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CONTRIBUTIONS OF NON-METHANE VOLATILE ORGANIC COMPOUNDS TO THE ATMOSPHERE FROM UK AGRICULTURE

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ABSTRACT

Agriculture produces a variety of non-methane volatile organic compounds (NMVOCs) from livestock and crop sources that have not been estimated in terms of their contribution to total atmospheric concentrations, or health and environmental damage. NMVOCs contribute to the production of secondary pollutants such as ozone which damages crops and natural fauna. Crops have been identified as emitting only small amounts of NMVOCs, but we identified some significant NMVOCs that may contribute to health problems. There have also been numerous types of NMVOCs identified from livestock sources, but it has not been possible to determine the amounts emitted. An inventory was constructed utilizing ratios of individual NMVOCs identified by gas chromatography-mass spectrometry, to ammonia emissions from livestock wastes, from the well-researched ammonia inventory. These projections have identified the total emission of NMVOCs from UK livestock as being of the order of over a hundred thousand tons annually, which is comparable to that from other biogenic sources and the larger industrial and transport sectors. Such inventories can help plan pollution reduction to the atmosphere. Our estimates show that 138 kt of NMVOCs are emitted annually from livestock agriculture and about 4.6 kt yr⁻¹ from crops and grassland. These values exceed the 50-100 kt yr⁻¹ currently originating from biogenic sources that includes both 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 modelling 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 mostly oxidizing agents, with ozone being the highest concentration. 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 oxidise VOCs, which in turn produce ozone during photolytic decay. 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 sulphide 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

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 analysed by gas chromatography-mass spectrometry (GC-MS) to determine the emission rate. 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) recognised 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).

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 sulphur(Hobbs and Mottram, 2000). Dairy cows are usually the greatest contributors to the atmospheric flux of DMS by ruminants. DMS oxidises to sulphuric acid that initiates cloud formation via particle nucleation in the atmosphere. (Dimethyl sulphide is an important component

of the bio-geochemical sulphur cycle and the second largest source of sulphur 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. 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 sulphur 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.

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 1). 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 1). Calculations assume the ratios to ammonia emission rates are constant for all situations such as housing and grazing.

Table 1 Projected UK annual emissions (kt yr⁻¹) of NMVOCs from Livestock.

Volatile compound	Sheep	Pigs	Cattle	Poultry
Dimethyl sulphide	3.91	7.60	10.27	4.80
Dimethyl disulphide				20.90
Dimethyl trisulphide				0.40
Acetone	1.62		3.42	
Acetic acid	5.25	8.06	40.68	Trace
Propanoic acid	0.14	0.36	1.07	Trace
2-methyl propanoic acid	0.07	0.22	0.52	
Butanoic acid	0.05	3.09	0.42	
3-methyl butanoic acid	0.20	0.37	1.58	
2-methyl butanoic acid	0.13	0.36	0.98	
Pentanoic acid	0.005	0.080	0.040	
Phenol	0.010	0.100	0.080	Trace
4-methyl phenol	2.62	2.40	20.32	
4-ethyl phenol	0.026	0.150	0.200	
Indole	0.001	0.010	0.010	Trace
3-methyl indole	0.001	0.010	0.010	
TOTAL	12.4	22.8	76.2	26.1

Total emissions are expressed as a sum of these to give projected values of emissions of individual NMVOCs in Table 2. Knowledge was insufficient at this point to give an estimation of the error of each of these values.

Table 2 Numbers of livestock and ammonia emissions

	Crops	Sheep	Pigs	Cow	Poultry	Totals
Livestock numbers millions	-	44.7	7.7	11.7	141	205.1
Ammonia losses kt yr ⁻¹ as N	25.31	17.66	26.82	136.8	38.59	245.2
NMVOcs kt yr ⁻¹	4.65	12.4	22.8	76.2	26.1	142.2

Conclusion and recommendations

- The preliminary NMVOcs inventory identified emissions with a total of about 142 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 sulphides. 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 sulphides appeared significant and clarification of its role in regional atmospheric chemistry should be clarified.

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