Clymo R.S. & Hargreaves K. (1994) Methane emissions from UK
agriculture, forests, wetlands and wastes. A. Natural wetlands.
Watt Committee Report #28: Methane Emissions.
Ed. Williams A. London, Watt Committee on Energy
111-121

CHAPTER 11

A. NATURAL WETLANDS

11A.1 INTRODUCTION

Methods for measuring methane emission from wetlands range from studies of emission from small (< 1 m^2) plots using flux chamber techniques, through to estimates for emission at the regional scale (1000 km^2) based on measurements made using aircraft to collect air samples. In both cases the estimating of an annual methane emission rate for a country requires careful scaling up from these measurements. This chapter describes work being carried out in the UK to estimate this emission rate for the UK and compares the results obtained from several different approaches.

The industrial sources of methane emissions share the characteristic that most of their gas passes through well-defined, if somewhat leaky, conduits within which concentrations and flows can be measured. Natural wetlands, in contrast, are diffuse sources which vary in intensity with time and space, and which occupy large areas. Methods for estimating gas effluxes from wetlands must be adapted to these characteristics.

11A.2 THE SORTS OF WETLAND

The common feature of all wetlands is that their substratum (soil, peat) is porous and at least partly waterlogged, and it contains microorganisms and matter which they can attack. Close to the interface of water with air the microorganisms use dissolved oxygen. It is replaced by diffusion from the air, but the rate of diffusion of most gases in water is only about 1/10,000 of the rate in air. More important, it is usually lower than the rate at which the microorganisms use it up. All but the surface of the porous matrix becomes anoxic. It is in these anoxic conditions that methane is produced by microorganisms. Maintenance of suitable anoxic conditions is dynamic and depends on the continued activity of one set of aerobic microorganisms, while methane production is also dynamic and depends on a different set of microorganisms.

Wetland terminology is confused, but it is convenient to distinguish wetlands which have a predominantly inorganic substratum from those which have a predominantly organic substratum. The former dominate in the Tropics and include many swamps, both forested and non-forested including rice paddies; the latter dominate in Temperate and Boreal latitudes and are mostly peatlands (Table 11.1). In the UK, peatlands are the dominant type of wetland, and the rest of this article concerns them only.

11A.3 THE STRUCTURE OF PEATLANDS

Peat is the dead and only partly decomposed remains of the plants that grow, or grew, on the suface of the peatland. When it dies the plant matter is in, or falls into, a surface layer which is damp, porous, and with ample oxygen. It decays relatively rapidly at first as the result of attack by fungi and bacteria. As more matter falls on the surface the original material becomes compacted and this impedes water flow. Excess water therefore runs off laterally while the peat below remains saturated. During summer drought the watertable drops into the peat but autumn rain refills the pores and the watertable rises again. The anoxic zone follows the watertable down and up.

There seem to be two main places where methane is produced in peatlands. There is a highly active zone just below the watertable, and methane is also produced continuously, though at a much lower rate, throughout the full depth of peat. The highly active zone near the surface may be perhaps 10-20 cm below the surface, while the peat mass as a whole may be 200-1000 cm deep. The methane produced in the main peat mass diffuses upward, but diffusion is a slow process so this deep methane produces a relatively low background efflux throughout the time that the surface is not frozen. The rate of production of methane in the surface zone is very dependent on temperature, increasing markedly in spring and summer while the watertable remains high (Table 11A.2).

The profile of partial pressure of methane in the main peat mass and details of the surface profile are shown in Figure 11A.1.

(i.e. the distance of uniform upwind terrain) are approximately 100-200 m per 1 m equilibrated surface layer (Monteith & Unsworth,(4)). Measurements of methane at a single location thus integrate over a large upwind area and overcome the problem of extrapolating from measurements on individual flux chamber samples to a whole area of peatland.

