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PATTERNS OF METHANE EMISSION FROM EXCRETA OF GRAZING ANIMALS

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Summary—Emissions of methane from dung pats under field and laboratory conditions have been determined. A range of dung materials from cattle and sheep and from cattle with different background managements was used and results indicated that all acted as significant sources of CH_4 over a relatively short period, usually less than 10–15 days. The patterns of release were similar, although modified by environmental conditions. A strong exponential relationship was determined between total CH_4 released and the C-to-N status of the dung, i.e. a greater rate of release with higher N status. Similar trends and patterns were displayed under controlled conditions. It was clear that the major effect came from dung itself with only a relatively small positive interaction when soil was present. Emission was stopped completely by a fumigation (chloroform)–evacuation procedure; evacuation alone (i.e. with the sample under vacuum) changed the pattern of release and increased the total amounts emitted. Although the emissions of CH_4 from dung were significant, the amounts were small relative to the estimated total release from a complete livestock production system, i.e $<0.2\%$ of the total CH_4 output from a dairy farm.

INTRODUCTION

Rising atmospheric concentrations of methane have been implicated as an important contributing factor to global warming and potential greenhouse effects (Rhode, 1990). Although the general perceptions of the extent of change in concentration of this trace gas and of the relative importance of various sources may be altering as new information becomes available, it is clear that agricultural production systems are one of the most important sources especially within temperate regions (Bouwman, 1990; Crutzen, 1991; IPPC, 1992; Moss, 1993). In the main, most of the CH_4 produced within agricultural systems comes from animal husbandry. A review (Williams, 1993a), which provided an inventory for all known U.K. sources, showed that ca. 31% of the annual CH_4 output was derived from agriculture, most of which originated from animal production.

The most potent source of CH_4 generation is the ruminant digestion system and substantial quantities of CH_4 are released. Recent estimates for U.K. dairy cows indicated that 95 kg CH_4 are released each year by an adult productive dairy cow (Williams, 1993a). However, there are other components of livestock management which may contribute to the output of CH_4. Thus at a total farm system level, calculations indicate that farm waste (both during storage and after application to the field), silage effluent and dirty water may all make a substantial contribution to net emission (Jarvis and Pain, 1994). A further component has been an assumed contribution from the dung which is deposited whilst animals are grazing (Williams, 1993a).

Freshly voided dung has a considerable potential to be a source of CH_4. It carries an appropriate population of microorganisms (Dar and Tandon, 1987), it is warm, moist and has a readily available substrate carbon supply: contact with soil may enhance the potential for CH_4 generation. Only recently have measurements been made to quantify CH_4 emission from this source under field conditions (Williams, 1993b). Many budgeting estimates have therefore been made on the basis that an arbitrary proportion of the volatile solids of the dung will be converted to CH_4. Until recently this had been assumed to be 10%. At this rate the contribution from dung dropped in the field was recently estimated to be 20% of U.K. agriculture's contribution (Williams, 1993a). The assumption that 10% of volatile solids would be converted is now seen to be an over-estimate and Hashimoto and Steed (1993) have suggested that this should be reduced to 1% of the volatile solid content with therefore major effects on calculations of the potential release of CH_4 from this source.

However, there is still little information upon which to base firm conclusions and decisions on source strength from dung. Our objective was therefore to determine CH_4 emissions from a number of faecal materials when these are dropped in the field using both field and laboratory-based experiments. The aim was not only to be better able to describe and define a firmer basis upon which to make estimates

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of the effects at a national level, but also to follow patterns of release and possible mechanisms.

MATERIALS AND METHODS

Field studies

The measurements undertaken in the field were on an area of permanent grassland on an inherently poorly drained soil of the Halstow series. All measurements were made using a static enclosure technique. Rectangular metal enclosure chambers, each of 50 × 15 × 20 cm dimensions, and each with a removable airtight lid which could be clamped to the chamber, were used to enclose treated areas. During periods of measurement the chambers were inserted into the ground to a depth of 2.5 cm. When the soil was dry, a narrow slit was cut into the turf to provide a lead into the soil, otherwise the chambers were pushed or hammered gently into the soil to provide a good seal. Each chamber enclosed a single rectangular "dung pat" which had been applied by hand to the sward (cut to a height of 2 cm) to cover half of the enclosed area of 750 cm^2. A total of 1 kg (wet wt) dung was applied in all treatments. The quantities of dung and areas covered were reduced proportionately in scale from that of normal dung pats deposited by adult cattle under grazing conditions. The pats were left exposed to the atmosphere except during periods of measurement which was normally 30 min but ranged up to 60 min. During each sampling day there were a number (up to 8) of sampling periods, and measurements were taken alternately from paired dung pats so that the effects of enclosure were minimized. Four replicate chambers were used for each experimental run and a fifth chamber was used to provide background measurements in the absence of excreta.

