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The scope and contribution of volatile organic compounds to pollution from livestock

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Abstract. *Livestock and their wastes produce a variety of non-methane volatile organic compounds (NMVOCs) from a range of biochemical processes, which are emitted into the atmosphere. They range from acetone and dimethyl sulfide (DMS) in ruminants breath, to over 150 NMVOCs produced from the anaerobic storage and management of livestock manure. The latter are principally comprised of sulfides, volatile fatty acids (VFAs), phenols and indoles. In the wider context they can contribute to man-made emissions and reduce air quality in rural areas. DMS from ruminants breath for example has been identified as contributing 10% of sulphur to the global atmosphere which was estimated to be between 2.1 and 5.5 Tg S yr⁻¹. However, there has been no recognition of contributions from livestock to DMS that regulates*

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global climate by inducing cloud formation and other NMVOCs that pollution on a regional or smaller scale. VFAs and other oxygenated hydrocarbons can contribute to atmospheric oxidant production such as ozone and peroxy acetyl nitrate (PAN).

There have been numerous types of NMVOCs identified from livestock sources but we only recognized sixteen. A NMVOC inventory was constructed utilizing ratios of individual NMVOC emissions to those from the better-understood ammonia inventory. Such projections have identified emissions of individual NMVOCs from the UK livestock as being of the order of thousands of tons annually. Thus making livestock sources necessary to be considered alongside those from the larger industrial and transport sectors. Such inventories can help plan reductions of pollution in the atmosphere and reduce the concentration of more harmful secondary chemicals that can be produced by reactive VOCs. Our estimations show that 133kt of NMVOCs are emitted annually and that this exceeds 50-100 kt determined by current methods for biogenic sources which includes agriculture and the natural environment.

Keywords. Air pollution, livestock, ozone, non-methane volatile organic compound

Introduction

Emissions of volatile organic compounds from livestock should be placed in relevant context of other such emissions and the potential pollution possible. We will only consider the UK non-methane volatile organic compounds (NMVOCs) as methane has been the subject of extensive studies. NMVOC emissions from livestock are considered with other biogenic sources that include for example vegetation and wetlands (Simpson et al., 1999). Other countries may have greater biogenic emissions because their ecosystems have not been destroyed since prehistoric times. Approximately 2337 kt yr⁻¹ of NMVOCs are emitted from the UK with 70% from transport and solvent sources. About 50-100 kt yr⁻¹ are estimated as being emitted from biogenic sources (PORG 1997).

Such uncertainty of course makes modeling atmospheric processes difficult, therefore the objectives of improving data quality will be to make more realistic assessment of local atmospheric budgets of NMVOCs and photochemical oxidant production. On a larger scale, determination of background concentrations will enable realistic reduction targets for anthropogenic sources to be established.

Biogenic NMVOCs in the atmosphere encompass a range of organic compounds from C₂ to about C₁₂ although they may extend up to C₁₅. Many isomers may be present as well as those with different chemical functional groups (Simpson et al., 1999). The task of providing information on such a broad band of volatile compounds proved challenging. Several different adsorption trapping materials were required for the concentration of these compounds prior to separation on the GC and identification by mass spectrometry system. These compounds are numerous in the troposphere and are often in the ppb or ppt concentration range, so collectively they contribute to atmospheric pollution and/or chemistry.

Some atmospheric NMVOCs present a health risk and an environmental problem in their own right. However, secondary pollutants are produced that are mostly oxidizing agents, ozone generally has the highest concentration, both are driven by sunlight intensity (PORG 1997). Photolytic ozone production is increased by higher nitrogen dioxide concentrations. In turn, nitrogen dioxide concentrations are increased by NMVOC and peroxide radicals. NMVOCs (and methane) can also undergo oxidation and produce ozone as a by-product. The oxidation of NMVOCs are dependent on the concentration of catalytic hydroxyl radicals produced primarily by sunlight and the presence of ozone or formaldehyde. Ozone is also a major producer of hydroxyl radicals in rural areas but formaldehyde is the major producer in urban areas. Ozone can be self-sustaining because it produces radicals that oxidize VOCs, which in turn produce ozone during photolytic decay.

