it is reasonable to assume near steady-state conditions. When adjusted for methanotrophic consumption, the methane concentration $[CH_4]'$ is then given by

$$[CH_4]' = [CH_4]_i - [CH_4]_c \qquad (5)$$

where $[CH_4]_i$ is the initial methane input and $[CH_4]_c$ is the methane consumed. Similarly,

$$[CO_2]' = [CO_2]_d + [CH_4]_c \qquad (6)$$

where $[CO_2]_d$ is the CO_2 level after initial displacement and $[CH_4]_c$ is the equivalent amount of CO_2 produced by methanotrophic oxidation. And

$$[O_2]' = [O_2]_d - 2\,[CH_4]_c \qquad (7)$$

$$[N_2]' = [N_2]_d \qquad (8)$$

At this point it is necessary to readjust for conservation of mass, because the two units of water formed in the oxidation reaction (Equation 4) would be expected to condense out in liquid form. The net loss of gas in the system must be replaced either by additional input of natural gas or by drawing in atmospheric air to replace the losses. In the conditions of this study, consumption of gases by methanotrophic bacteria can only be maintained where both oxygen and methane have adequate rates of supply. It therefore seems reasonable to assume that the lost volume is replaced by a reinfusion of air and methane in proportion to their existing (measured) values. On this basis, all the soil gas concentrations are increased by a factor $1/(1 - 2[CH_4]_c)$. Since $2[CH_4]_c$ cannot be greater than $[O_2]_0$, the maximum value of this scaling factor is 1.27.

The measured gas values therefore become

$$\begin{aligned}[O_2]_m &= [O_2]' / (1 - 2[CH_4]_c) \\ &= ([O_2]_d - 2\,[CH_4]_c) / (1 - 2[CH_4]_c)\end{aligned}$$

$$= ((1 - [CH_4]_i/\mu)\, [O_2]_0 - 2[CH_4]_c) / (1 - 2[CH_4]_c) \qquad (9)$$

and

$$[CH_4]_m = ([CH_4]_i - [CH_4]_c) / (1 - 2[CH_4]_c) \qquad (10)$$

With some manipulation it is then possible to solve for the values of consumed and initial methane as follows:

$$[CH_4]_c = ([O_2]_0 (1 - [CH_4]_i/\mu) - [O_2]_m) / 2(1 - [O_2]_m) \qquad (11)$$

and

$$[CH_4]_i = ([O_2]_0(1 - 2 [CH_4]_m) - [O_2]_m + 2 [CH_4]_m) / (([O_2]_0/\mu)(1 - 2[CH_4]_m) + 2(1 - [O_2]_m)) \qquad (12)$$

To calculate $[CH_4]_i$ and $[CH_4]_c$, $[O_2]_0$ was assumed to be 0.21 and μ was taken as 0.92. The methane content of natural gas may in fact be variable: the value of 0.92 was chosen to avoid negative estimates of consumption; the analysis shows that μ is only important at high methane levels and error due to this factor is no more than 1%. With these parameters, the estimates of initial and consumed methane are shown in figure 4 for all data in the study. The average fraction of methane consumed throughout the study is estimated as 37%. However this fraction depends strongly on the initial methane concentration. At low initial methane concentrations, as much as 100% of the gas can be consumed. The peak absolute rate of consumption occurs at an initial methane level of about 10% when the O_2/CH_4 mixing ratio would be about 2, matching the ratio of gas consumption. Consumption efficiency drops rapidly with increasing methane above this point, limited by the availability of oxygen.

Temporal trends in gas consumption

Gas consumption estimates are shown in figure 5 for the early-gassed grass, wheat and bean crops. The data shown are derived from the model (equation 11) and have been slightly smoothed with a three point running median filter to reduce excursions due to measurement errors. The trends within each pair of plots are broadly similar. In grass and wheat, consumption levels increased to an early peak after about three months, declined for a period in late winter and then increased again in early summer, peaking (in grass) in early August. There is no evidence of any change in consumption pattern when fertiliser was added to these plots. In the bean plots, consumption peaked after about one month and showed a gradual decline from November onwards. Similar patterns occurred in the late-gassed plots, but methane consumption was generally less well developed. Methane consumption values are relatively consistent over periods of a week or so. By comparing the measured gases for plot D (figure 1) with consumed methane for the same plot in figure 5(a) it appears that consumption levels are somewhat more stable than the measured values of the constituent gases.

