Gaseous pollutants from organic waste use in agriculture

Invited Paper

Polluants gazeux liés à l'utilisation agricole de déchets organiques.

Brian Pain
Institute of Grassland and Environmental Research.
North Wyke, Okehampton, Devon, EX20 2SB, UK.
E-mail : brian.pain@bbsrc.ac.uk

Abstract

Manures from housed livestock, sewage sludges and other organic industrial wastes are commonly applied to agricultural land to exploit their value as fertilisers or for disposal. Emissions of environmentally important gases and volatile compounds may arise either directly from the organic materials or from perturbations of soil processes. The gases of greatest concern include ammonia (NH_3), nitrous oxide (N_2O), other oxides of nitrogen (NO_x) and methane (CH_4). Although certain volatile organic compounds (VOC) have an impact on atmospheric chemistry, those responsible for offensive odours from wastes have received most attention. The focus of research has been on manures from housed livestock because the amounts applied to land far exceed those of other organic wastes. This paper outlines the processes which result in the formation and release of gaseous pollutants, the contribution of organic wastes, the main factors influencing emissions and techniques for abatement.

Résumé

Les déjections animales issues de bâtiments d'élevage, les boues et autres déchets organiques industriels sont habituellement épandus en agriculture, à la fois pour une valorisation de leur potentiel fertilisant ou comme méthode d'élimination.

Des émissions indésirables pour l'environnement de composés gazeux et volatils peuvent intervenir, soit directement à partir de ces déchets organiques ou à la suite de perturbations des processus intervenant dans le sol.

Les gaz les plus concernés sont l'ammoniac (NH_3), le protoxyde d'azote (N_2O) et autres oxydes d'azote ($N0_x$) et le méthane (CH_4). Bien que certains composés organiques volatils (COV) présentent un impact sur la chimie de l'atmosphère, ce sont les composés malodorants qui ont été les plus étudiés.

Les recherches se sont principalement développées sur les déjections animales produites en élevage intensif car les volumes apportés au sol dépassent largement

ceux représentés par les autres types de déchets organiques.
Cet article présente un aperçu des processus qui engendrent la formation et l'émission de ces polluants gazeux, la contribution des déchets organiques, ainsi que les principaux facteurs influençant ces émissions et les techniques de réduction qu'il est possible d'envisager.

1. Ammonia

Following transport away from the source and deposition as ammonia gas (NH^0_3) or ammonium salts (NH_4^+), ammonia can have severe effects on sensitive ecosystems through direct toxicity to plants, nitrogen enrichment or eutrophication and soil acidification. Currently, there are negotiations within the EU which may give rise to controls over ammonia emissions from agriculture. Such controls already apply in some countries, particularly in the Netherlands.

Sources of ammonia.

Most of the ammonia emitted to the atmosphere is derived from the hydrolysis of urea (Equations 1 and 2)

Urea hydrolysis

$CO\,(NH_2)_2 + 3H_20 \longrightarrow 2NH_4^+ + HCO_3^- + OH$ Equation 1

Volatilisation

NH_3° Atmosphere

$\uparrow\downarrow$

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_2O + H^+$ Equation 2

Solution

Livestock production is the major source of this gas with emissions occurring from manure in livestock buildings, in stores and from spreading on land. Grazing animals, nitrogen fertilisers, especially urea, and sewage sludges are smaller sources. (Table 1) (ECETOC, 1994).

	% total NH_3-N
Livestock	
housing	34.5
manure spreading	31.5

grazing	7.7
Fertiliser application	12.2.
Crops	5.6
Industry	0.5
Miscellaneous	8.0

Table 1
Anthropogenic contributions to ammonia emissions in western Europe

Of all livestock classes, cattle are the largest source of ammonia. The importance of housing and landspreading manure is further emphasised by the estimates of ammonia emission from a dairy cow that are given in Table 2. This is based mainly on measurements made in the UK and also summarises the management options that are likely to influence emissions. (Pain, et al. 1989).

