Emissions of volatile organic compounds originating from UK livestock agriculture

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Abstract: In this paper we estimate the quantity of non-methane volatile organic compounds (NMVOCs) emitted from UK livestock. The final estimate is derived from published values and from direct measurements of NMVOC emissions from dairy cattle slurry and laying hen manure. Emission rates of NMVOCs were determined for fresh dairy cattle slurry and laying hen manure using a 40 m³ emissions chamber. Dimethyl sulphides dominated emissions from laying hen manure at $753 \pm 263\,\mathrm{g\,m^{-3}\,day^{-1}}$. Emissions from dairy cattle slurry were dominated by volatile fatty acids (C_2–C_5, $6.3 \pm 3.1\,\mathrm{g\,m^{-3}\,day^{-1}}$) and phenols ($2.4 \pm 1.2\,\mathrm{g\,m^{-3}\,day^{-1}}$). Many of these NMVOCs are decomposition products from protein sources from which ammonia is also a by-product. There is a close association between ammonia and NMVOC production from manure, and on this basis we estimated the annual NMVOC emissions from UK livestock as $165 \pm 56\,\mathrm{kt}$ for 2002. These emissions compare to those from the larger industrial and transport sectors and exceed the 50–100 kt C year⁻¹ currently determined as originating from biogenic sources including agriculture. These findings have implications for air quality, and these NMVOCs may affect the cleansing capacity of the troposphere.
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Keywords: air pollution; agriculture; livestock; crops; ozone; non-methane volatile organic compounds

INTRODUCTION

Non-methane volatile organic compounds (NMVO-Cs) are becoming an increasing topic of investigation because of their effect on air quality. There is pressure on EU member states to reduce emissions to the atmosphere from agricultural sources as defined by the UNECE Gothenburg Protocol,[1] the EU National Emissions Ceilings Directive[2] and the Kyoto Protocol.[3] To be able to demonstrate that current emission estimates are correct will also help to justify any economic costs of abatement. NMVOCs comprise a wide range of chemicals that promote the formation of atmospheric oxidants, eg ozone and peroxyacetyl nitrate (PAN),[4] and contribute to the greenhouse effect. NMVOCs also make a significant contribution to ozone formation in rural areas.[5] The average concentration of ozone at ground level has more than doubled in the last 100 years,[6] and the frequency of episodes of high concentration is increasing.[7]

Approximately 2337 kt NMVOCs year⁻¹ are estimated as being emitted from the UK, with 70% arising from transport and solvent sources and about 50–100 kt year⁻¹ from biogenic sources.[7] However, recent measurements have been above and below this range.[8] Such uncertainty makes modelling atmospheric processes difficult. Knowledge of the emission rates from livestock should initially provide a more realistic assessment of the contribution of local (or farm)-scale emissions of NMVOCs to atmospheric budgets. Once annual emissions from agricultural sources have been quantified, reduction targets for the much greater anthropogenic sources can be made on a more realistic basis. NMVOCs from agriculture have normally been classified as belonging to biogenic sources, with little research having been performed to define the mass or type of chemical species originating from livestock. Agriculture may contribute to increasing ozone concentrations in the troposphere, causing stress to trees and crops as well as toxic or stress factors in human populations as in the case of livestock odours.[9] The main complaints have been recognised as eye, nose and throat irritation and potential mood or memory effects.

Values of NMVOC emission rates from livestock have not been collated, but other inventories have focused on ammonia[10] and recently nitrous oxide.[11]