11A.4.2.1. Flux-Gradient Technique

In this method methane concentrations at a series of heights above the bog surface are determined using a flame-ionisation detector fitted upstream with a platinum catalyst to remove higher hydrocarbons. Measurements of windspeed, temperature and vapour pressure are also made at several heights above the surface. Each "profile" measurement takes ten minutes giving potentially six estimates of methane emission flux per hour. Fluxes are calculated according to the equation:

$$F = -k^2 \frac{du}{dln(z-d)} \frac{d\chi}{dln(z-d)} (\phi_m \cdot \phi_h)^{-1} \qquad 11.2$$

where:
F = methane flux ($\mu g\ m^{-2}\ s^{-1}$),
k = 0.41 (von Karmann's constant),
u = windspeed ($m\ s^{-1}$) at height z (m),
d = zero plane displacement (m),
χ = methane concentration ($\mu g\ m^{-3}$)

and the terms ϕ_m and ϕ_h are correction factors introduced to correct for buoyancy effects present in stable and unstable conditions. The derivation of this equation and calculation of the correction factors are described extensively in the literature: Monteith & Unsworth (4), Hicks et al (5), Garland (6), Webb et al (7). An example of a concentration profile for methane is shown in Figure 11A.3.

The sensitivity of this technique depends on instrument response and meteorological conditions. The minimum detectable flux with the existing system is of the order of 30-50 ng $m^{-2}\ s^{-1}$ in favourable (low windspeed) conditions.

11A.4.2.2 Eddy Correlation Technique

This technique is theoretically simpler and more elegant than the flux gradient technique. It relies on the fact that transport of methane away from the surface must be via the vertical component of windspeed, and hence that there must be a correlation between fluctuations in vertical wind velocity and fluctuations in methane concentration. The methane flux is thus calculated from the equation:

$$F = w' \cdot \chi' \qquad 11.3$$

where:

w' is the instantaneous departure of the vertical wind velocity from the mean wind velocity, w (both in $m\ s^{-1}$) and χ' is the instantaneous departure of the methane concentration from the mean methane concentration, χ (both in $\mu g\ m^{-3}$).

Whilst this requires only two measurements to be made it does require the instruments to have very fast response times (better than 10 Hz). Measurement of w' is fairly straightforward using a conventional (but expensive) ultrasonic anemometer capable of logging three components of wind velocity and temperature at 21 Hz. An instrument capable of measuring rapid fluctuations in methane concentration (a tunable diode laser or TDL) has recently been developed commercially and has been used by ITE during 1993. It is capable of detecting methane fluxes of the order of 5 ng $m^{-2}\ s^{-1}$.

11A.4.2.3 Eddy Accumulation or Conditional Sampling

This method, like eddy correlation, depends on the fluctuations in methane concentration which occur with variations in the vertical component of windspeed. However, in this case the only expensive equipment required

A characteristic of most peatlands is that they have a heterogeneous surface with low (30-50 cm) hummocks and intervening lawns and wet hollows. As methane passes slowly up through the anoxic layer of hummocks it seems that some of it, at least, is oxidised to carbon dioxide and reaches the atmosphere in that form. These three habitat types interdigitate on a scale of a few metres. The efflux of methane differs among types by more than one order of magnitude and this makes extrapolation of point measurements to whole peatlands an error-prone process.

11A.4 TYPES OF METHODS FOR MEASURING METHANE EFFLUX

There are four main types of method for measuring gas effluxes from peatlands:

(i) flux chambers ('upturned buckets') in which the rate of change in methane concentration gives the efflux over distances of 0.1 - 1 m^2;

(ii) micrometeorological measurements of concentration profiles at a point which integrate fluxes over areas of 10^3 - 10^5 m^2 upwind;

(iii) measurements of concentration increase over long path (typically 25-100 m) under low level inversions (10^4 - 10^6 m^2);

(iv) concentration profiles measured by equipment in aircraft which gives averages over 10^8 - 10^9 m^2 (100 - 1000 km^2).

The next sections describe these four in more detail.