Peroxyacetyl nitrate (PAN) and hydrogen peroxide (H₂O₂) are significant secondary oxidants in mainland Europe. However this is not so in the UK because they are not produced in sufficient concentrations. Generally, both are below concentrations of 1 ppb with maximums of 2 to 3 ppb present for about 10 days a year (PORG 1997).

Nitric oxide produced from road traffic will scavenge ozone and is the major reason for low ozone concentrations in urban areas. Increasing water vapor can decrease the production of hydroxyl radicals by about 10%. Wind may play a role in atmospheric mixing which can be modeled. Models are difficult to produce without considerable amounts of resource and data. During anticyclones the highest concentrations of ozone are observed. Wind flows from the European continent will increase ozone concentration over the UK. Ozone occurs on average at about 20-40% higher concentrations in rural areas and increases with increasing altitude and

proximity to the coast. Large areas of the UK exceed critical concentrations for damage to crops and human health (PORG 1997).

In this study we will scale the NMVOCs emitted from livestock manure as a ratio to the ammonia emissions determined in the recent UK ammonia emissions inventory (Pain et al., 1998). Measurement of the ratio of emissions will be performed the major livestock types to determine annual emission rates. Recent studies have identified that ruminants also emit dimethyl sulfide as well as acetone and other minor NMVOCs (Elliott-Martin et al., 1997). Based on the initial discovery we will calculate emissions from ruminant breath based on dietary intake.

NMVOCs emitted from livestock manure and excreta

Three major sources of excreta from livestock were identified as significant contributors to NMVOCs emissions. NMVOCs samples were captured using selected adsorbents to collect the widest range from the headspace of manure from pig, dairy cattle slurry and laying hens. The headspace was analyzed by gas chromatography-mass spectrometry (GC-MS) to determine the emission rate. Results are presented in Table 1. Although some authors have identified over 130 volatile compounds as originating from livestock (O'Neill and Phillips, 1992) we identified less than twenty (Hobbs et al., 1996). There is some uncertainty over which NMVOCs originate from each of the manure type. The scope of NMVOCs may be greater than we have identified. Zahn (1997) recognized first some unusual compounds and several hydrocarbons from a swine waste lagoon. Second C₂ to C₉ organic acids demonstrated the greatest potential for decreased air quality, since these compounds exhibited the highest transport coefficients and high airborne concentrations. Those identified can depend upon the adsorbent material used for their collection and the means of desorption into a detection system, but not all NMVOCs are odorous. As the manure ages, emission rates of volatile fatty acids, phenols and CO₂ decreases with increasing storage period, while those of CH₄ and NH₃ increase (Hobbs et al., 1999).

Table 1 Emission rates of NMVOCs from different livestock using an enclosed emission chamber

	pig slurry	Cattle slurry	Layer manure
	g m ⁻³ d ⁻¹	g m ⁻³ d ⁻¹	g m ⁻³ d ⁻¹
dimethyl sulfide	7		156
dimethyl disulfide			683
dimethyl trisulfide			14
Ammonia	21.7	13.8	984
Acetic acid	7.43	5.7	Trace
Propanoic acid	0.34	0.15	Trace
2-methyl propanoic acid	0.20	0.07	
Butanoic acid	2.85	0.06	Trace
3-methyl butanoic acid	0.34	0.22	
2-methyl butanoic acid	0.34	0.14	
Pentanoic acid	0.07	0.01	
Phenol	0.09	0.01	Trace
4-methyl phenol	2.21	2.8	Trace
4-ethyl phenol	0.14	0.0	
Indole	0.01	0.0	
3-methyl indole	0.01	0.0	