Conclusions and Discussion

The results of this study support earlier findings that methanotrophic bacteria act as a significant sink for methane in aerobic soils, with a strong development of methane oxidising capacity within a few weeks of injection of gas into the soil (Hoeks, 1972; Whalen *et al*, 1990). Our calculations indicate that on average more than one-third of the gas was oxidised, but with marked variability associated, but only in part, with treatment and seasonal factors. Soil moisture was not measured in this study and although a weak correlation with soil temperature was found, Smith *et al*. (2003) suggested that the effect of soil temperature on oxidation is small with Q_{10} values of the order of 1.4 and that increases in oxidation rates in summer are due mainly to drier soil, and only secondarily to increases in temperature. These comments referred to natural exchanges of gases between soil and atmosphere and may not apply to the bacterial populations that operate at the high methane levels typical of forced systems. However, it is worth noting that methane oxidation itself generates a certain amount of moisture (equation 4): if one third of the input (100 l h^{-1}) were oxidised, within a region corresponding to 1 m^2 at the surface, the water released would be equivalent to 1.4 mm of precipitation per day. The summer of 2003 was very dry at our site and this supply of moisture might have been significant.

In calculating methane consumption rates, two critical assumptions were made in the model. Direct uptake of carbon into the bacterial mass would remove methane without the corresponding loss of soil oxygen. If carbon uptake were significant, this would have the effect of increasing the proportion of methane consumed relative to our estimates. The assumption made in this analysis is that this factor, although certainly present, is small relative to the overall metabolism. The second assumption is that reinfusion of soil gases occurs in proportion to their measured values. Since two units of oxygen are consumed for every unit of methane, this assumption may fail when oxygen is limiting. However, while a change in the reinfusion proportions would affect the calculations of consumed and initial methane their ratio, which gives the fraction, consumed, is relatively insensitive to this assumption.

An important feature of the soil sink for methane is that it is dynamic and adaptive. Methanotrophic activity appears to increase almost without limit with methane supply, which is especially remarkable given that the bacteria appear to be able to lie dormant almost indefinitely. Hanson and Hanson (1996) note that methanotrophic bacteria have survived up to 90 tears in anoxic conditions. This adaptive capacity acts as a constraint on higher intensity underground methane sources and may provide a greater resilience to gas leaks and other intense local sources than would be the case if soils had a fixed capacity for methane metabolism. However, the amount of methane consumed also depends on the supply of oxygen, which is limited by diffusion. In the context of the gas industry, the mitigating effects of methanotrophic bacteria on natural gas leakage are therefore probably limited to relatively slow leaks typical of low-pressure systems. Moreover, while this adaptive methanotrophic capability responds rapidly to changes in methane supply, it does not make a significant contribution to the sink for methane already in the atmosphere, which is much more restricted because of the very slow diffusion rates of methane from the atmosphere into the soil.

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References

Adamse, A.D., Hoeks, J. and De Bont, J.A.M. (1971) Microbial activities in soil near natural gas leaks. *Antonie van Leeuwenhoek* **37**:251-252

Baggott, S.L., Davidson, I., Dore, C., Goodwin, J., Milne, R., Murrells, T.P., Rose, M., Watterson, J.D. and Underwood, B.: 2003, 'UK Greenhouse Gas Inventory,1990 to 2001(Annual Report for submission under the Framework Convention on Climate Change).'

Bender, M. and Conrad, R. (1995) Effect of CH_4 concentrations and soil conditions on the induction of CH_4 oxidation activity. *Soil Biol. Biochem.* **27**:1517-1527

Boeckx, P. and van Cleemput, O. (1996) Methane oxidation in a neutral landfill cover soil: influence of moisture content, temperature and nitrogen turnover. *Journal of Environmental Quality* **25**:178-183

Bognor, J., Meadows, M. and Czepiel, P. (1997) Fluxes of methane between landfills and the atmosphere: natural and engineered controls. *Soil Use and Management* **13**:268-177

Börjesson, G. and Svensson, B.H. (1997) Seasonal and diurnal methane emissions from a landfill and their regulation by methane oxidation. *Waste Management and Research* **15:**33-54.