Annual emission in kg ammonia-N/animal						
			MANURE			
HOUSE	**YARD**	**STORE**		**LAND**	**GRAZING**	**TOTAL**
7.0	2.4	3.3		8.8	2.4	23.9
OPTIONS:-						
Cubicles		Slurry :				
Straw bedded			Tanks	DM content	N fertilizer	
			Lagoons		use	
				Grass or arable		
				Time of year		
				Method		
		FYM :				
			Concrete pad	Grass or arable		
			Field heap			
		Dirty water				

Table 2
Estimate of ammonia emission from dairy cow management.

Factors influencing ammonia emission.

Although the process of ammonia volatilisation is well understood chemically and described by equations 1 and 2, the rate and extent of emission from organic wastes is influenced by the wide range of factors summarised in Table 3. Thus, in practice, the process is very complex and mathematical models are being developed to describe the process or to predict the rate and extent of loss for given sets of circumstances (Hutchings,et al., 1996; Genermont & Cellier, 1997).

WASTE PROPERTIES	WEATHER
Dry matter content	Solar radiation
NH_4-N content	Temperature
pH	Rainfall
	Wind speed

SOIL	MANAGEMENT
Porosity CEC Vegetation pH	Application rate Application method Waste treatment

Table 3
Some factors influencing ammonia emission from organic wastes.

The factors listed in Table 3 relate mainly to emissions following the application of manures or sewage sludges to land but some, such as wastes composition and weather, will also have an impact on emissions from animal housing and manure stores. Following application to land, the rate of ammonia emission is high for a few hours but rapidly declines to much lower levels which may continue for several days. Over 60% of the NH^+_4-N, or plant available N, can be lost from livestock slurries (Pain, et al. 1989) or liquid sewage sludges (Beauchamp, et al. 1978) with most of this loss occurring within a few hours of application. In addition to environmental effects, ammonia emission also decreases the fertiliser value of manures. Losses from solid manures, such as those produced from loose housed cattle on straw bedding, are generally lower but continue for a longer time. Large losses can occur during composting of these materials (Amon, et al. 1998). The dry matter (DM) content of slurries has a large effect on emissions from landspreading with losses decreasing with decreasing DM content. (Sommer and Olesen 1991; Smith and Chambers 1995) (Fig 1). This is because more dilute materials infiltrate into the soil more rapidly which results in the cessation of ammonia volatilisation.
Temperature and wind speed also have an important influence with warm, drying conditions in summer favouring high rates of emission.

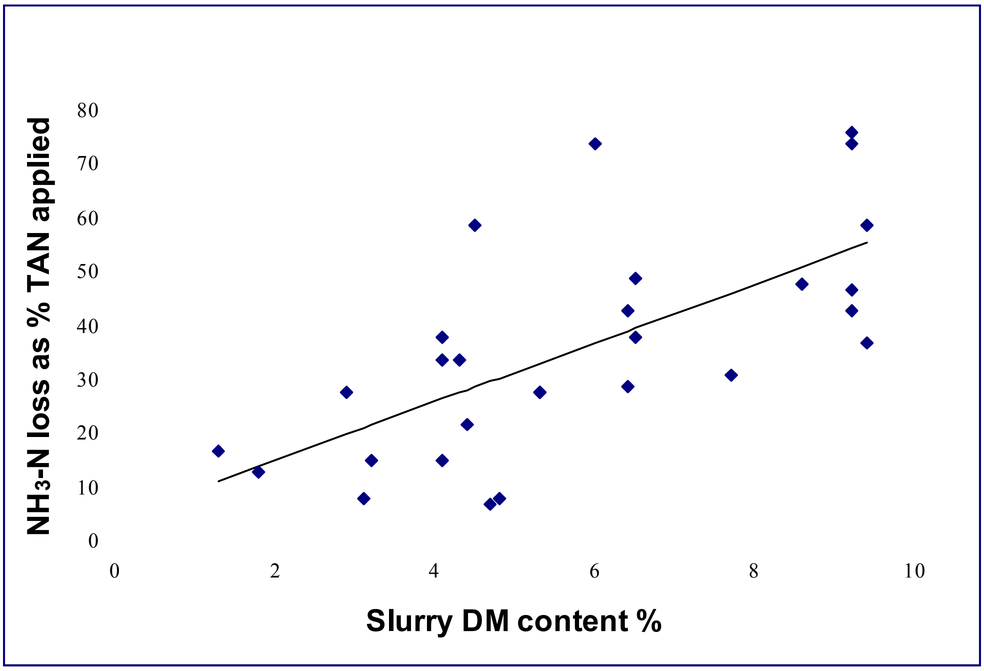

Figure 1
The relationship between ammonia loss and slurry dry matter content

2. Nitrous oxide

Nitrous oxide strongly absorbs radiation in the infra-red band in the atmosphere and so contributes to the greenhouse effect and there is evidence that atmospheric concentrations are increasing.