NMVOCs emitted from breath

Recent analysis at IGER on ruminant breath reveals that the formation and exhalation of dimethyl sulphide (DMS) is the means by which ruminants expel excess sulfur (Hobbs and Mottram, 2000). Dairy cows are usually the greatest contributors to the atmospheric flux of DMS by ruminants. DMS oxidizes to sulfuric acid which initiates cloud formation via particle nucleation in the atmosphere. (Dimethyl sulfide is an important component of the biogeochemical sulphur cycle and the second largest source of sulfur in the troposphere.) Contributions by ruminants to the global flux of DMS were evaluated by means of measurement and by dietary studies of lactating cattle in a mass balance model. The average dairy cow has a daily diet of 20kg of dry matter, which contains 19.2g of sulfur. At peak lactation 16.8g d⁻¹ of sulphur will be excreted in the milk and this will decline with the possibility that at least 2.4g d⁻¹ of sulphur may be exhaled as DMS from the rumen. We have determined that the breath contains between 0 and 25 ppm DMS at various stages of the reproductive cycle with an average of 9.4 ppm (or about 3.5g of sulphur d⁻¹). We estimate that with a population of 12 million cattle in the UK there will be 10.3 kt yr⁻¹ of DMS produced from cattle alone. On a body weight basis UK sheep produce about 3.85 kt yr⁻¹ of DMS. We approximated acetone emissions on breath to be about one third of those of DMS as reported on a paper concerning ketotic cattle (Mottram et al., 1999).

Assuming the emissions of other ruminants is proportional to body weight then farmed ruminants contribute 0.42 Tg S yr⁻¹ of sulphur to the global atmosphere in the form of DMS from breath. The global flux of sulfur to the atmosphere as DMS from biogenic sources was estimated to be between 2.1 and 5.5 Tg S yr⁻¹ (Badr and Probert, 1994) but there was no recognition of a possible contribution from livestock. Ruminant exhalation would not be of interest if it were not for DMS being an agent that regulates the global climate by cloud formation and that contributions vary on a regional or smaller area basis.

Confirmation of DMS emissions was sought in a cubicles shed using a thermoluminescence detector that monitors reduced sulfides (Figure 1) so may include hydrogen sulfide and methanethiol traces. The first peak shows when silage was distributed and the second when the dairy cattle passed directly underneath the detector on their way to the milking parlor.

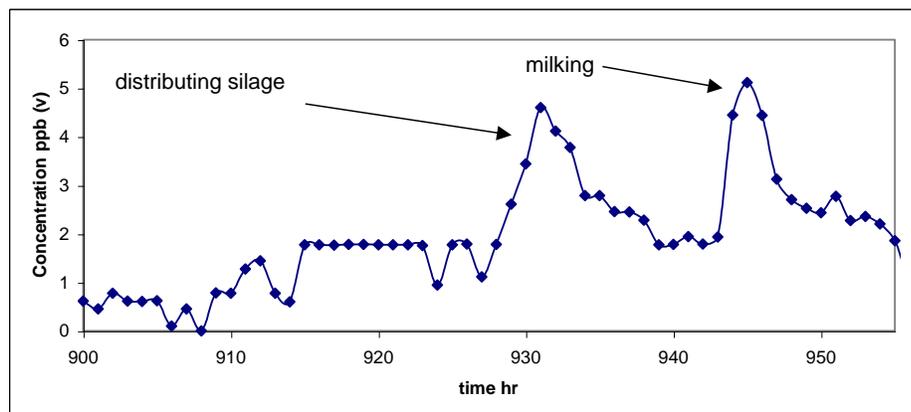


Figure 1 Total reduced sulfide concentration in dairy cattle cubicles

Preliminary emissions inventory of NMVOC from livestock

Emission rates of NMVOCs from different manure types and ruminant breath sources of DMS and acetone were used to build a preliminary inventory (Table 2). Additional determinations were performed to include a greater range of NMVOCs. Projections of NMVOCs were made as a ratio to those from the ammonia inventory (Pain et al., 1998) to give values for UK annual emissions of individual compounds. These are expressed for each animal type (Table 2). Calculations assume the ratios to ammonia emission rates are constant for all situations such as housing and grazing.

Table 2 Projected UK annual emissions of NMVOCs from cattle, pig and poultry sources.

Volatile compound	kt yr ⁻¹			
	Sheep	pig	Cattle	Poultry
dimethyl sulfide	3.85	7.6	10.27	4.8
dimethyl disulfide				20.9
dimethyl trisulfide				0.4
Acetone	1.62		3.42	
Acetic acid		8.06	40.68	trace
Propanoic acid		0.36	1.07	trace
2-methyl propanoic acid		0.22	0.52	
Butanoic acid		3.09	0.42	
3-methyl butanoic acid		0.37	1.58	
2-methyl butanoic acid		0.36	0.98	
Pentanoic acid		0.08	0.04	
Phenol		0.10	0.08	trace
4-methyl phenol		2.40	20.32	
4-ethyl phenol		0.15	0.20	
Indole		0.01	0.01	trace
3-methyl indole		0.01	0.01	
TOTAL	5.47	22.8	79.60	26.1

Total emissions are expressed as a sum of these to give projected values of emissions of individual NMVOCs in Table 3. Knowledge was insufficient at this point to give an estimation of the error of each of these values.