Christophersen, M., Kjeldsen, P., Hoslst, H. and Chanton, J. (2001) Lateral gas transport in soil adjacent to an old landfill: factors governing emissions and methane oxidation. *Waste Management Research* **19**:126-143.

Conrad, R. (1996) Soil microorganisms as controllers of atmospheric trace gases (H2, CO, CH4, OCS, N2O and NO). *Microbiological Reviews* **60**:609-640.

Czepiel, P.M., Crill, P.M. and Harriss, R.C. (1995) Environmental factors influencing the variability of methane oxidation in temperate zone soils. *Journal of Geophysical Research* **100**:9359-9364.

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**:16,721-16,729.

Haarstad, K. (1997) Methane in landfills: production, oxidation and emissions. In *Proceedings Sardinia 97, Sixth International Landfill Symposium,* S. Margherita di Pula, Cagliari, Italy; 13-17 October 1997, pp 33-44.

Hanson, R.S. and Hanson, T.E. (1996) Methanotrophic Bacteria. *Micobiological Reviews* **60**:439-471.

Hoeks, J (1972) Changes in the composition of soil air near leaks in natural gas mains. *Soil Science* **113**: 46-54

Hütsch, B.W. (2001) Methane oxidation in non-flooded soils as affected by crop production. *European Journal of Agronomy* **14**:237-260

IPCC (1996) Climate Change 1995: The Science of Climate Change: Contribution of Working Group I to the Second Assessment of the Intergovernmental Panel on Climate Change (JT Houghton, LG Meira Filho, BA Callender, N Harris, A Kattenberg and K Maskell, - Eds) Cambridge University Press

IPCC (2001) Climate Change 2001: The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change (J. T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P. J. van der Linden and D. Xiaosu, - Ed.) Cambridge University Press

Jones, H.A. and Nedwell, D.B. (1990) Soil atmosphere concentration profiles and methane emission rates in the restoration covers above landfill sites: Equipment and preliminary results. *Water Management and Research* **8**:21-31

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

Kightly, D., Nedwell, D.B., Cooper, M. (1995) Capacity for methane oxidation in landfill cover soils measured in laboratory-scale soil microcosms. *Applied and Experimental Microbiology* **61**:592-601

Knowles, K. (1999) Factors affecting the localisation of transformations of nitrogen and methane in soils. In *Microbial Biosystems: New Frontiers, Proceedings of the 8th International Symposium on Microbial Ecology, Bell, C.R., Brylinsky, M. and Johnson-Green, M. (Ed).* Atlantic Canada Society for Microbial Ecology, Halifax, Canada.

Lamb, B.K., Westberg, H., Kashinkunti, R, Czepiel, P.M., Crill, P.M., Harriss, R., Kolb, C.E., and McManus, J.B. (1996). Oxidation of methane in soils from underground natural gas pipeline leaks. Final Report on contract no. 5091-254-2148 for Gas Research Institute, Chicago, USA. (GRI-94-0257.35)

Smith, K.A., Ball, T., Conen, F., Dobbie, K.E., Massheder, J. and Rey, A. (2003). Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *European Journal of Soil Science* **54**:779-791.

Smith, K L Colls J J and Steven M D. (2004) A facility to investigate effects of elevated soil gas concentration on vegetation. *Water Air and Soil Pollution* (in the press)

Smith, K.L., Steven, M.D. and Colls, J.J. (2004) Use of hyperspectral derivative ratios in the red-edge region to identify plant stress responses to gas leaks. *Remote Sensing of Environment* **92**:207-217

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.