Sources of nitrous oxide.

Nitrous oxide is produced by the of burning biomass and fossil fuels and, more importantly in the context of this paper, from soil microbial processes. The gas may be released as a by-product during nitrification of NH_4^+-N and, more significantly, from incomplete denitrification of nitrates (NO^-_3). (Equation 3 and 4).

Nitrification

$$\begin{tikzcd} NH_4^+ \arrow[r] & NO_2^- \arrow[r] \arrow[d] & NO_3^- \\ & N_2O & \end{tikzcd}$$

Equation 3

Denitrification

$$NO_3^- \longrightarrow NO_2^- \longrightarrow [NO] \longrightarrow N_2O \longrightarrow N_2$$

Equation 4

Agriculture and related land-based activities are, therefore, important sources particularly where large amounts of inorganic or organic fertilisers are used (see Table 4) (Grosslinger et al. 1996)

	% total N_2O
Agriculture, forestry and land use change	47
Production processes	31
Combustion	13
Road transport	6
Other industry	3

Table 4
Anthropogenic contributions to nitrous oxide emissions in EU 15 countries.

The inventories of nitrous oxide emission for the UK and the Netherlands presented in Tables 5 and 6 illustrate the significant contributions that arise from manure management. The data for the UK (Chadwick, et al.) is for farmed livestock but includes fertilisers whilst that for the Netherlands (Kroeze, 1995) is more broadly based and also includes nitrous oxide emissions arising from the subsequent denitrification of losses via other pathways such as nitrate leaching.

	% total N_2O
Livestock	
housing	22.5
manure storage	31.0
manure spreading	6.1
outdoor (incl. grazing)	11.0
Fertilizers	29.4

Table 5
Contributions to nitrous oxide emissions from farmed livestock in the UK

	% total N_2O
Livestock	
housing	3.0

manure spreading	32.0
Fertilizers	26.0
Enhanced background	17.8
N losses	21.2

Table 6
Contributions of nitrous oxide emissions from agriculture in the Netherlands

Factors influencing nitrous oxide emissions

Livestock manure and sewage sludges provide a suitable source of nitrogen (NH^{+}_{4} -N) for nitrification but, since they are mostly anaerobic, may temporarily inhibit this aerobic process. The provision of nitrifiable nitrogen together with a freely available carbon (C) source and moisture favours denitrification. Data on the impact of these materials on nitrous oxide emissions from land is limited but is likely to be influenced, amongst other factors, by differences in the composition of wastes as illustrated by the data in Table 7 (Chadwick et al. 1998; Mosier, et al. 1982). Nitrous oxide emission is also mediated by soil type and conditions

	g N_2O/t
Pig slurry	34.8
Cattle slurry	12.6
Cattle FYM	21.7
Poultry manure	29.0
Digested sewage sludge	23.5

Table 7
Nitrous oxide emissions following application of livestock manures and sewage sludge to land

NO_X

NO_X denotes nitric oxide (NO) and nitrogen dioxide (NO_2). The conversion of NO to NO_2 in the lower atmosphere is the primary source of ozone which is deleterious to air quality. These chemically reactive gases are also involved in reactions in the stratosphere which erode the efficiency of the ozone layer as a protective shield against ultra violet radiation. They are also implicated in acid rain.

Sources of NO_X

The primary sources of NO_x are combustion of fossil fuels, biomass burning, lightening and the soil processes outlined for nitrous oxide. (Table 8) (Lee, et al. 1997).