11A.4.1 Flux chambers

A box with one open face of known area (A) is placed with the open face on the ground and sealed to it. The concentration of methane is measured in gas samples taken at intervals from inside the box. The slope ($\Delta C/\Delta t$) is calculated. Usually it is positive and constant. The volume of air (V) inside the box is measured. The efflux of methane (F) is then:

$$F = (V/A) \;.\; \Delta C/\Delta t \qquad 11.1$$

Technical details differ considerably. Usually a cylinder or rectangle of a material impermeable to gases is sunk in the ground and left as a permanent base. The box is sealed to the top of the base when needed. Simply treading on the ground can markedly affect the efflux so samples of gas may be withdrawn through long (15 m) nylon tubes. Wet sites are easily damaged and need to be protected with wooden walkways. The concentration of methane in gas samples is usually measured by gas chromatography, but on-site quadrupole mass spectrometry (QMS) has been used too.

In the Alaskan Arctic the efflux has been found to change by 3 - 4 orders of magnitude as the seasons change (Whalen & Reeburgh,(4)) and to differ by an order of magnitude at sites only a few metres apart, being generally greater at the wetter sites. The same sorts of difference have been found in the UK but the size of differences among sites is smaller: typically 1-5 fold (Table 11A.2).

Flux chamber measurements are useful in the study of processes, and are sufficiently simple to be repeatable at frequent intervals but integration over large areas requires assumptions which may be difficult to justify. The methods which follow integrate automatically but require more complex apparatus and are therefore difficult to keep going for protracted times.

11A.4.2 Micrometeorological methods

Micrometeorological techniques for determining methane emissions rely on the use of fast-response instruments to measure methane concentrations together with simultaneous measurements of windspeed, temperature and vapour pressure over the site. For the first three techniques described here a uniform, even site is required in order to allow the surface layers of air to equilibrate with the surface emissions to an adequate depth and to permit the detection of vertical flux gradients in the absence of any horizontal fluxes. "Fetch" requirements is an ultrasonic anemometer to determine the three components of turbulence. A computer control/logging system is used to divert sample gas into either an "updraft" bag or a "downdraft" bag according to the sign of w. These samples may then be analysed by a more conventional technique such as gas chromatography or flame ionisation detector and the flux of methane calculated as:

$$F = b(\zeta) \cdot \sigma_w(\overline{\chi^+} - \overline{\chi^-}) \qquad 11.4$$

where $b(\zeta)$ is an empirical coefficient determined by experiment, and has been shown to be constant over a wide range of stabilities (Businger & Oncley, (8)), σ_w is the standard deviation of w (m s^{-1}) and χ^+ and χ^- are methane concentrations in the "up" and "down" bags respectively. The main problems in this technique are the need for very fast response valves and the careful tuning of the system to ensure that lag times in sample lines are consistent. Failure to do this leads to "up" sample entering the "down" bag and vice versa.

11A.4.3 Accumulation under low level inversions

This method has the advantage of not requiring the large uniform areas demanded by micrometeorological techniques, and yet retains the ability to make estimates of fluxes integrated over many square kilometres. However, the technique only succeeds in relatively calm conditions when a temperature inversion occurs close to the ground. Such conditions are usually found only at night, or during the winter when net radiation is small. In these circumstances the top of the boundary layer acts as a "lid" on a large box. Emission of methane from peatlands thus results in an increase in methane concentration under the inversion which can be measured using a long-path infra-red absorption detector for methane (Siemens-Plessey Hawk). Measurement of the inversion height and upper air windspeeds is performed using a doppler sodar instrument (Remtech). The methane flux is then calculated from the rate of increase of methane concentration and the depth of the inversion layer.

11A.4.4 Aircraft-borne equipment

This technique involves using an aircraft fitted with air sampling equipment to measure the emission plume from a large area. Sampling is carried out in line with the wind direction across the region, and ascents are made taking samples from different heights to determine concentration gradients within the boundary layer. Samples are returned to the ground for analysis by a conventional technique (such as a flame ionisation detector). Additional samples are taken concurrently at ground level to assist in assessing spatial and temporal variability of emissions. Boundary layer depth and mean windspeeds are determined using data from instruments such as a doppler sodar and aircraft soundings, and data from nearby radio-sonde ascent stations. The measurements of methane concentration both upwind and within the area of the emission source allow an estimate of the landscape methane emission flux to be made using a simple one-dimensional diffusion model.