During each sampling period of 30(+) min, the enclosure was placed over the pat and the lid clamped to the top. A sample of the head space was then taken after the defined enclosure period for analysis of CH_4 by removing a 10 ml sample with a syringe through a Suba seal fitted into the lid. The enclosure and lid were then removed, and the next sampling period initiated on the paired treatment area. This procedure was repeated through the day and daily emission rates were then calculated from the mean over the day. In the earlier experimental runs, the head space samples were injected into evacuated 13 ml "Exutainer" tubes (Europa Scientific, Cheshire, U.K.) and stored for later analysis. Prior to analysis, sufficient He was added to each tube so that after withdrawal of a 1 ml subsample, the gas in both tube and syringe remained at atmospheric pressure. The tubes were analysed as soon as possible, and a 1 ml subsample was analysed for CH_4 concentration with a g.c. (FID detector) against standards prepared in He. Where analysis could not be undertaken rapidly, appropriate standards were stored in the same way as the samples and a correction factor derived from any decay in concentration was applied. Emissions were calculated throughout as $\mu g\ CH_4\ m^{-2}\ min^{-1}$. During the later experiments head space samples were sealed within 30 min of collection. Proving trials indicated that emissions from treatment areas were completed on most occasions after 10 days. Our measurement periods therefore extended, in the main, over 10–15 day periods. Samples of each dung were taken at the start of each experiment, air dried at room temperature and analysed for total N and C contents (using an automated Dumas procedure on a Carlo-Erba NA 1500 analyser).

There were five experimental runs using excreta from animals under a range of managements. On each occasion, dung was collected immediately after excretion either (in the case of dairy cattle) while tethered at milking or in the grazed paddock. Sufficient dung was obtained for the experimental run, mixed and applied as described above within 1 h of collection. A range of different excretal types was examined from a wide range of animal types and background managements (Table 1). In the final field experiment, as well as dung, a sample of dairy cow urine was included as a treatment. In this case, urine was applied in the same volume-to-area ratio as

Table 1. Experimental details and background characteristics of dung samples used to determine CH_4 emissions

Experimental material	Animal type	Animal diet	Date of dung application	Dung characteristics		
				C (% dry matter)	N (% dry matter)	Moisture %
1. Dung	Grazing dairy cows (at milking)	Grass–clover + concentrates	6 Sept	38.6	2.5	84
	Grazing calves	Fertilized (N) grass	5 Oct	38.0	2.9	84
2. Dung	Grazing heifers	(i) Grass–clover	30 Sept	34.1	2.2	82
		(ii) Grass—low N		39.5	1.9	86
3. Dung	Grazing beef steers	(i) Grass–clover	19 Oct	27.4	1.6	80
		(ii) Fertilized (N) grass		29.6	1.6	85
		(iii) Unfertilized (N) grass		35.7	1.7	82
4. Dung	Housed dairy cows (at milking)	Silage + concentrates	4 May	41.9	2.5	89
	Housed sheep	Hay + concentrates	4 May	39.5	2.7	75
5. Dung	Grazing dairy cows	Fertilized grass + concentrates	15 June	32.0	2.5	90
	Grazing (upland) cows	Rough grazing (Dartmoor)	15 June	37.5	2.6	88
Urine	Grazing dairy cows (at milking)	Fertilized grass + concentrates	17 June	—	—	—

occurs in typical urine patches in the field (Doak, 1952) i.e. 3 l over an area of 0.5 m^2. Thus 450 ml were applied to cover the enclosed area of 0.075 m^2. Enclosure and sampling procedures were as before.