An inventory of NMVOCs from agriculture may be considered irrelevant (and ambitious) because of the small concentration of each NMVOC (although large in numbers of species present), making qualitative and quantitative analysis difficult. NMVOCs are mostly polar and require specialist approaches for collection and detection. Although some authors have identified over 130 volatile compounds originating from cattle, pigs and poultry,[12] there is some uncertainty over which NMVOCs originate from each manure type. Less than 20 volatile compounds were present in different manure types but at different concentrations or ratios in the headspace of pig, cattle and chicken manure.[13,14] NMVOCs originate from undigested protein that decomposes in manure.[15] Those collected from the headspace of manure will reflect the nature of the adsorbent used and the means of desorption into the selected separation/detection system. Zahn et al[16] recognised that some non-polar hydrocarbons are emitted from pig slurry lagoons. This comprehensive study also demonstrated that fluxes of NMVOCs from deep basin or pit manure storage systems in Iowa, USA were 500–5700 times greater than those from biogenic sources. Wind velocity was positively correlated with total NMVOC emissions between 0.2 and 9.4 m s^{-1}, with a maximum concentration of 9 μg l^{-1} occurring at 3.6 m s^{-1}. Zahn et al[16] also recognised that NMVOCs identified in small-scale laboratory studies did not necessarily represent the compounds produced in the field or their rates of emission. The determination of emission rates from sources to produce an NMVOC inventory is further complicated by many climatic and management factors. Sources include animal housing, yards, manure storage, land-spreading and grazing livestock. Manure can be stored in solid form as farmyard manure or as slurry. Differing amounts of straw and organic matter will also alter degradation and emission rates. Further, as the manure ages, emission rates change. Emissions of volatile fatty acids (VFAs), phenols and CO_2 appear to decrease with increasing storage period.[17] Recently, dimethyl sulphide (DMS) was identified as originating from ruminant breath.[18,19] Dairy cows were calculated to be the greatest ruminant contributors to the atmospheric flux of DMS. This may explain some of the unknown DMS of terrestrial origin that was previously thought to be small, but still important, because DMS is oxidised to sulphuric acid, which initiates cloud formation via particle nucleation.[20]

Little information on emissions from poultry and cattle manure sources was found in the literature, the latter being the greater emitter of ammonia. Our experimental emissions chamber (EC) was used to determine emission rates from pig manure in an earlier study.[21] The same approach was used here to determine NMVOC emission rates from dairy cattle slurry and laying hen manure. Emission rates of NMVOCs from sheep breath[19] (the emission rates from cattle were used to estimate emissions from sheep on a body weight basis and pigs[21]) were obtained from the literature and used to construct an inventory for the UK.

MATERIALS AND METHODS
Experimental
Sufficient fresh manure (1 m^3) necessary for duplicate analysis was collected from laying hens and dairy cattle at commercial farms. Samples were stored in 200 l containers at 15 °C over a 3 day period, and emission measurements were made in an enclosed 40 m^3 emissions chamber (EC).[22]

The EC initially encloses 40 m^3 of air which is circulated at 1 m s^{-1} over the surface of the manure held in a 200 l capacity container (2 m × 0.5 m × 0.25 m). The manure was placed in the EC immediately before measurement. The temperature of the EC was 5 °C higher than that of the manure maintained at 15 °C in a water bath to minimise condensation onto the chamber surfaces. A full account of the EC operating conditions, analysis of NMVOCs by thermal desorption gas chromatography/mass spectrometry (GC/MS) and experimental determination of emission rates can be found in Ref 21.

Sampling and analysis
Samples were periodically taken from the EC and analysed to determine emission rates. Analysis required samples to be concentrated using an adsorbent before presenting the sample to the GC/MS system. The widest range of NMVOCs from 500 ml of headspace sample of manure from dairy cattle and laying hens was captured using a polar adsorbent silica (Orbo 52, Supelco Inc, Bellefonte, PA, USA) and a carbon-based adsorbent (Orbo 32) for hydrophobic components. The concentrated headspace sample was thermally desorbed and analysed by GC/MS to determine the NMVOCs' identity and concentration. Chromatographic retention time and mass spectral matching were used to confirm odorant identity. A Hewlett Packard (HP Ltd, Stockport, UK) GC/MS system consisting of a 5890 II Series gas chromatograph and a 5972A mass-selective detector (MSD II) was used for analysis. A 25 m fused silica (crosslinked methyl siloxane) DB-225 column with an internal diameter (id) of 0.2 mm and a 0.25 μm film with a 1 m deactivated fused silica guard column (0.25 mm id) were used. The flow rate of the eluting gas helium was 0.70 ml min^{-1}. An Optic temperature-programmable injector (Ai Cambridge Ltd, Cambridge, UK) was used to desorb headspace samples from the adsorbents and was initially at 40 °C and heated to 220 °C at 16 °C s^{-1} for 1 min for headspace samples. An electronic pressure controller was used to offset peak pressure broadening with increasing GC column temperature. The GC oven conditions were an initial temperature of 40 °C, increasing to 220 °C at 15 °C min^{-1} and remaining at 220 °C for 1 min. The GC/MS interface was at 280 °C.

The mass spectrometer scanned from 35 to 250 mass units every 0.2 s to give responses in the ppb range.