For the remainder of this chapter measured fluxes will be expressed as mg m^{-2} day^{-1} to abide by the accepted conventions. However, it must be realised that most micrometeorological measurements of methane emissions take place over typically 10-100 minutes, so the extrapolation to a daily flux must be treated with care. If the carbon balance of an ecosystem is of interest the use of molar rather than mass units would be preferable. For methane:

$1.0 \text{ mg m}^{-2} \text{ day}^{-1} = 11.6 \text{ ng m}^{-2} \text{ s}^{-1} = 62.5\ \mu\text{mol m}^{-2} \text{ day}^{-1}$.

11A.5 CURRENT ESTIMATES OF METHANE EFFLUXES FROM PEATLANDS

11A.5.1 World estimates

World estimates are the sum of products of areas of wetland type and unit fluxes specific to that type. The estimates of area have begun to stabilise: the most detailed up-to- date ones are those of Matthews & Fung (1987) summarised in Table 11A.1. Estimates of unit rates of methane efflux are still changing by factors of 3-5 though the changes for different wetland types have recently been compensating so that five recent estimates for the world total annual wetland efflux all fall in the range 80-111 Mt/yr (Bartlett & Harriss, (2)).

11A.5.2 Area of peatland in the UK

Estimates of the total area of peatland in the UK are rather variable, partly owing to uncertainties in surveying, and partly to changes in afforestation and peat cutting. However, the best available estimate at present is based on a 10 by 10 km grid map of the UK, and suggests a total area of peat in the UK of 12,307 km^2 (Smith and Cresser, (9)).

11A.5.3 Fluxes from unit areas

The annual rates (Table 2) estimated by workers at Queen Mary and Westfield College from measurements by QMS in flux chambers at Ellergower Moss (SW Scotland) are similar to those measured by the same group at Moor House (Cumbria) 21 years ago using more primitive sampling methods and measuring methane by IRGA (Infra-red gas analysis). In both cases there were occasional high values. At Moor House, with 3 replicates in each habitat on each of 5 monthly samples, the high values were sporadic, but at Ellergower, with measurements on 6 replicates in each habitat, the results on a single occasion were usually similar to one another while they differed between sample dates.

For Ellergower, the proportions of the three habitat types within the hectare around the sampling point multiplied by the unit habitat effluxes give a weighted mean annual efflux of 9.5 $g/m^2/yr$. If this rate applied to the whole UK area of peatland the annual efflux of methane would be **120 kt/yr.**

11A.5.4 Fluxes measured at the field scale

Measurements of methane emission at the field scale were carried out during a joint field experiment at Strathy Bog, Sutherland, Scotland in July and August 1992. Collaborating institutes were:

Institute of Terrestrial Ecology, Edinburgh (ITE);
University of Manchester Institute of Science and Technology (UMIST);
University of Edinburgh (IERM).

All the above field scale techniques were employed at the site with the exception of the eddy correlation method, and only limited data were obtained from the eddy accumulation system as the analytical instrument was still under development.

11A.5.5 Ground-based Measurements

From the data analysed to date, methane emission fluxes were found to be in the range 4 to 21 mg m^{-2} day^{-1}. However, these fluxes were observed during periods of very low windspeed conditions and errors in the calculation of the fluxes are relatively large. It is also significant that no fluxes were detected in the early stages of the experiment. In the two months prior to the experiment virtually no rain fell and the bog, which would normally have had extensive wet, anoxic areas, was atypically dry. The fluxes measured towards the end of the experiment occurred after rainfall which restored anoxic conditions to some parts of the bog. Even so, the surface was still drier than would be expected in an ordinary year. These conditions would have led to a reduction in the methane emission rate when compared with the same period in more normal years.