Laboratory controlled-temperature studies

Two experiments were conducted. In each case dung was incubated (either in the presence or absence of soil) in polyethylene storage containers, with air-tight lids. The boxes had dimensions of 15 × 15 × 15 cm and each lid was fitted with a Suba seal sampling port. In those treatments where soil was present, intact turfs (15 × 15 × 10 cm) were collected and placed into each box leaving a head space of 1125 cm^2. Grass was trimmed to soil level immediately before the application of dung. In those treatments where soil was not used the boxes were filled to the same depth with dry sand. Within 1 h after collection dung was mixed and quickly applied directly onto the soil surface or a plastic tray placed on the sand. In each case, 170 g samples of dung were formed into 9 cm dia pats (60 cm^2), i.e. again in proportion to the weight:surface area of pats deposited in the field by adult cattle. In both experiments the source of dung was dairy cows at milking (and maintained on a diet of grazed herbage plus concentrates).

The experiments took place in a controlled temperature room at 16/17°C. Except for the periods when head space samples were taken, the boxes were left open with the lids resting on the tops. The boxes were sampled over a 10–15 day period and each day a number of head space samples were taken whilst the boxes were sealed for timed periods of from 10 to 30 min. Each box was opened for a comparable time to the sampling period prior to the next. Daily emission rates were then calculated from the mean value from a number (from 4 to 6) of samples taken during any one day. Head space samples were collected with a 10 ml syringe via the Suba seal port and analysed by FID g.c. within 30 min. In each experiment, empty boxes, sealed over the same sampling period provided samples for background, control measurements.

Effect of soil type

In the first incubation experiment the possible interaction between dung addition and two distinct soil types was examined. The first soil (Halstow Series, i.e. that used in the field experiments) was a poorly-drained, clay loam with a moisture content of 47.7% at the start of the incubation. The second soil (Bromsgrove Series) was a coarse sandy loam, a moderately-drained loosely-structured soil with an initial moisture content of 16.9%. There were four replicate boxes of each soil treatment with or without dung applications and of dung alone in the absence of soil.

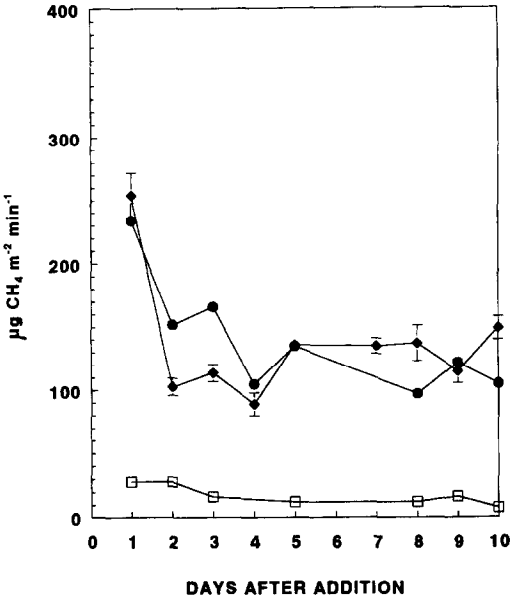

Fig. 1. Emission of methane from dairy cow (●) and calf (◆) dung and background soil (□) after deposition in the field in September. Standard errors greater than ±5 μg CH_4 m^{-2} min^{-1} shown as vertical bars.

Effect of evacuation–fumigation

For this experiment dung was collected from dairy cows at milking as before, mixed and divided into three equal parts for prior treatment before the incubation period. There were three treatments, the first of which was fumigation—dung was placed in a glass container inside a desiccator containing a small beaker of chloroform. The desiccator was then evacuated for 24 h at room temperature and then the vacuum was released and the chloroform removed. This was followed by repeated evacuations to remove residual chloroform. The procedure follows that used to deactivate the microbial biomass in soils (Brookes *et al.*, 1985). The second treatment was evacuation alone in which dung was treated in the same manner as in the first treatment except that no chloroform was present. The final portion of dung remained at room temperature until application to the soil to provide an untreated dung sample. There were four replicate incubation boxes for each treatment.

