Discussion paper, Task 6

Emissions of NMVOC from manure management (NFR 4B)

The current Guidebook (GB) discusses NMVOC (Non-Methane Volatile Organic Compounds) from manure management but do not include emission factors for NMVOC. In the UNECE protocol to address reducing VOC emissions and their transnational flows (United Nations Economic Commission for Europe (UNECE), 1991) a list of the principal NMVOCs, from the main emission sources, and a classification of the VOCs according to their importance, is included. The protocol classifies NMVOCs into three groups, according to their importance in the formation of ozone episodes, considering both the global quantity emitted and the VOCs reactivity with OH-radicals, (UNECE, 1991 Table 1 and 3). Over 200 volatile compounds originating from cattle, pigs and poultry have been identified (Shiffmann et al., 2001), although only ca. 20 compounds were considered significant by Hobbs et al. (2004) and US EPA (2012) covering up to 80-90 % of the total emission. Some of the major NMVOCs released from agricultural barns can be seen in Appendix A.

In the context of the Guidebook, NMVOCs are defined as 'all those artificial organic compounds other than methane which can produce photochemical oxidants by reaction with nitrogen oxides in the presence of sunlight' (UNECE, 1991). These compounds also contribute greatly to the odour associated with manure.

The wide range of compounds has very different physical and chemical properties. Some are relative active, some are rather inactive, some are water soluble some aren't, some binds to surfaces other not - altogether giving a mixture giving high challenges to the measuring methodology which again may yield high uncertainties and to the interpretation of measured data. A large US study (US EPA, 2012) showed that up 50% of the NMVOCs from animal handling is iso-propanol and n-propanol followed by acetaldehyde and short chained acids (acetic acid, propionic acid, butanoic acid). Ethyl acetate was only found in major quantities in cattle barns. According to the classification made by UNECE (1991) the major part of the emissions from animal handling can be classified as "Less important". Hobbs et al. (2004) has previously noted that sulphur compounds could be a major source. In the US study Dimethylsulphide (DMS) covered approximately 1-3 % of the NMVOC emission. Dimethyl disulphide (DMDS) was only found in larger concentrations in poultry barns, which is consistent with Hobbs et al. (2004).

The EMEP area covers a wide range of climatic conditions, from boreal to warm temperate/sub tropic conditions and from coastal to continental climates. Within this area the NMVOC emission per year for an animal type may vary due to differences in:

- Feeding
- Housing
- Manure storage
- Manure application
- Number of grazing days
- How the different NMVOCs react on the local climatic conditions.

The development of Tier 2 emission factors for the different animal types listed in the current guidebook is therefore a challenge considering the limited amount of data available.

1. General emission physics

The emission of NMVOCs depends primarily on the physical and chemical properties. The emission of NMVOCs from animal farm operations can generally be divided two sources:

1. surface dependent sources
2. surface independent sources

1.1. Surface dependent sources

The release of NMVOCs from silage piles, feeding tables and fouled areas in the barns, manure stores and application of manure in the field depends on the amount of NMVOCs and concentration in the organic substrate. They are then transported from the organic substrate to the gas phase (air above the substrate) across the air-liquid system due to a difference in the partial pressure of dissolved and gaseous compounds between the surface area and the atmosphere. Transport across the air-liquid system may be referred to as release.

A difference in the partial pressure is essential for the release of gasses from a solution of dissolved gasses to the atmosphere, so the release is a function of the concentration of gas dissolved. So, the release is a function of the concentration of gas dissolved in the organic layer. In their ionised form (i.e. charged or dissolved), chemical compounds cannot exchange between the liquid phase and the gas phase. Because many of the gases and odorous compounds are weak acids or bases, the form of these compounds in the aqueous phase (and hence their potential to be released) will depend on the chemical equilibria and will be affected by the pH. In general terms manure has a pH of 7-8, silage a pH of 3.5-4.5 and fresh forage a pH of 5.5-6.0.

Several studies (Angelidaki et al., 1993, Sommer & Husted, 1995) have shown that the main buffer components controlling the pH are the total inorganic content, total ammonium nitrogen and total acetic acid.