Operational and computational parameters

Emission values were calculated by measuring the increase in concentration in the EC headspace volume. The emission rates were calculated at zero time of the EC run. The reasons for this are threefold. First, the suppression of emission by the mass present in the headspace would be minimised as inferred by Henry's law, because an increasing headspace concentration would reduce the chemical potential or energy for emission to occur and would not reflect the real situation where odorants are rapidly removed. Second, physical and chemical interactions with other odorants which are polar and reactive will complicate the results unnecessarily. Third, oxidative processes that occur in the slurry because of stirring may introduce another factor into the calculation that is difficult to evaluate. The most appropriate solution was therefore to differentiate the equation of the total mass emitted over time and determine the slope. The equation of the total mass emitted was the sum of the integrated equations for the mass leaked and that present in the chamber, and this was best expressed in a quadratic form. The emission rates are expressed as mass emitted per unit area.

Basis for the inventory

Origin of NMVOCs

The majority of NMVOCs originate from the decomposition of undigested protein in livestock faeces,[23] and some are exclusive to the protein sources identified in Table 1.[15,23] Of the nitrogen in the faeces, 50% occurs as undigested protein.[15] Our research studies of emissions of VOCs from pig manure have shown that NMVOC emissions, excluding hydrogen sulphide, change during the aging of manure.[17] NMVOC emissions remain in a relatively constant ratio to those of ammonia ($p < 0.001$), even though volatile fatty acids can decay to lower-molecular-weight gases such as CO_2 and CH_4.

Physical basis of emission rates

Four reasonable assumptions have been made: (1) emissions from manure from grazing and housed livestock are the same as those determined from a

stored manure surface; (2) aging waste has a similar reduction in emission rates of NMVOCs to that for ammonia; (3) emissions of ammonia, NMVOCs and odours from manure are a result of decay processes of organic matter; (4) stored solid manure has similar ammonia and NMVOC emissions to those of liquid manure (2–8% dry matter). These assumptions, which relate to ammonia emissions having some proportionality to NMVOC emissions, have a physical basis. Henry's law recognises proportionality between the concentration in the liquid phase and that in the gaseous phase at equilibrium and can be approximated from the ratio of vapour pressure to solubility.[24] The implications are that those compounds that are virtually insoluble in water, such as the hydrocarbons and alkyl sulphides, have a greater presence in the air than those that are soluble or react with water, such as the phenols and volatile fatty acids (VFAs). However, this is for pure solutions and assumes that the kinetic rates of emission are similar, which is so for compounds of similar molecular mass. Zahn *et al*[16] and the present authors (unpublished data) have identified some evidence for behaviour close to Henry's law for phenols and VFAs. Sources of error can include the adsorption of volatile compounds onto aerosols and particles.

Structure of the inventory of NMVOCs from livestock sources

The inventory was constructed by multiplying the emission rate of an NMVOC by the ratio of the ammonia emission rate and the ammonia inventory value to give values as kt year^{-1}, using the numbers of animals from the MAFF 2002 agricultural census[25] (Table 2). It must be stressed that it is the ratio of the NMVOC to ammonia and not the NMVOC emission rate *per se* that is important for the collation of an inventory. The proportionality of each NMVOC to ammonia can be calculated from Table 4 (see 'Results and discussion'). Total ammonia emissions for each of the livestock sources (Table 2) include those for outdoor and indoor sources as well as for different waste management approaches to manure storage and land application. Variability within the ammonia inventory was therefore translated into the NMVOC inventory. Uncertainty analysis was performed using @RISK software (Palisade, Europe, London, UK). Normal distributions were assumed for multiple measurements of three or more. A simulated

Table 1. Amino acid sources of NMVOCs

NMVOC	Amino acid
2-Methyl propanoic acid	Valine
3-Methyl butanoic acid	Isoleucine
2-Methyl butanoic acid	Leucine
Methanethiol	Methionine
Dimethyl sulphide	Cysteine
4-Methyl phenol	Tyrosine
4-Ethyl phenol	Tyrosine
Indole	Tryptophan
3-Methyl indole	Tryptophan

Table 2. Summary of NMVOC and ammonia emissions and livestock numbers in the UK (2002)

	Sheep	Pigs	Cattle	Poultry	Total
Livestock numbers (millions)	44.7	6.3	11.4	165	227.4
Ammonia losses (kt year^{-1} as N)	15.6	26.1	133.6	35.0	210.3
NMVOCs (kt year^{-1})	6.6	25.3	102.4	30.4	164.6

Latin hypercube sampling technique was run using 3000 iterations and identified an overall variation of 29% in the mean annual emission value.[26]

Collection of sufficient sheep manure proved difficult. Projected emission rates were calculated on the basis of ammonia emission figures from cattle. The assumptions were that 10 sheep were equivalent to one cow and that they have similar digestive pathways. This has been verified by unpublished data (Webb J) used by ADAS which identify the annual production of total nitrogen (TN) from one sheep as 11 kg and from one cow as 106 kg. For both animal types, about 60% reverts to total ammonia nitrogen (TAN).