RESULTS

Field measurements

Methane emission was always stimulated by the addition of dung (Figs 1–5). Typically, CH_4 emission rates were greatest immediately after application, and usually declined to background levels over the 10 + day period. This was not always the case, especially in the first experiment where CH_4 emission from both dung types had not ceased by day 10 (Fig. 1). The other major divergence from the general trend was in the experiment shown in Fig. 4 where there was no

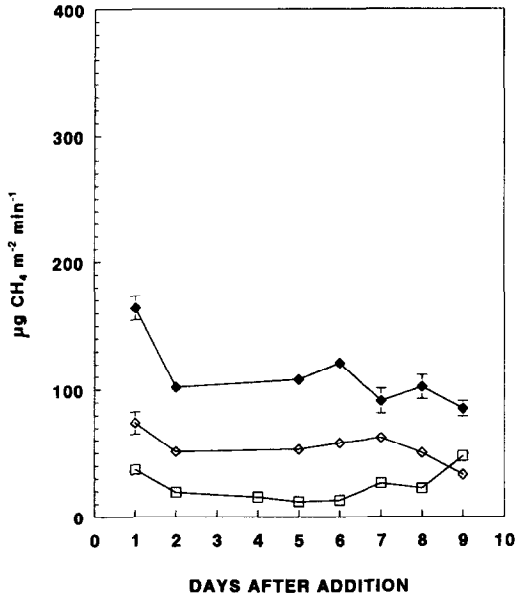

Fig. 2. Emissions of methane from dung from heifers grazing grass–clover (◆), or low-N grass (◇) and background soil (□) after deposition in the field in September. Standard errors greater than ±5 μg CH_4 m^{-2} min^{-1} shown as vertical bars.

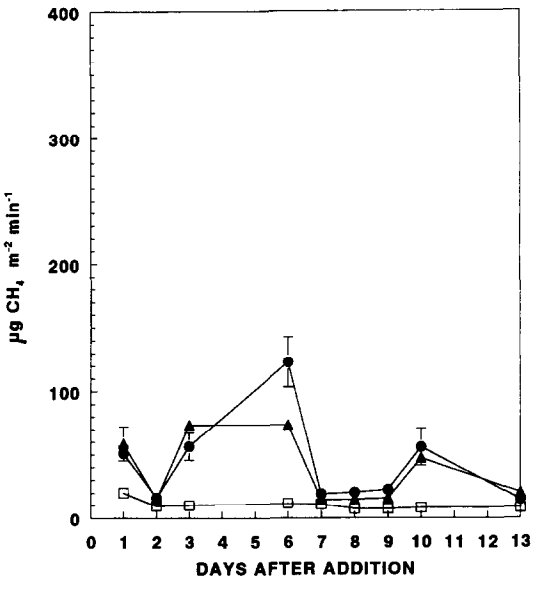

Fig. 4. Emissions of methane from housed dairy cow (●) and sheep (▲) dung and background soil (□) after deposition in the field in May. Standard errors greater than ±5 μg CH_4 m^{-2} min^{-1} shown as vertical bars.

peak emission immediately after application, and rates were generally low and variable. The experimental and dung handling procedures for all field experiments were the same so this should not have influenced emission. The similarity in the pattern for the two dung types illustrated in Fig. 4 suggests that there may have been something particular to dung from housed animals that influenced CH_4 generation.

Interaction with current environmental factors would also have been important and no attempt was made to standardize these. Because measurements were made over a long period, changes in moisture or temperature regimes would have been substantial, making comparisons between experiments difficult

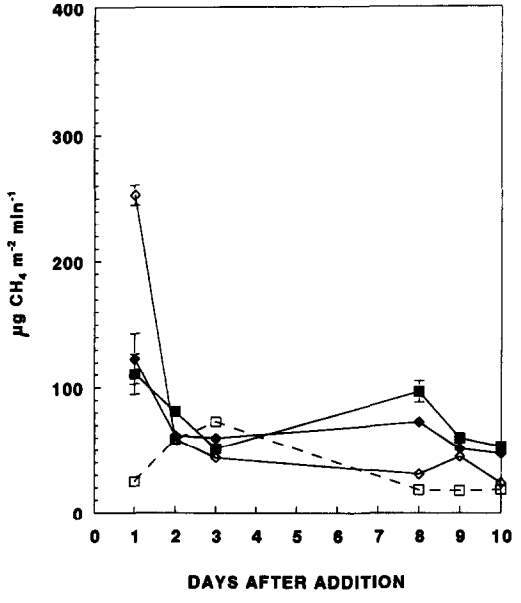

Fig. 3. Emissions of methane from dung from steers grazing grass–clover (◆), fertilized (■) or unfertilized (◇) grass and background soil (□) after deposition in the field in October. Standard errors greater than ±5 μg CH_4 m^{-2} min^{-1} shown as vertical bars.