On the basis of these effluxes and taking into account the large assumptions made in extrapolating from a few days measurements at one site to the whole of the UK, the annual efflux for the UK would be in the range **18 - 95 kt/yr** and of the same order as those for the flux chambers.

11A.5.6 Aircraft-based Measurements

Sampling was carried out by the UMIST Cessna 182 aircraft on several days during the experiment, generally in westerly flow situations. Samples were taken over a 1 minute period during horizontal flight at airspeeds of 40 to 50 m s^{-1}. Results showed a clear increase in concentration from west to east, and a decrease in concentration with height over the experimental site. Seven case studies were chosen during conditions of constant flow and near-neutral atmospheric stability. Using these data in the one-dimensional model produced seven estimates of the flux ranging from 85 to 340 mg m^{-2} day^{-1}. On the basis of these estimates the annual UK efflux of methane would be 380 - 1530 kt/yr. This is an order of magnitude larger than the ground- based measurements.

11A.6 CONCLUSIONS

A wide range of estimated annual methane emission rates (effluxes) were obtained: the minimum was 18-95 kt/yr (using micrometeorological techniques), and the maximum 380-1530 kt/yr (using aircraft measurements). An estimate based on flux-chamber techniques yielded an emission rate of 120 kt/yr. The reasons for the large discrepancies between the aircraft values and the others are not readily apparent, but further study should produce closer agreement between the estimates.

11A.7 REFERENCES

1. Matthews, E. & Fung, I. (1987). Methane emission from natural wetlands: global distribution, area, and environmental characteristics of sources. Global Biogeochemical Cycles 1 61-86.
2. Bartlett, K.B. & Harris, R.C. Review and assessment of methane emissions from wetlands. Chemosphere (in press).
3. Clymo, R.S. & Reddaway, E.J.F. (1971) Productivity of Sphagnum (bog moss) and peat accumulation. Hidrobiologia 12 181 - 192.
4. Whalen, S.C. & Reeburgh, W.S. (1992). Interannual variations in tundra methane emission: a 4-year time series at fixed sites. Global Biogeochemical Cycles 6 139-159.
5. Monteith, J.L. & Unsworth, M.H. (1990). Principles of Environmental Physics. Edward Arnold, London.
6. Hicks, B.B., Matt, D.R. & McMillen, R.T. (1989). A micrometeorological investigation of surface exchange of O3, SO2 and NO2. A case study. Boundary Layer Meteorology 47 321-336.
7. Garland, J.A. (1977). The dry deposition of sulphur dioxide to land and water surfaces. Proceedings of the Royal Society of London A 354 245-268.
8. Webb, E.K., Pearman, G.I. & Leuning, R. (1980). Correction of flux measurements for density effects due to heat and water vapour transfer. Quarterly Journal of the Royal Meteorological Society 106 85-100.
9. Businger, J.A. & Oncley, S.P. (1990). Flux measurement with conditional sampling. Journal of Atmospheric and Ocean Technology 7 349-352.
10. Smith, C & Cresser, M. (1993). *Personal Communication.* University of Aberdeen, Dept. of Plant and Soil Science.

TABLE 11A.1 WORLD WETLAND AREA AND METHANE EFFLUX.

	Latitude Range	Area $10^3 km^2$						CH_4 efflux Mt/yr					
Type		FB	NFB	FS	NFS	A	Total	FB	NFB	FS	NFS	A	Total
Arctic	80N-60N	929	506	7	26	0	1467	8.9	4.8	0.1	4.8	0.0	14.1
Boreal	60N-15N	889	381	35	87	0	1392	12.6	5.0	0.5	5.0	0.0	19.6
Temperate	45N-20N	174	3	80	114	10	381	2.0	0.0	1.0	0.0	0.1	4.1
Tropical	20N-30S	80	12	905	736	152	1884	2.4	0.5	24.3	0.5	5.0	63.1
Temperate	30S-50S	5	0	51	47	33	135	0.1	0.0	0.6	0.0	0.2	1.4
Total							5263						102.3

FB=Forested bog; NFB=Non-forested bog; FS=Forested swamp; NFS=Non-forested swamp; A=Alluvial.