In addition, new emission values for DMS and acetone[18] from cattle breath were used to determine additional amounts for inclusion in the annual NMVOC total. We have assumed that, by using the same ratio of expiration rate of sheep to cattle as the body weight ratio of one-tenth, we can project a value for sheep. Contributions by ruminants to the global flux of DMS were evaluated by measurement and dietary studies of lactating cattle in a mass balance calculation.[19] With a population of 12 million cattle in the UK there will be 10.3 kt DMS year^{-1} produced from cattle. We estimated acetone emissions in breath to be about one-third of those of DMS as reported for ketotic cattle.[27] There are 47.4 million sheep in the UK and, assuming that they have one-tenth of the body weight of a cow, they produce ca 3.91 kt DMS year^{-1}.

RESULTS AND DISCUSSION
Emission rates from cattle slurry and chicken manure

Dry matter (DM) content and pH (Table 3) were determined in duplicate for each manure sample. The concentrations of NMVOCs in the manure prior to the determination of emission rates are shown in Figs 1 and 2 for dairy cattle slurry, where fatty acids predominate. Figs 3 and 4 show a high concentration of acetic acid for laying hen manure. Other compounds present include volatile fatty acids, phenols and indoles.

Table 4 shows the emission rates of NMVOCs from both manure types. The variability of emission from these manures was determined as ±20% of the mean for those emitted at a low rate of 10 g m^{-3}day^{-1} and ±5% for those emitted at a higher rate. Table 4 also includes averaged emission rates of NMVOCs from aging pig slurry over a 112 day period from Ref 17. As expected, pig and hen manure emit

Table 3. Manure analysis

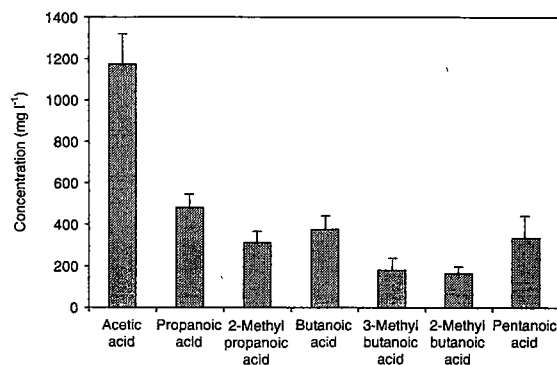| Manure	Dry matter (g kg^{-1})	pH	NH$_4$ content (kg m^{-3})
Laying hen	501.2 ± 144.8	8.3	7.52 ± 0.66
Dairy cattle slurry	53.7 ± 9.5	7.1	1.09 ± 0.7

Variation given as one standard deviation.

Figure 1. Concentrations of NMVOCs present in dairy cattle slurry investigated for emission rates in the emissions chamber (bars indicate standard error).
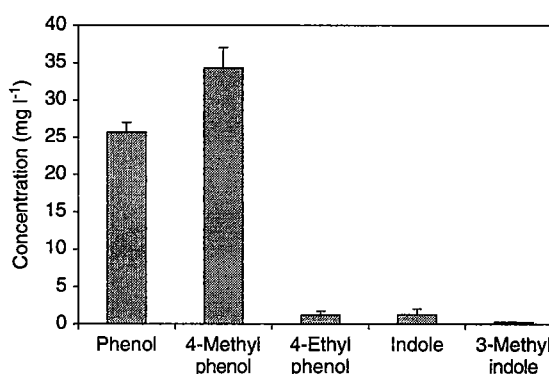