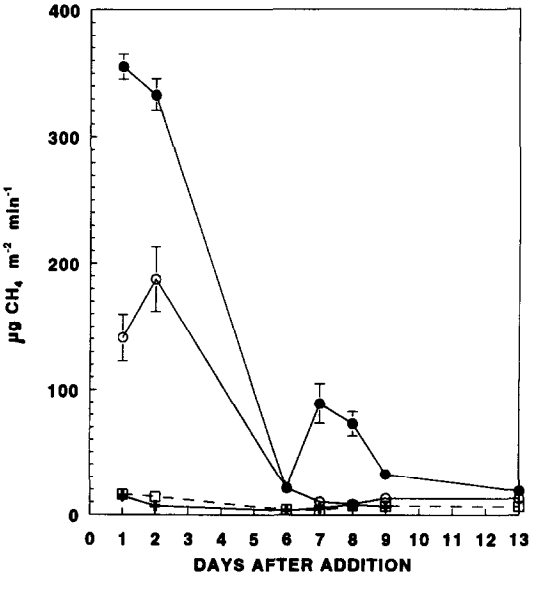

Fig. 5. Emissions of methane from dairy cow (●) and suckler cow (○) dung, dairy cow urine (+) and background soil (□) after deposition in the field in June. Standard errors greater than ±5 μg CH_4 m^{-2} min^{-1} shown as vertical bars.

Table 2. Total emissions of CH_4 from dung in field over measurement periods (ca. 10 days*)

Experimental material	Animal type	Diet	CH_4 emitted (mg CH_4 m^{-2})
1. Dung (Fig. 1)	Dairy cow	Grass–clover (grazed)	1702**
	Calf	+ N grass (grazed)	1655**
2. Dung (Fig. 2)	Heifer	Grass–clover (grazed)	1143
		Low N grass (grazed)	423
3. Dung (Fig. 3)	Steer	Grass–clover (grazed)	406
		Low N grass (grazed)	503
		No N grass (grazed)	300
4. Dung (Fig. 4)	Dairy cow	Silage + concentrates (housed)	716
	Sheep	Hay + concentrates (housed)	598
5. Dung or urine (Fig. 5)	Dairy cow (dung)	Fertilized grass + concentrates	2040
	Suckler cow (dung)	Rough grazing (upland)	922
	Dairy cow (urine)	Rough grazing (upland)	0

*See relevant figures for actual measurement periods.
**Indicates that emission was still occurring at a low rate.

without detailed day-to-day measurement of environmental variables in soil, dung and atmosphere. Within experiments some marked differences between dung sources were evident on occasion. Thus in one experiment (Fig. 1) emission rates were greater with dairy cow than with calf dung. The next experiment, using dung from heifers grazing grass–clover, had higher emission rates ($P < 0.001$) than that using dung from animals on a low-N input pasture (Fig. 2). In the case of dung from steers (Fig. 3) although initially a higher rate ($P < 0.05$) of CH_4 emission was recorded from material from animals on no fertilizer or clover N input, this difference did not persist. Initial emission rates were again higher ($P < 0.01$) from the intensively managed animals in a comparison between intensively managed dairy cows and extensive upland suckler cows.

Total amounts (as interpolated from the measured values) of CH_4 emitted from dung ranged between 716–2040 mg CH_4 m^{-2} for dairy cows (Table 2); the overall mean for all cattle was 981 mg CH_4 m^{-2}. This is equivalent to 73.6 mg CH_4 per dung pat (assuming an average area of 0.075 m^2 in the field). There was no effect of urine on CH_4 emission (Fig. 5; Table 2).

Laboratory studies

It was clear from the experiments under controlled environment conditions that emission rates were of the same order as those found in the field and the same trends with time were displayed (Figs 6 and 7). There was no effect of soil type (Fig. 6). Emission of CH_4 from dung on both soils followed exactly the same trends and over the 10 day period, 2774 and 2577 mg CH_4 m^{-2} dung were emitted on the poorly-drained (Halstow) and well-drained (Bromsgrove) soils, respectively. There was no significant release of CH_4 from soils on their own without added dung. Dung in the absence of soil emitted substantial amounts of CH_4 which followed the same patterns as from dung in contact with soil. In total, there was an overall emission over the 10 day period of 1839 mg CH_4 m^{-2} from dung alone, i.e. 69% of that emitted from the dung–soil combinations.