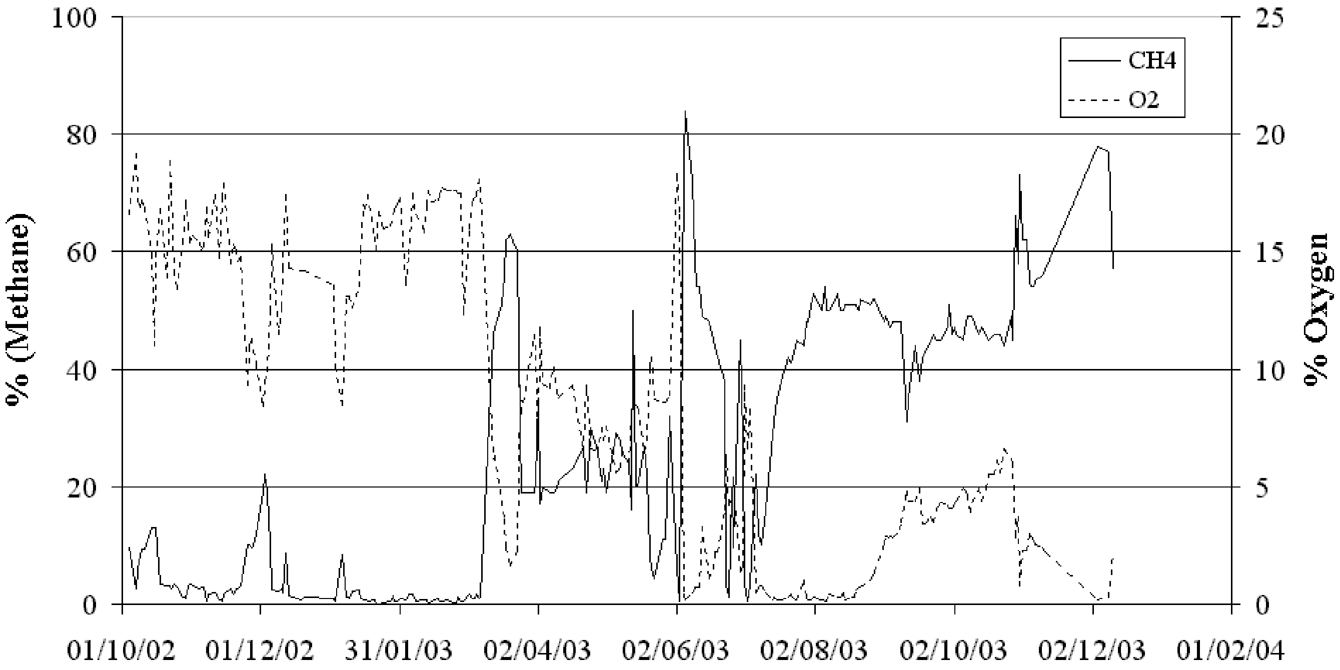


Figure 1: Methane and oxygen levels in early-gassed grass plot D.

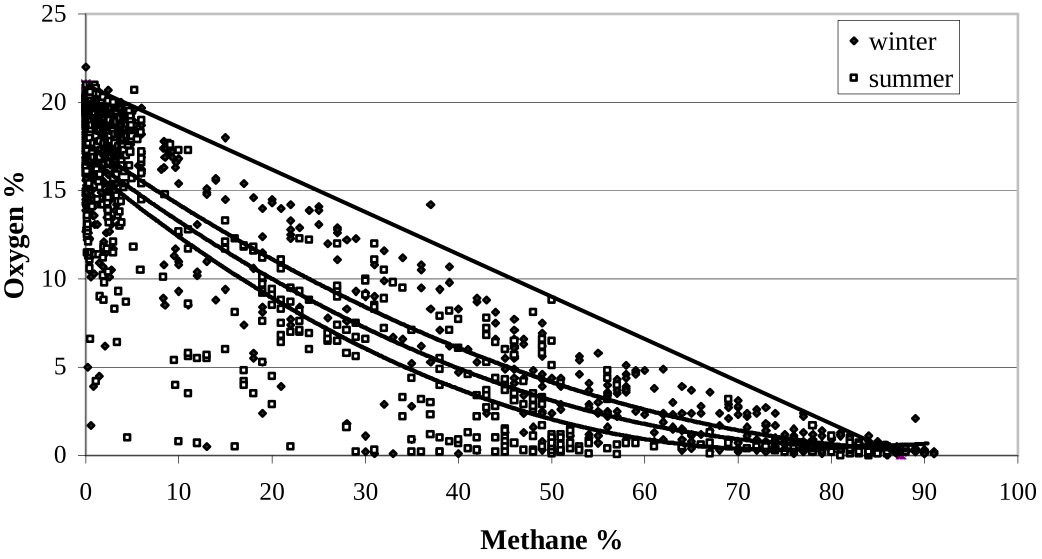


Figure 2. Soil oxygen expressed as a function of soil methane. The straight line represents the relationship expected with simple displacement. The fitted curves represent averages (from bottom to top respectively) of summer (April – September 2003), annual (October 2002 – December 2003), and winter (September – March, both years) data.