Figure 2. Concentrations of NMVOCs present in dairy cattle slurry investigated for emission rates in the emissions chamber (bars indicate standard error).
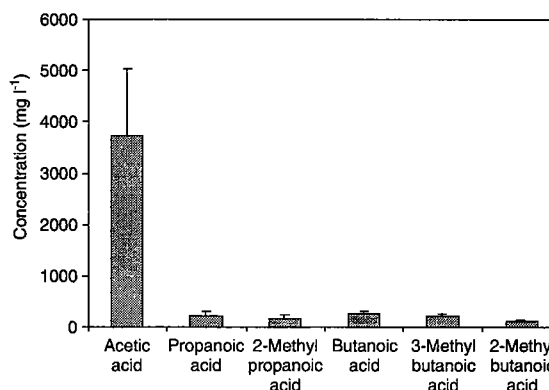

Figure 3. Concentrations of NMVOCs present in laying hen manure investigated for emission rates in the emissions chamber (bars indicate standard error).

more NMVOCs than cattle manure per unit volume and are more odorous. The volume of manure or slurry is significant to NMVOC emission rates for an absolute determination, but here the ratio to ammonia emissions is relevant. The ratio of the NMVOC to the ammonia value should overcome the complexities of determining the effect of manure or slurry depth.
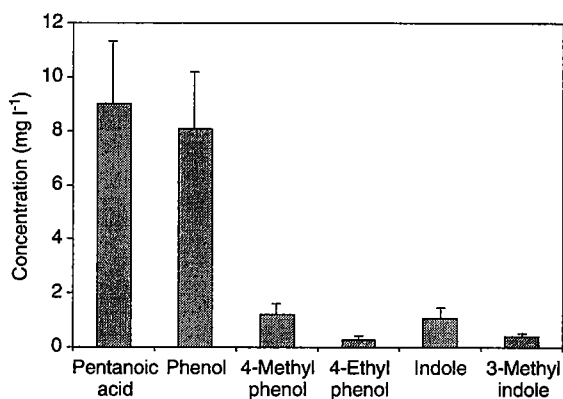
Figure 4. Concentrations of NMVOCs present in laying hen manure investigated for emission rates in the emissions chamber (bars indicate standard error).

Table 4. Emission rates (g m⁻³day⁻¹) of NMVOCs from different types of livestock manure using the emissions chamber

Volatile compound	Pig slurry[a]	Cattle slurry	Laying hen manure
Dimethyl sulphide	7.00	ND	156
Dimethyl disulphide	ND	ND	683
Dimethyl trisulphide	ND	ND	14
Ammonia	21.70	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	ND
Butanoic acid	2.85	0.06	Trace
3-Methyl butanoic acid	0.34	0.22	ND
2-Methyl butanoic acid	0.34	0.14	ND
Pentanoic acid	0.07	0.01	ND
Phenol	0.09	0.01	Trace
4-Methyl phenol	2.21	2.80	Trace
4-Ethyl phenol	0.14	Trace	ND
Indole	0.01	Trace	ND
3-Methyl indole	0.01	Trace	ND

[a] Values from Ref 17. ND, none detected.

Emissions include sulphides and phenols and, in the case of pig slurry, indoles. The emission rate of acetic acid gave the greatest variability for the three different manure types. Acetic acid and many of the odorous NMVOC species are readily water-soluble (with the exception of the sulphides and indoles) and are prone to displacement on the surface of the adsorbent material during collection. This is illustrated by the absence or low concentration of acetic acid in the emission profile from some manure types, although at high pH for the chicken manure the acetate ion would predominate rather than the undissociated acetic acid that readily volatilises. Emission rates of ammonia and the sulphides from laying hen manure were high. The NMVOC species originating from the different manure types were the same but were emitted at different rates.

Validation of the relationship between ammonia and NMVOC emissions

The EC measurements showed a significant correlation ($p = 0.01$) between NMVOC and ammonia emissions for laying hen manure. We did not find a significant correlation between NMVOC and ammonia emissions for dairy cattle slurry, as the former were too low. However, as stated above, we have identified that the ratio of ammonia to NMVOCs is good ($p > 0.001$) for pig slurry even during the process of aging.[17] This provides evidence that there is the potential to use the NMVOC/ammonia emission ratio as a factor to predict NMVOC emissions.