Understanding and quantification of the emissions is generally based on the two-film theory (Lewis and Whitman, 1924), which assumes that the overall resistance to mass transfer across the air-liquid system results from resistance through two thin films (air and liquid) adjacent to the air-liquid interface. The emission is a transport model and does not consider the biological formation in the organic layer. The transport of gases from the liquid surface to the atmosphere can be illustrated as:

1. An upward transport of dissolved gases from the bulk of the organic matter
2. A transfer of gases between the surfaces across the liquid phase and the air phase
3. An upward transport of gas from the air phase immediately above the liquid across the air film layer to the free atmosphere.

Above the film layer, convection or turbulence created by the wind over the surface will decrease the air concentration and increase the release. Below the liquid layer (the bulk of the organic layer) turbulence can be increased by stirring of manure, handling of feed or ebullition of gasses in the manure.

The transport of gases across the liquid film is mediated by molecular diffusion. At the gas-liquid interface, Henry's constant (H_{CC}, unitless, gas/liquid) controls the partitioning of the compound between the gas and

the liquid phases and hence the transport of gases across the air film layer which again is influenced by local climate properties affected by the convection of turbulence created by wind over the surface.

In Figure 1 is shown some values of H_{CC} (Parker et al. 2010). The Figure shows that some of the easiest NMVOCs to be released are the short chained acids. These are also among the major released compounds (Appendix A).

As the partial pressure of a compound depends on the actual temperature the absolute release can be simplified to a function of concentration, temperature, wind speed and H_{CC}.

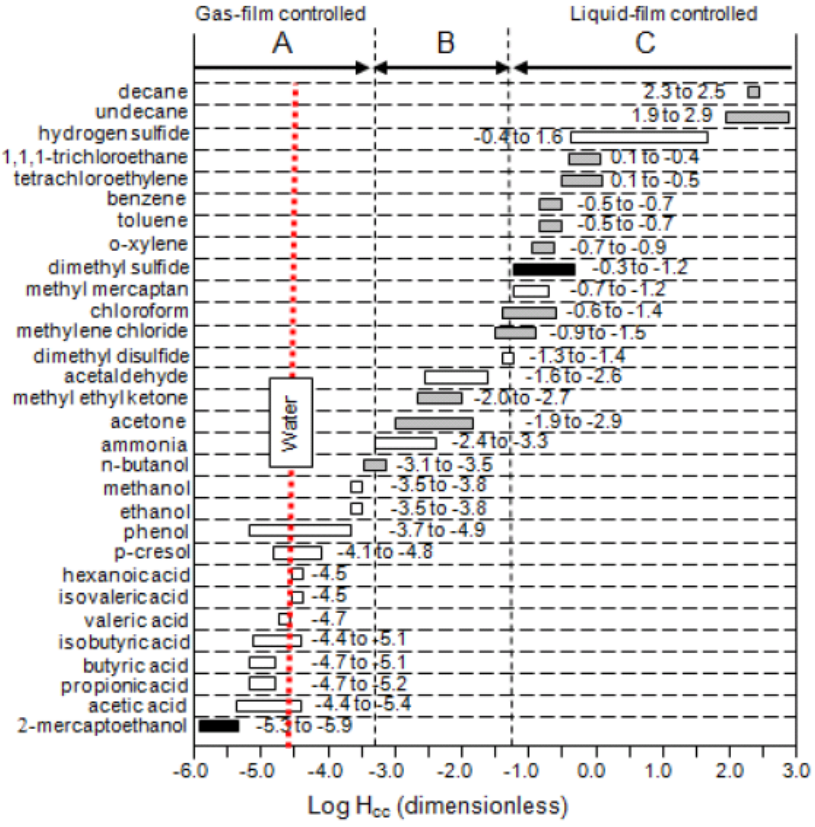


Figure 1.Henry's Law constants and the emission controls for VOCs (Parker et al. 2010).

1.2. Surface independent emissions

The surface independent sources are from animal breath or excreted gases from the anus. These can to some extend be seen as independent of the actual climatic conditions as the animals are expected to have an exhalation and excretion rate independent of temperature and wind speed as these can be assumed to be constant between regions. However, differences in feeding especially for ruminants may cause differences in the emission as this is known to affect the function of the stomach.

2. Data references

As background for the following is used the current GB and published literature data as well as contact with researchers in the area. Within the last five years several studies have been made where the NMVOC emission has been measured. Following the discussions on odours from animal production facilities there has also been a high number of odour measurements. The latter is often focused on measuring the compounds with the highest odour as concentrations and not absolute emitted amounts. Such data are therefore not easily included in emission estimates for NMVOC.