Table 3 Numbers of livestock and ammonia emissions

	Sheep	Pig/swine	Cow	Poultry	Totals
Livestock numbers millions	43.9	7.7	11.7	141	203.9
Ammonia losses kt yr-1 as N	12.7	23.6	98.6	30.2	165.1
NMVOCs kt yr-1	5.47	22.8	79.60	26.1	133.7

Conclusion and recommendations

- The preliminary NMVOCs inventory identified emissions with a total of about 133 kt yr⁻¹. Uncertainty of this value is currently difficult to determine.
- While the results show profiles of numerous types of NMVOCs the greater mass were acidic VFAs and phenols or sulfides. To improve the confidence of these analysis further research and monitoring efforts should be made.
- Different livestock management styles may alter the emissions rates of NMVOCs so improved quantification of emission rates from the major means of livestock production should be performed.
- Emissions rates of organic sulfides appeared significant and clarification of its role in regional atmospheric chemistry should be clarified.

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References

- Badr, O. and S.D. Probert. "Atmospheric sulfur - trends, sources, sinks and environmental impacts." *Applied Energy* 47(1994):1-67.
- ElliottMartin, R.J., T.T. Mottram, J.W. Gardner, P.J. Hobbs, and P.N. Bartlett. "Preliminary investigation of breath sampling as a monitor of health in dairy cattle." *Journal Of Agricultural Engineering Research* 67(1997):267-275.
- Hobbs, P. and T. Mottram. "New Directions: Significant contributions of dimethyl sulphide from livestock to the atmosphere." *Atmospheric Environment* 34(2000):3649-3650.
- Hobbs, P.J., T.H. Misselbrook, and T.R. Cumby. "Production and emission of odours and gases from ageing pig waste." *Journal Of Agricultural Engineering Research* 72(1999):291-298.
- Hobbs, P.J., B.F. PAIN, R.M. KAY, and P.A. LEE. "Reduction of odorous compounds in fresh pig slurry by dietary control of crude protein." *Journal Of The Science Of Food And Agriculture* 71(1996):508-514.
- Mottram, T.T., P. Dobbelaar, Y.H. Schukken, P.J. Hobbs, and P.N. Bartlett. "An experiment to determine the feasibility of automatically detecting hyperketonaemia in dairy cows." *Livestock Production Science* 61(1999):7-11.
- Oneill, D.H. and V.R. PHILLIPS. "A review of the control of odor nuisance from livestock buildings .3. Properties of the odorous substances which have been identified in livestock wastes or in the air around them." *Journal Of Agricultural Engineering Research* 53(1992):23-50.
- Pain, B.F., T.J. van der Weerden, Chambers B.J, V.R. PHILLIPS, and S.C. JARVIS. "A new inventory of ammonia emission from UK agriculture." *Atmospheric Chemistry* 32(1998):309-313.
- PORG United Kingdom Photochemical oxidants review group 1997 4th Report, Department of Transport and Industry, London.

- Simpson, D., W. Winiwarter, G. Borjesson, S. Cinderby, A. Ferreiro, A. Guenther, C.N. Hewitt, R. Janson, M.K. Khalil, S. Owen, T.E. Pierce, H. Puxbaum, M. Shearer, U. Skiba, R. Steinbrecher, L. Tarrason, and M.G. Oquist. "Inventorying emissions from nature in Europe." *Journal of Geophysical Research-Atmospheres* 104(1999):8113-8152.
- Zahn, J.A., J.L. Hatfield, Y.S. Do, A.A. DiSpirito, D.A. Laird, and R.L. Pfeiffer. "Characterization of volatile organic emissions and wastes from a swine production facility." *Journal Of Environmental Quality* 26(1997):1687-1696.