	% total
Fossil fuel combustion	49.7
Biomass burning	17.9
Soil microbial processes	15.8
Lightening	11.3

Stratospheric decomposition of N2O	1.4
Ammonia oxidation	2.0
Aircraft	2.0

Table 8
Best estimates of contributions to global emissions of NO_x

The contributions from agriculture and from organic waste use are not well defined but best estimates suggest that agricultural soils account for 15% of global emissions (Lee, et al. 1997).

There is evidence for increasing nitric oxide emission form soils with increasing rates nitrogen fertiliser application. (Skiba, et al. 1997; Yeinger and Levy, 1995). There are very few data on the impact of organic wastes but application of these to land has potential for increasing emissions of nitric oxide (Watanabe, et al.. 1997; Veldcamp and Keller, 1997).

3. Methane

Methane strongly absorbs infra-red radiation and is one of the major greenhouse gases. It is also implicated in the reactions involving ozone.

Sources of methane

Methane is produced by the microbial process of methanogenesis which occurs in all anaerobic environments in which organic matter undergoes decomposition. On a global scale, natural wetlands and rice paddy fields are major sources of this gas accounting for about 40% of the total emission. Estimates of contributions to methane emission in Europe are summarised in Table 9 (Grosslinger ,et al. 1996)

	% total CH_4
Agriculture, forestry & land use change	46
Waste treatment and disposal	35
Extraction/distribution of fossil fuels	16
Miscellaneous	3

Table 9
Anthropogenic contributions to methane emission in EU 15 countries

Agriculture is a significant source because methane is produced and released in large amounts from enteric fermentation in ruminant livestock. Estimates of methane emissions from farmed livestock in the UK (Table 10) illustrates that ruminant livestock, whether housed or grazing outdoors, are the main source of methane emission. (Sneath,et al. 1997)

	% total CH_4
Livestock	

housing	43.9
manure storage	5.0
manure spreading	0.1
outdoor (incl. grazing)	51.0

Table 10
Contribution to methane emission from farmed livestock in the UK

Organic wastes are generally anaerobic and may contain high concentrations of volatile fatty acids, precursors of methane formation, so their use leads to some emission but this is very small compared to that from enteric fermentation. Methane is released, probably from that entrapped in the slurry, for a brief period following the application of livestock slurries to land but ceases as oxygen diffuses into the manure. There is evidence that the manure and/or soil may sometimes act as a sink for methane.

Factors influencing methane release

Unlike nitrous oxide, it appears unlikely that methane emission from waste application is mediated by soil processes although more anaerobic conditions may result in higher emissions. The composition of the waste is important and, for livestock manures, how this is influenced by the animals` diet. Storage conditions, especially temperature, is likely to have a large impact on emission from stores. Anaerobic digesters are designed to exploit the process by ensuring conditions favour biogas (methane+carbon dioxide) production for use as a fuel.

4. Odours

Although not damaging to the environment, offensive odours from organic wastes are a major source of complaints from the public. The focus of research has been on livestock manures although complaints about odours from sewerage works and other industrial sources are common.

Sources of odour emission

Livestock manures are significant sources of odour emission particularly when they are applied to the land surface with conventional machinery. The pattern of odour emission is similar to that describe for ammonia although the frequency and number of complaints may be a reflection of social attitudes as well as the concentration of odour in air. Odour are complex mixtures of gases and volatile organic compounds with over 160 odorous compounds being identified in piggeries. (O`Neil and Phillips, 1992). Because of this complexity, odour concentration in air is difficult to measure chemically and this has led to the development and use of olfactometric techniques. An olfactometer is used to present clean: odorous air dilutions to a panel of people to determine the 50% detection threshold, i.e. the number of dilutions at which 50% of the panel can just detect an odour, which is often expressed as Odour Units m^{-3} air .More recently, GC-MS has been to used to study odour chemistry (Hobbs et al. 1995). This has shown that 15 compounds, which include VFAs, sulphides, phenols and indoles, are mainly responsible for odours from livestock manures. These are mainly derived from the digestion, and subsequent degradation in wastes, of nitrogenous compounds in the animals diet.

Factors influencing odour emission

Many of the factors which influence ammonia emission (see Table 3) also affect odour emission (see Pain, 1994). The class of stock and their diet is also important, because these influence the concentrations of different odorous compounds in manure, together with the period of manure storage prior to spreading on land.