The longer preparative stages for the fumigation–evacuation experiment (Fig. 7) were probably responsible for the overall lower loss rates. The emission pattern with untreated dung (Fig. 7) was typical of those observed earlier and interpolation from the measured values indicated that 447 mg CH_4 m^{-2} dung were emitted. The chloroform treatment stopped CH_4 emission completely: there was no significant difference between this treatment and the background blank measurements. Evacuation alone had a marked effect on both the pattern and extent of emission. After evacuation, instead of an initial high emission rate on day 1 followed by a rapid decrease, the initial rate was much lower than untreated dung, but also declined at a much slower rate and had not ceased by day 15. The overall effect of this was that 986 mg CH_4 m^{-2} dung were released

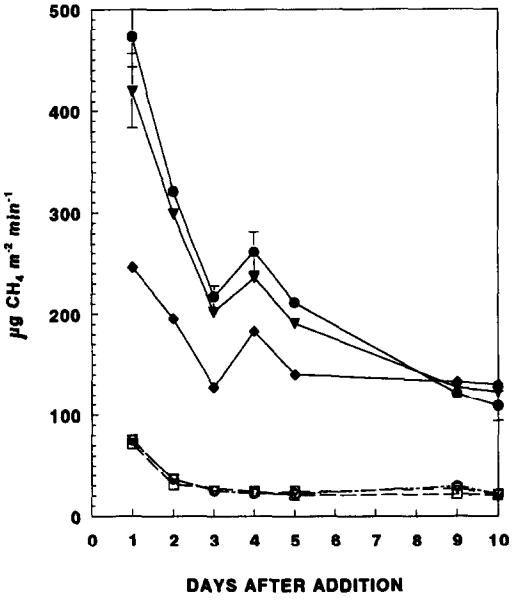

Fig. 6. Emission of methane from dairy cow dung applied to poorly-drained (●) or well-drained (▼) soils, and from dung (◆) and poorly-drained (○) or well-drained (▽) soils alone. Background measurements shown as (□) and standard errors greater than ±5 μg CH_4 m^{-2} min^{-1} shown as vertical bars.

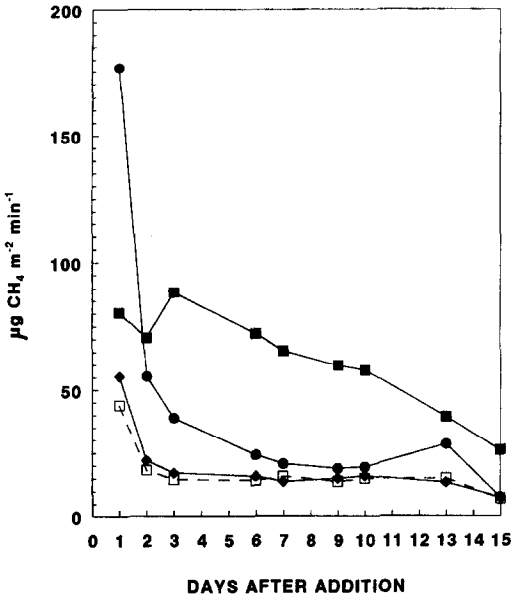

Fig. 7. Emissions of methane from dairy cow dung either untreated (●), evacuated (■) or fumigated and evacuated (◆). Background measurement shown as (□) and standard errors greater than ± 5 μg CH_4 m^{-2} min^{-1} shown as vertical bars.

over 15 days from this treatment, i.e. 2.2 times more than from untreated dung.