Areas from Matthews & Fung (1987).
Effluxes from Bartlett & Harris (in press) using areas from Matthews & Fung with more up-to-date estimates of unit CH_4 effluxes.

TABLE 11A.2 METHANE EFFLUX FROM PEATLAND: ELLERGOWER MOSS, SW SCOTLAND DURING 1992 EXPESSED ON A MASS AND A MOLECULAR BASIS.

Units : (mg m^{-2} day^{-1})

Month	Hummock	Lawn	Hollow	
April	-ve	-ve	-ve	
May	4	1	6	
June	166	362	317	
July	23	41	36	
August	19	70	63	
September	26	52	50	
October	(10)	(12)	(12)	
November	+ve	+ve	+ve	
*Sum	7.5	16.1	14.2	Units:g m^{-2} yr^{-1}
Clymo & Reddaway+	2.3	5.3	9.5	

+ve, -ve indicate slopes too small for reliable measurement. Values in parentheses are estimates.

Units : (mmol m^{-2} day^{-1})

Month	Hummock	Lawn	Hollow	
April	-ve	-ve	-ve	
May	0.3	0.1	0.4	
June	10.4	22.6	19.8	
July	1.4	2.6	2.3	
August	1.2	4.4	3.9	
September	1.6	3.3	3.1	
October	(0.6)	(0.6)	(0.6)	
November	+ve	+ve	+ve	
*Sum	0.5	1.0	0.9	Units:mol m^{-2} yr^{-1}

* Calculated as sum of (30 * each monthly value). Assumes no significant efflux from Nov - Mar.

+ Results from Clymo & Reddaway (1971) for Moor House, Cumbria. (11.50 - 24.96)