5. Other emissions

Most of the information in this paper is about emissions from livestock manures which reflects the research activity in this area. The use of other organic wastes, particularly sewage sludges, may give rise to emissions of other trace organic contaminants and potentially toxic elements such as mercury (Hg). It is, however, a general view that the impact of sludge treated soils is probably small compared with background levels in the aerial environment. (Smith, 1996)

6. Strategies and techniques for abatement

Modifying the design of buildings, installing air scrubbers or filters or covering stores offer a means of abating emissions from these sources. Incorporating a treatment stage in waste management offers a range of options as discussed by Burton in this volume. Options for the abatement of emissions from the use of organic wastes on land include :

- controlling the rate and time of application
- improved methods of application
- incorporation into the soil
- modifying the diet of livestock.

Rate and time of application

Matching the rate and time of application of nitrogen in manures etc to a crop requirements ensures good recovery by plants with less opportunity for losses, for example, as nitrous oxide through denitrification.

Method of application

Methods have been developed and used for decreasing the surface area of slurries exposed to the air so reducing ammonia emission. (Huijsmans 1997). These include bandspreaders, comprising trailing hoses or trailing shoes, and injectors making open or closed slots in the soil. Trailing hoses apply slurries in parallel bands to grassland or between the rows of cereals whilst trailing shoes are designed to place slurry on the soil surface rather on the grass sward and need a grass height of about 10cm to be effective. Open slot injectors normally operate to a depth of about 5cm whilst closed slot injectors commonly employ 15cm deep, winged tines. The efficiencies of these types of machine for reducing ammonia emission are compared with surface "broadcast" application in Table 11. These machines can also be used to reduce odour.

	% reduction compared with « broadcast »
Bandspreader	
Grassland	10
Arable	30
Trailing shoe	40
Injection	
Open slot	60
Closed slot	80
Incorporation	
Immediate	80
Same working day	40

Table 11
Ammonia abatement efficiencies of slurry application machinery compared with « broadcast » application.

Incorporation into soil

Incorporation of organic wastes into the soil is an effective means of reducing ammonia and odour emission. (see paper by Huisjmans in this volume). Since rates of emission are very high for the few hours after spreading on the soil surface, incorporation must be done as soon as possible and preferably within 3-4 hours. The equipment used for incorporation will depend upon soil type but, in general, ploughing to bury completely the manure is most effective. (Table 12). Odour emission is decreased also.

Method of incorporation	Immediate	3 hr delay	6hr delay
Plough	90	68	54
Rotavator	68	55	43
Tines	40	37	34

Table 12
Effect of time and method of incorporating slurry into soil on ammonia emission

Modifying the diet of livestock

More accurately adjusting the protein contained in the diet of livestock to their requirements can lower the amount of surplus nitrogen excreted. This is more straightforward for pigs than for cattle because diets for the latter can be formulated accurately using synthetic amino acids.

Although more costly, such diets significantly decrease nitrogen excretion and subsequent emissions of gaseous nitrogen compounds and odours. (Hobbs et al. 1996; Misselbrook et al. 1998).

Interactions

It is well established that controlling emissions may a) increase emission of the same compound at a “downstream” stage of management or, b) increase emission of another compound. For example, reducing ammonia emission from storage of slurries or composting of solid manure may increase emission of this gas from spreading on land unless an appropriate abatement technique is used. Similarly, deep injection of slurry may reduce ammonia emission but increase emission of nitrous oxide through enhanced rates of denitrification.

7. References

Amon B, Boxberger J, Amon Th, Zaussinger,A and Pollinger A (1998) Emissions of ammonia, nitrous oxide and methane from a tying stall for milking cows during storage of solid manure and after spreading, See this volume.

Beauchamp E G, Kidd G E and Thurtell G (1978) Ammonia volatilization from sewage sludge applied in the field. Journal of Environmental Quality 7, 141-146

Chadwick D R, Sneath Rw, Phillips V R and Pain B F (1998) Methane and nitrous oxide emissions from the UK livestock sector. See this volume.