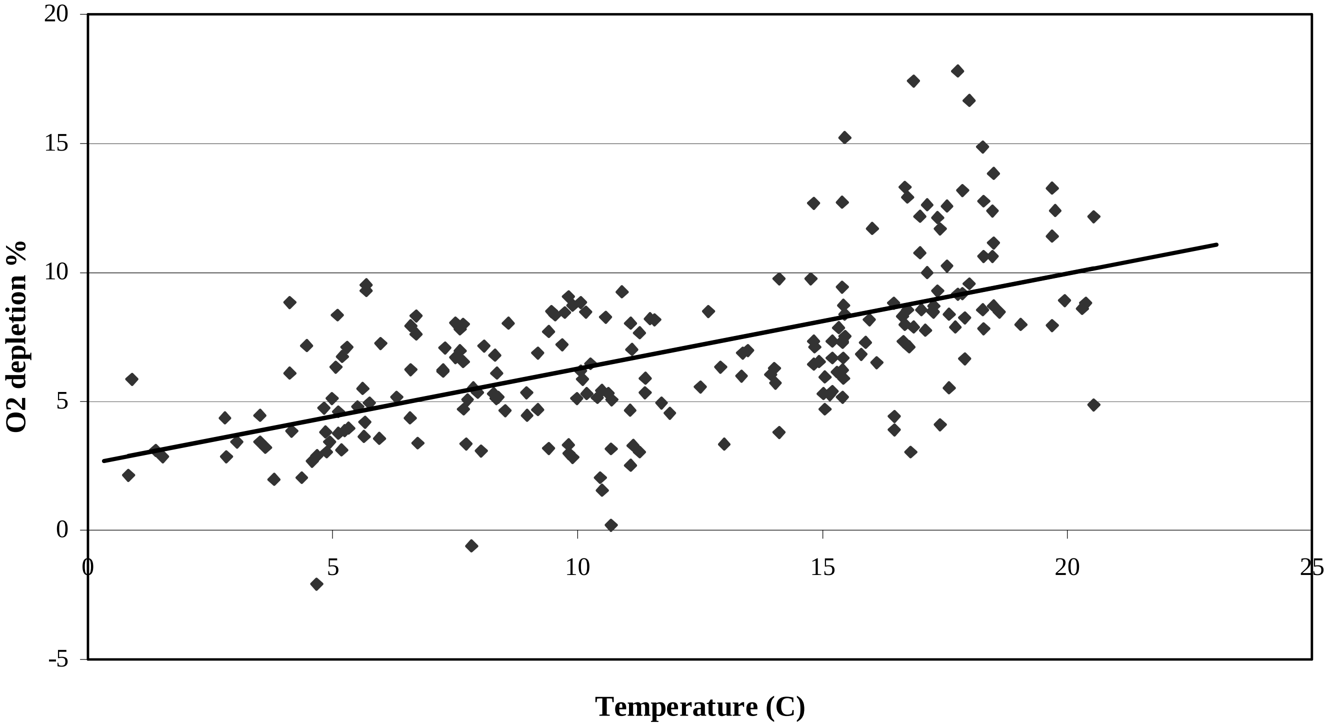


Figure 3. Oxygen depletion in grass plots as a function of soil temperature at 10 cm depth, for the measured methane range 10-60%.