Figure 11A.1

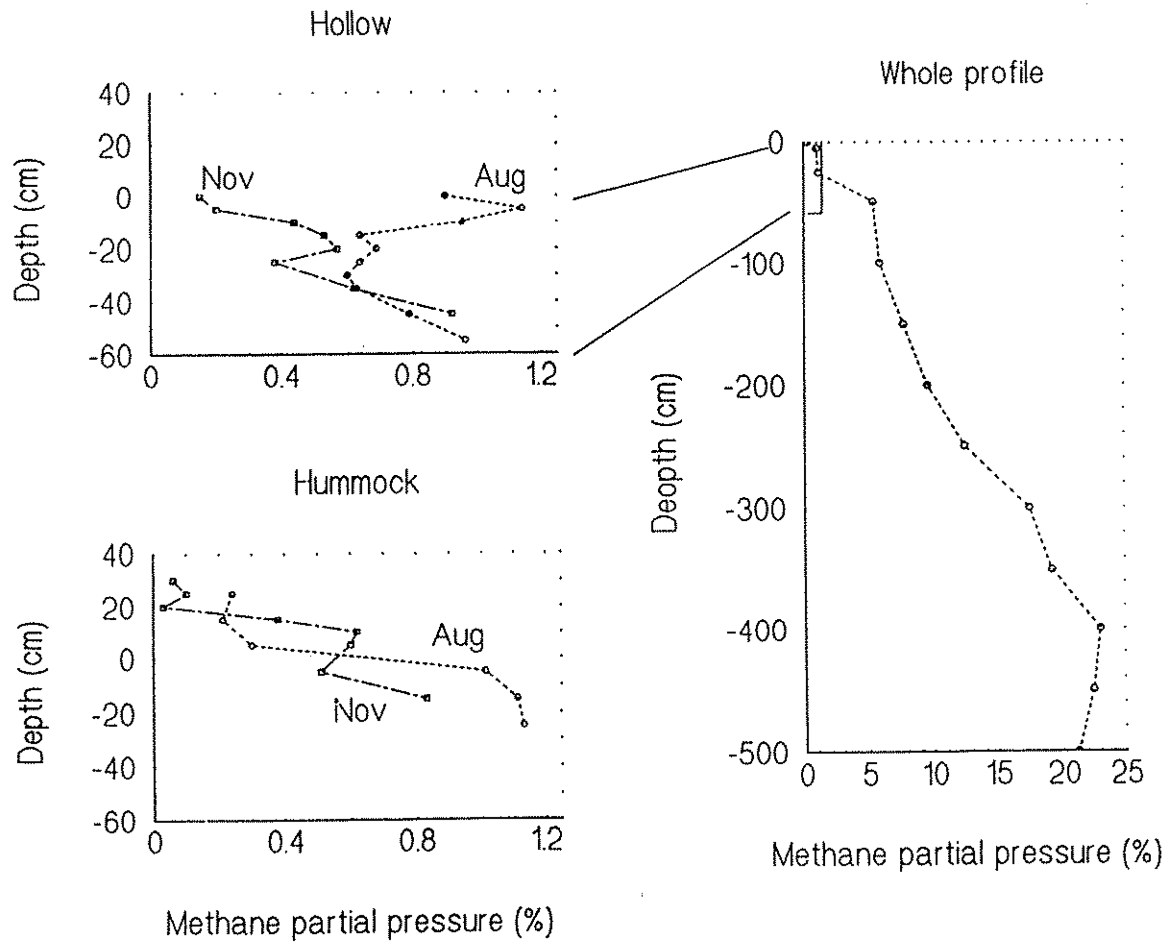

Hollow
Depth (cm)
40
20
0
-20
-40
-60
0
0.4
0.8
1.2
Nov
Aug
Hummock
Depth (cm)
40
20
0
-20
-40
-60
0
0.4
0.8
1.2
Aug
Nov
Methane partial pressure (%)
Whole profile
Deopth (cm)
0
-100
-200
-300
-400
-500
0
5
10
15
20
25
Methane partial pressure (%)