ECETOC (1994) Ammonia emissions to air in Western Europe. Technical Report No62. Brussels 196pp

Genermont S and Cellier P (1997) A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil Agricultural and Forest Meteorology 88, 145-167

Grosslinger E, Radunsky K and Ritter M (1996) CORINAIR 1990 Summary Report. European Environment Agency, Copenhagen.

Hobbs P J, Misselbrook T H and Pain B F (1995) Assessment of agricultural odours by a photoionisation detector, an electronic nose, olfactometry and gas chromatography-mass spectrometry. Journal of Agricultural Engineering Research 60, 137-144.

Hobbs P J, Pain B F, Kay R M and Lee P A.(1996) Reduction of odorous compounds in fresh pig slurry by dietary control of crude protein. Journal of the Science of Food and Agriculture 71, 508-515.

Huijsmans J F M, Hol J G M and Bussink D W (1997) Reduction of ammonia emission by new slurry application techniques on grassland. In: Gaseous Emissions of Nitrogen from Grassland. S C Jarvis and B F Pain (eds) CABI Wallingford, pp281-285.

Hutchings N J, Sommer S G and Jarvis S C (1996) A model of ammonia volatilization from a grazing livestock farm Atmospheric Environment 30, .589-599

Kroeze C (1995) Comparison of inventory methods for estimating national emissions of nitrous oxide. Quarterly Journal of the Hungarian Meteorological Service 9, 209-225

Lee D S, Bouwman A F, Asman W A H, Dentener F J, Van Der Hoek K W and Olivier J G J (1997) Emission of nitric oxide, nitrous oxide and ammonia from grasslands on a global scale. In: Gaseous Nitrogen Emissions from Grassland. S C Jarvis & B F Pain (eds) CABI, Wallingford. 452pp

Misselbrook T H, Chadwick D R, Pain B F and Headon D (1998) Diietary manipulation as a means of reducing N losses, methane emissions and improving herbage N uptake following applications of pig slurry to grassland. Journal of Agricultural Science, Cambs. 130, 183-191

Mosier A R, Hutchinson G L, Sabey B R and Baxter J (1982) Nitrous oxide emission from barley plots treated with ammonium nitrate or sewage sludge. Journal of Environmental Quality 22, 78-81.

O`Neil D H and Phillips V R (1992) A review of the control of odour nuisance from livestock buildings: Part 111 Properties of the odorous substances which have been identified in livestock wasts or in the air around them. Journal of Agricultural Engineering Research 53, 23-50.

Pain B F (1994) Odour nuisance from livestock production systems. In: Pollution in Livestock Production Systems. L Ap Dewi, R F E Axford, I F M Marai and H Omed (eds) CABI Wallingford, pp241-263.

Pain B F, Phillips V R, Clarkson C R and Klarenbeek J V (1989) Loss of nitrogen through ammonia volatilization during and following the application of pig or cattle slurry to grassland. Journal of the Science of Food and Agriculture 47, 1-12

Sommer S G and Olesen (1991) Effects of dry matter content and temperature on ammonia loss from surface applied cattle slurry. Journal of Environmental Quality20, 679-683.

Skiba U, Fowler D and Smith K A (1997) Nitric oxide emissions from agricultural soils in temperate and tropical climates : sources, controls and mitigation options. Nutrient Cylcing in Agroecosystems 48, 139-153.

Smith K A and Chambers B J (1995) Muck from waste to resource-utilisation:the impacts and implications. Agricultural Engineering, Autumn 1995, 33-38.

Smith S R (1996) Agricultural Recycling of Sewage Sludge and the Environment. CABI, Wallingford. pp382

Sneath R W, Chadwick D R, Phillips V R and Pain B F (1997) A UK inventory of methane emissions from farmed livestock, Final Report to MAFF, London. pp55.

Veldkamp E and Keller M (1997) Fertiliser induced nitric oxide emission from agricultural soils. Nutrient Cycling in Agroecosystems 48, 69-77

Watanabe T, Osada T, Yoh M and Tsurata H (1997) N_2O and NO emissons from grassland soils after application of cattle and swine excreta. Nutrient Cycling in Agroecosystems 49, 35-39.

Yeinger J J and Levy H (1995) Empirical model of global and soil-biogenic NO_X emissions. Journal of Geophysical Research 100, 11447-11464.