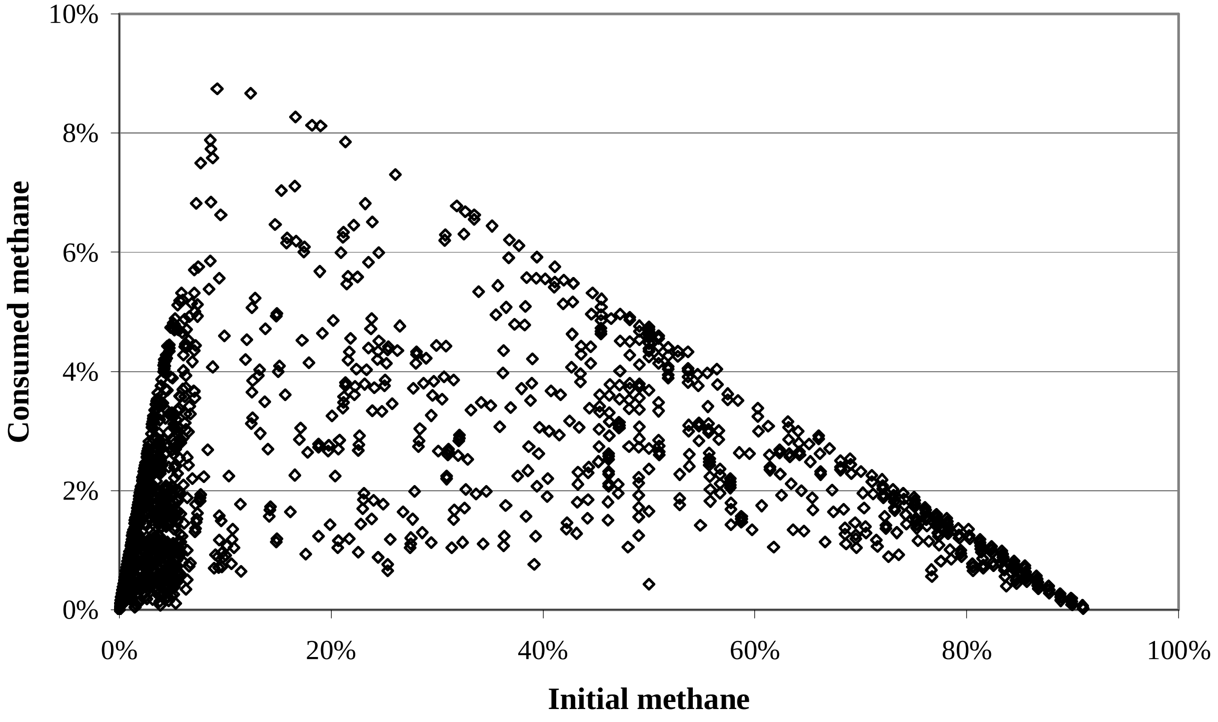
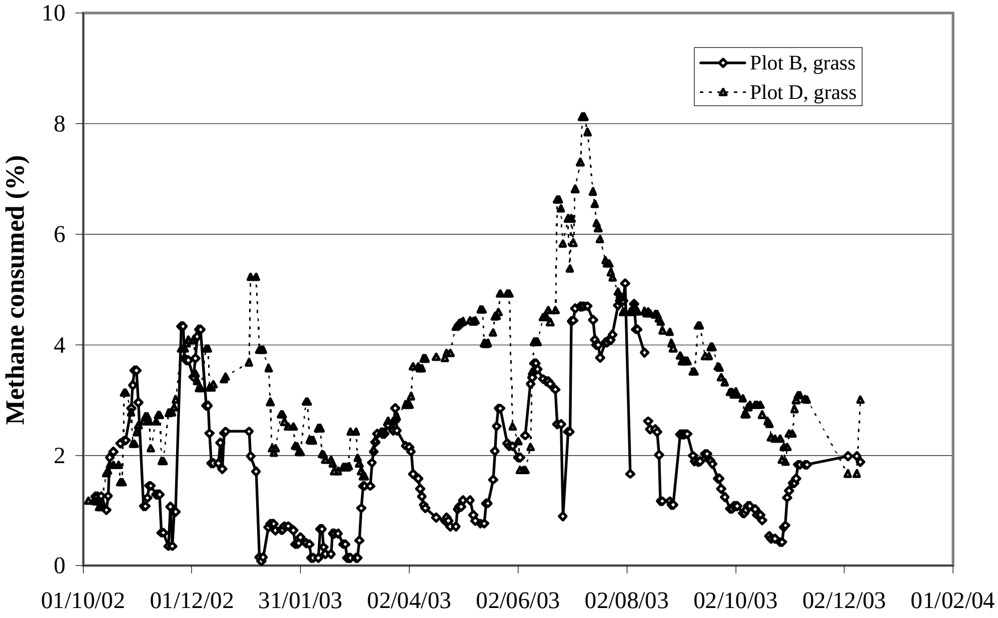
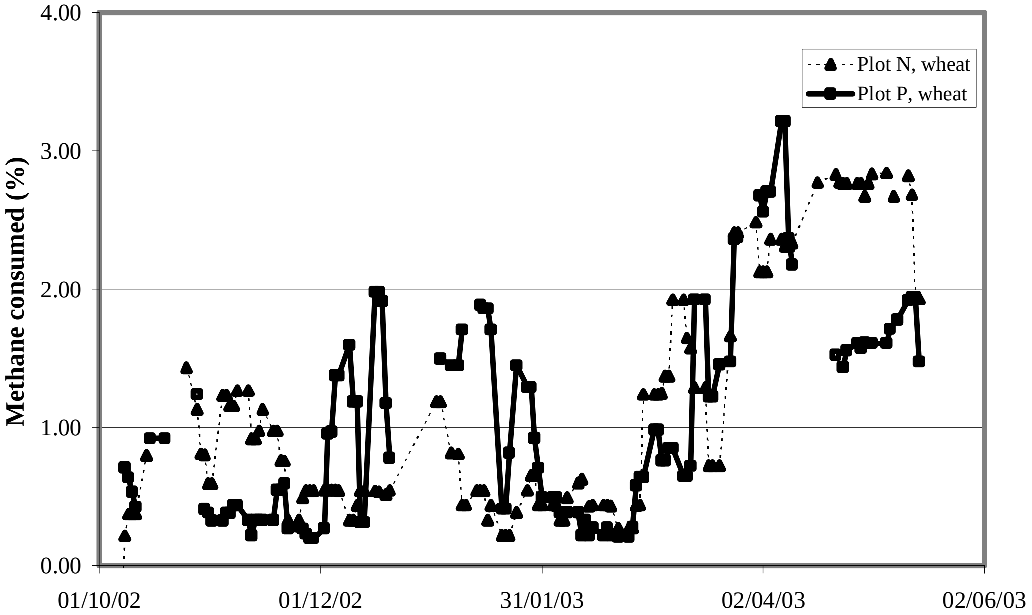