Figure 11A.2

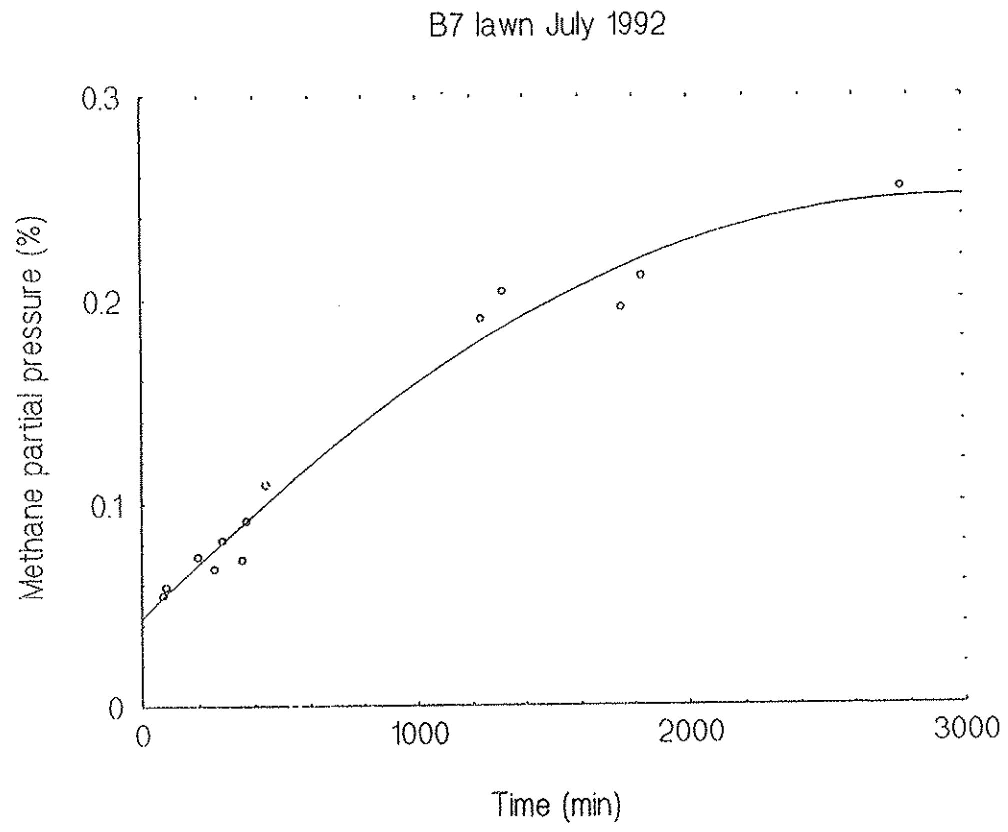
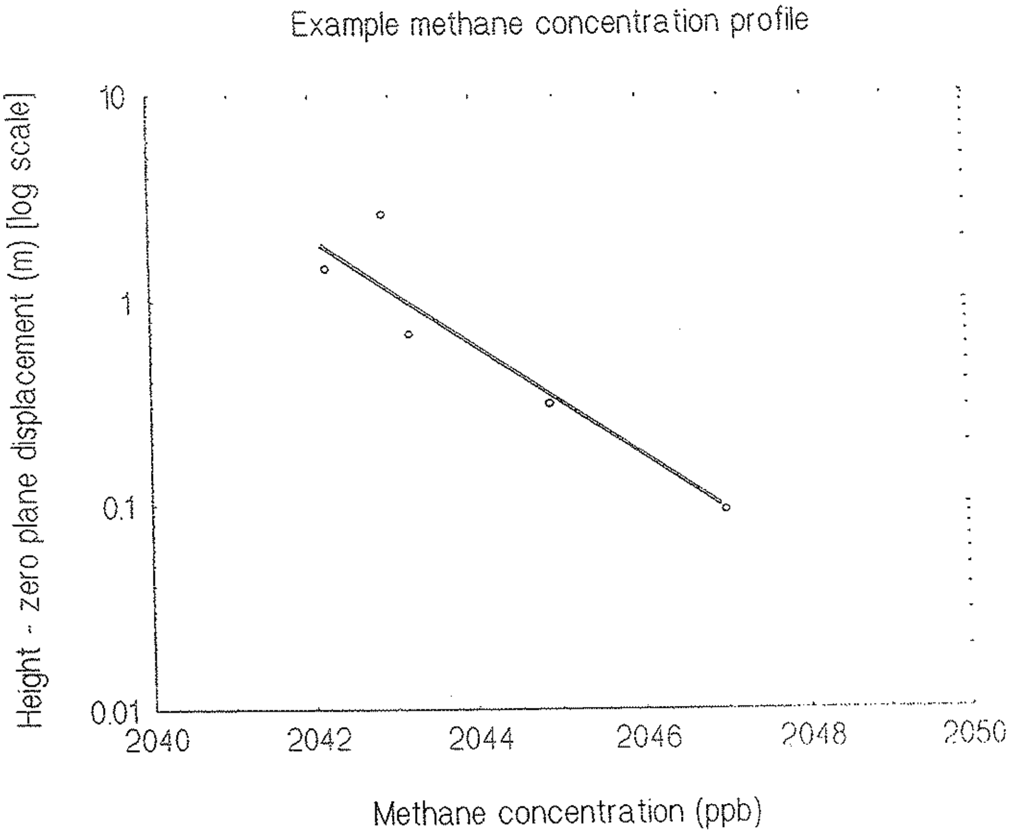

B7 lawn July 1992
Methane partial pressure (%)
0.3
0.2
0.1
0
0
1000
2000
3000
Time (min)

Figure 11A.3


Example methane concentration profile
Height - zero plane displacement (m) [log scale]
10
1
0.1
0.01
2040
2042
2044
2046
2048
2050
Methane concentration (ppb)

METHANE EMISSIONS

Report of a Working Group appointed by the Watt Committee on Energy

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