DISCUSSION

It has been suggested that faeces have the potential for anaerobic production of CH_4 which if fully achieved would exceed the amounts of CH_4 emitted by the rumen by a factor of 2 (Johnson *et al.*, 1992). The present simple studies demonstrate that dung pats in the field under U.K. conditions do emit significant amounts of CH_4 which can be readily detected. The few other studies that have examined this aspect of the CH_4 cycle have provided similar evidence (Williams, 1993b; Lodman *et al.*, 1993). Overall amounts emitted in our studies are comparable to those determined under very different environmental conditions, i.e. in field experiments in Australia (Williams, 1993b) and laboratory enclosures (Lodman *et al.*, 1993) where humidity and drying out conditions were very different to those experienced in SW England. Our approach in the field, whilst introducing some effects during the short enclosure period, would have minimized these to a large extent so that variance from what would have occurred under natural conditions would not have been great. A good deal of variation between experiments and between dung types was demonstrated. This is not surprising. Methane production by dung pats has been shown to have a strong temperature dependence, although even at 6°C significant amounts of CH_4 can be released (Williams, 1993b). Many factors will have contributed to the variation. Firstly, there will have been much interaction between temperature and moisture status. Methane production will only take place under strictly anaerobic conditions (Tiedje *et al.*, 1984). High temperatures, whilst stimulating microbial activity and CH_4 production would also have stimulated crust formation on the pat and not only helped to maintain the anaerobic status of the pat, but at the same time changed the CH_4 exchange characteristics between the pat and the atmosphere. Rainfall would also have contributed to the anaerobic status of the system, but may also have removed a good many of the substrates for methanogenesis by washing them into the ground. The nature of our studies does not allow firm conclusions to be drawn about environmental effects and interactions other than to indicate that these might be complex.

A good deal of variability in rates of emission was noted by Williams (1993b) with dung from similar animals and it was suggested that this might reflect variation in the numbers of microorganisms present which are responsible for generating CH_4. This aspect of variability will have influenced our studies. Dietary quality will have also influenced the nature of the materials being excreted, especially those volatile solids likely to form potential substrates for CH_4. Differences in emission rates between grain and hay fed animals were noted by Lodman *et al.* (1993); over 7.5 times more CH_4 kg^{-1} dung (dry matter basis) was emitted when animals were fed on grain. There may have been substantial differences in dietary quality within the various animal groups that we investigated. Clearly the N status of the herbage differed between the dung samples used in the field experiment resulting in C-to-N ratios in the dung ranging from 12.8 to 21.0 (Table 1). It is interesting to note that, across all dung types, and despite the probable interactions between moisture, temperature and CH_4 generation, there was a strong relationship between C-to-N in the dung and total amounts of CH_4 emitted, i.e. increasing CH_4 with lower C-to-N. The exponential relationship was best described by: $\ln y = 3.24 \times 54.69/x$ ($r^2 = 0.738$), where x is the C-to-N ratio and y = μg CH_4 m^{-2}.

If environmental constraints had been constant, variation in the C-to-N properties of the dung would have accounted for an even greater proportion of the variability. Furthermore, both qualitative and quantitative information of the volatile solids content within the dung may also be useful in providing an explantation for differences in CH_4 emissions.

The changing emission rate with time must reflect the changing degree of aerobicity within the pat: it is unlikely that substrates would have been depleted. Previous studies (Williams, 1993b) have shown that under Australian conditions cattle dung pats acted as significant sources of CH_4 for up to 3 days after deposition in winter and up to 2 days in summer. The fact that our dung pats emitted for longer periods

reflects the differences in moisture contents in the different systems. Holter (1991) has shown that methane is present in detectable amounts within the gas phase of the dung itself for only 28 days and peak concentrations were observed between 5–10 days but these declined with an increased aerobicity after this time. The manner in which the internal concentrations are transmitted to the exterior will depend upon environmental conditions and result in the typical decay patterns shown in our measurements.

Interaction with soil appeared to be relatively minor. The laboratory incubation showed that the major direct source of CH_4 was the dung itself. Soils were likely to have had large populations of potential methanogens, and deposition of dung would have increased and maintained soil moisture status and provided additional mobile organic compounds. Effects, however, were small, and likely to have resulted from the maintenance of a greater degree of anoxic conditions within the dung when it was in contact with the soil. Methane production was completely stopped when dung was treated with chloroform treatment indicating that the microbial population contained within the dung was largely responsible for the measured CH_4. The effect of evacuation is of interest. The low rate of emission on day 1 probably results from a physical removal of CH_4 during the evacuation process. The reason for sustained rates over longer periods is not so clear. These may have been the results of an increase in anaerobic conditions through O_2 removal during evacuation. Alternatively, removal of high concentrations of CH_4 at the sites of production may have reduced an unidentified feedback mechanism limiting CH_4 production. Whatever the mechanism, it is clear that the population of micro-organisms responsible for CH_4 generation is present at the time of deposition, is capable of rapid activity and that some CH_4 may be entrapped within the dung when it is voided by the animal.

No effect of urine was noted. Although the rapid addition of a large volume of water, with an additional, although small, content of soluble carbon may have increased the soils methanogenic potential this would have been small and not have produced significant amounts of CH_4.