Figure 4. Estimated values of consumed and initial methane


10
8
6
4
2
0
Methane consumed (%)
01/10/02
01/12/02
31/01/03
02/04/03
02/06/03
02/08/03
02/10/03
02/12/03
01/02/04
Plot B, grass
Plot D, grass


4.00
3.00
2.00
1.00
0.00
Methane consumed (%)
01/10/02
01/12/02
31/01/03
02/04/03
02/06/03
Plot N, wheat
Plot P, wheat

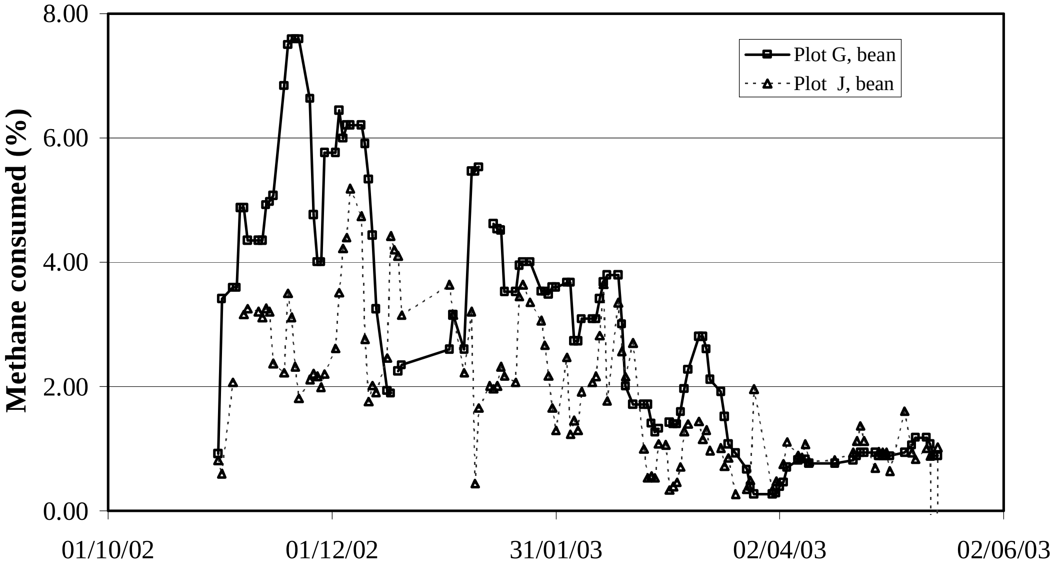


Figure 5: Methane consumption estimates in early-gassed crops

(a) grass; (b) wheat; (c) bean