Inventory of NMVOCs from livestock

The approximate annual emission masses for each NMVOC from the different livestock sources were used to calculate the nation's emissions (Table 5) and gave a total value of 165 kt + 56 kt for 2002 (Table 2). Variability for these annual emission rates was calculated to be from 35% for the highest-concentration components to 50% for the lower-concentration components. This includes factors from chamber and analytical variance together with a 30% addition for the variance from the ammonia inventory.[26]

Our results help to reduce the uncertainty over the origins and types of other NMVOCs[28] currently unaccounted for in the atmosphere. Air pollution associated with NMVOCs originating from agriculture is complex and concerns the interaction of point or diffuse sources, climatic conditions, air chemistry and atmospheric sinks. Recently recognised atmospheric VOC sinks include the formation of[29,30] and attachment to aerosols or particles.[31] Also the role of heterogeneous adsorption and reactions of NMVOCs on aerosols[32] that may contain moisture[33] is not well understood.

Table 5. Projected annual emissions (kt year⁻¹) of NMVOCs from livestock in the UK (2002)

Volatile compound	Sheep	Pigs	Cattle	Poultry
Dimethyl sulphide	3.91	8.4	10.3	5.6
Dimethyl disulphide	ND	0.0	ND	24.3
Dimethyl trisulphide	ND	0.0	ND	0.5
Acetone	1.62	0.0	3.4	ND
Acetic acid	0.6	8.9	55.2	Trace
Propanoic acid	0.0	0.4	1.5	Trace
2-Methyl propanoic acid	0.0	0.2	0.7	ND
Butanoic acid	0.0	3.4	0.6	ND
3-Methyl butanoic acid	0.0	0.4	2.1	ND
2-Methyl butanoic acid	0.0	0.4	1.4	ND
Pentanoic acid	0.0	0.1	0.1	ND
Phenol	0.0	0.1	0.1	Trace
4-Methyl phenol	0.3	2.7	27.1	ND
4-Ethyl phenol	Trace	0.2	Trace	ND
Indole	Trace	0.0	Trace	Trace
3-Methyl indole	Trace	0.0	Trace	ND
Total	6.6	25.3	102.4	30.4

ND, none detected.

Each NMVOC will have specific atmospheric chemistry and require a robust inventory to predict effects of air quality.

Evaluation of the impact of NMVOCs resulting from livestock production requires some form of categorisation with regard to the effect on air quality and tropospheric air chemistry. Zahn et al[16] demonstrated that a plume of 24 odorous compounds changed composition upon dispersion in the atmosphere and that there was a linear relationship between concentration and distance. Transport efficiencies over 100 m ranged from 100–40% for C_2-C_9 VFAs respectively to about 10% for the phenolic compounds. This clearly shows that localised atmospheric events occur and may reduce air quality and that high concentrations can rapidly disperse, but there are no indications of the transportation factors. Zahn et al[16] related transport efficiencies to the physical properties of the NMVOCs, such as solubility or the ability to collect water molecules, and to other atmospheric conditions. The majority of NMVOCs from livestock sources are polar and water-soluble and may adsorb onto particles depending on humidity.[33] Particles in drier atmospheres are better able to adsorb alkanes, polycyclics and long-chain fatty acids.[34] These findings have implications for building larger intensive animal-housing units that may compromise livestock health and produce subclinical level effects other than the obvious direct toxicity that may occur with ammonia or sulphides. To define the effects of NMVOC emissions from livestock, the focus should be directed at how NMVOCs travel and impact upon the rural or regional air quality. Once we can determine atmospheric concentrations of NMVOCs, the collective, and probably not insignificant, impact on the greenhouse effect can be assessed.

CONCLUSIONS

Emission rates of NMVOCs were determined for fresh dairy cattle slurry and laying hen manure using an enclosed emissions chamber. NMVOC emissions of odorous dimethyl sulphides were $753 \pm 263\,\mathrm{g\,m^{-3}day^{-1}}$ and dominated those from laying hen manure. NMVOC emissions from dairy cattle slurry were predominantly volatile fatty acids (C_2-C_5, $6.3 \pm 3.1\,\mathrm{g\,m^{-3}day^{-1}}$) and phenols ($2.4 \pm 1.2\,\mathrm{g\,m^{-3}day^{-1}}$). A collated value of $165 \pm 56\,\mathrm{kt}$ NMVOCs year^{-1} originating from agriculture was derived from the best available estimations and clearly shows that NMVOCs from biogenic sources have been underestimated. Emissions from livestock agriculture effectively double current estimates from biogenic sources of $50-100\,\mathrm{kt\,C\,year^{-1}}$,[8] which would be about 20% greater for comparison (if considered as alkanes with a general formula of C_rH_{2n+2}). Improving the accuracy of current NMVOC emission estimations will enable air quality to be improved and emission target options from anthropogenic sources to be realistically achieved.

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