Our studies indicate that dung pats in the field emit significant amounts of CH_4. The extent, however, is small. The studies of Williams (1993b) have also indicated that only small proportions of the potential CH_4 release is achieved under field conditions. Our results confirm this and show that this is low in comparison with other sources within animal production systems. Jarvis and Pain (1994) and Jarvis and Moss (1994) have attempted to estimate CH_4 emission at a farming systems scale. Thus for a 76 ha dairy farm sustaining 165 livestock units, the estimated annual emission of CH_4 was 24,016 kg, CH_4. If the following assumptions are made: (i) that all the animals on the dairy farm graze, on average, 180 days each year and defecate 11 times (Marsh and Campling, 1970) each day; (ii) that dung pat size is 0.075 and 0.05 m^2 for adult cows and young cattle, respectively; and (iii) that, on average, 1486 and 657 mg CH_4 m^{-2} are emitted from dung pats from cows and young cattle, respectively; then 30 kg CH_4 are released each year from this source, i.e. 0.12% of the estimated total farm output from all sources (rumen, slurry, dirty water, etc). On an individual adult cow basis, the annual emission rate of 0.22 kg is very much lower that the estimated output from the rumen of 105 kg CH_4 per animal in the farm study. The immediate effects of this source within a farming system context are therefore relatively small. Nevertheless, over a global scale dung excreted at grazing will have some significance and the mechanisms of, and controls over, release will be of some importance.

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REFERENCES

Bouwman A. F. (1990) *Soils and the Greenhouse Effect*. Wiley, Chichester.

Brookes P. C., Landman A., Pruden G. and Jenkinson D. S. (1985) Chloroform fumigation and the release of soil nitrogen: a rapid direct extraction method to measure microbial biomass N in soil. *Soil Biology & Biochemistry* **17,** 837–842.

Crutzen P. J. (1991) Methane sinks and sources. *Nature London* **350,** 380–381.

Dar G. H. and Tandon S. M. (1987) Response of a cattle dung fermentation to nickel. *Biological Wastes* **22,** 261–268.

Doak B. W. (1952) Some chemical changes in the nitrogenous constituents of urine when voided on pasture. *Journal of Agricultural Science, Camb.* **42,** 162–171.

Hashimoto A. and Steed J. (1993) *Methane emissions from typical US Livestock Manure Management Systems*. Draft Report, U.S. E.P.A., Washington.

Holter P. (1991) Concentration of oxygen, carbon dioxide and methane in the air within dung pats. *Pedobiolgica* **35,** 381–386.

IPPC (1992) *Climate Change*. The IPPC Scientific Assessment. (J. T. Houghton G. J. Jenkins and J. J. Ephraums, Eds), Cambridge University Press, Cambridge.

Jarvis S. C. and Moss A. (1994) Methane emissions from dairy farming systems. In *Grassland and Society*. (L.'t Mannetje and J. Frame Eds), Proceedings 15th General Meeting of the European Grassland Federation. Workshop Proceedings, pp. 218–221.

Jarvis S. C. and Pain B. F. (1994) Greenhouse emission from livestock systems: their estimation and technologies for reduction. *Climatic Change* **30,** 1–12.

Johnson D. E., Branine M. E. and Ward G. M. (1992) *Methane emissions from livestock*. Proceedings of the Animal Feed Industry Association Symposium, St. Louis, p. 33.

Lodman D. W., Branine M. E. Carmean B. R., Zimmermans P., Ward G. M. and Johnson D. E. (1993). Estimates of methane emissions from manure of US cattle. *Chemosphere* **26,** 189–199.

Marsh R. and Campling R. C. (1970) Fouling of pasture by dung. *Herbage Abstracts* **40,** 123–130.

Moss A. (1993) *Methane: Global Warming and Production by Animals*. Chalcombe Publications, Canterbury.

Rhode H. (1990) A comparison of the contribution of various gases to the greenhouse effect. *Science* **248**, 1217–1219.

Tiedje J. M., Sexstone A. J., Parkin T. B., Revsbech N. P. and Shelton D. R. (1984) Anaerobic processes in soil. *Plant and Soil* **76**, 197–212.

Williams A. (1993) (Ed.) *Methane Emissions*. The Watt Committee on Energy, London.

Williams D. J. (1993) Methane emissions from manure of free-range dairy cows. *Chemosphere* **26**, 179–187.