The measuring techniques also vary, from canister sampling to acoustic measurements.

In this discussion paper the most recent literature data are used and it is attempted to quantify the differences in the different methodologies.

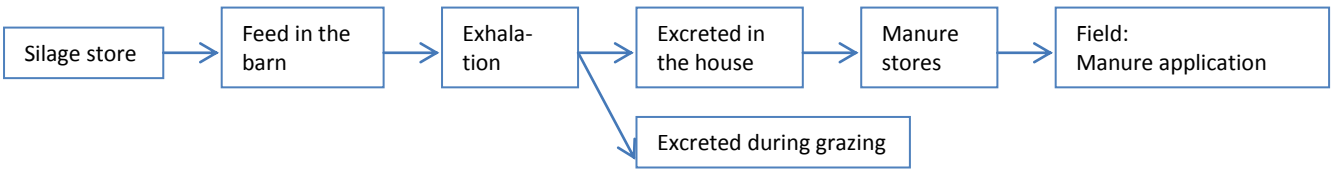
The major data source for NMVOC emission is US EPA (2012). In USA a National Air Emissions Monitoring Study (NAEM) was initiated in 2005 in order to measure ammonia, PM, H_2S, NMVOC and TSP from animal operations. The NAEM study has intensively measured the most relevant parameters for air emission from 25 different animal production facilities covering dairy cattle, sows, fatteners, egg layers and broilers for a range of climatic conditions in the USA over a two year period. The raw data are freely available but final conclusions from the study have not been made public yet.

2.1. NMVOC sources from agricultural activities

Agricultural activities may emit NMVOC from both feeding operations (Alanis et al. 2010), exhalation from animals (Elliot et al. 1997, Hobbs et al. 2004), from excreted manure and the processes occurring in the manure when it is inside the barns (slats and deep-pit) and from manure stores outside the barns (Malkina et al., 2010, Alanis et al., 2010, Ngwabie et al., 2008, Feilberg et al. 2010, Hobbs et al. 2004) and from composting (Kumar et al., 2011), manure application to the field and manure deposited during grazing.

NMVOC from agricultural activities are shown in Figure 2. In areas where cattle are fed with silage large emissions from the open areas in the silage store can occur. The emission from silage continues further from the feed when it is placed in front of the cattle. Exhalation may also be a large source, but here there is likely to be a large difference between ruminants and non-ruminants, from excreted manure in the housing, from the surface of the manure stores and finally when the animal manure is applied in the field.

Figure 2. Sources of NMVOC



Most attention has been drawn to the emission from manure as many of the compounds emitted are thought to evaporate from the surface of manure in barns and in stores.

3. Measuring of NMVOC data

There are three main methodologies: Air sampling in bags or canisters followed by flame ionization detector (FID) or simple GC-MS, by PRT-MS and or acoustic measurements. The difference in the methodologies should be understood before development of EFs can be made.

3.1. Air sampling

Air sampling in a bag or canister followed by Gas Chromatography and Mass Spectrum (GC-MS) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. The gas chromatograph utilizes a capillary column to separate the different molecules. The chemical properties between different molecules in a mixture will separate the molecules as the sample travels the length of the column. The molecules are retained by the column and then elute from the column at different times, and this allows the mass spectrometer downstream to detect the ionized molecules separately by using their mass to charge ratio. As the bags and canisters are only a grab sample over a very short time span the position of the sampling position are crucial as well as the air flow and other relevant conditions should be monitored. Many of the NMVOCs get bound to surfaces or react in the atmosphere. Special attention is therefore given to cleaning and coatings of the bags/canisters. Furthermore it is very time consuming. Because the air sampling is often made in a short time span the diurnal or annual emission pattern becomes a variable, when such data are used for establishing EF for NMVOCs.

3.2. PTR-MS

PTR-MS is the abbreviation for Proton Transfer Reaction - Mass Spectrometry, allowing for real-time measurement of volatile organic compounds (VOCs). The VOC trace gases in the sampled air undergo (mostly) non-dissociative proton transfer from H_3O^+ ions, which are injected into a drift tube and measured. The fundamental process in a PTR-MS instrument can be written as

$$H_3O^+ + R \longrightarrow RH^+ + H_2O$$

This means that protonated water (H_3O^+ interacts with the trace gas (R). During this interaction a proton transfers from the hydronium to the trace gas molecule, which leads to a protonated and therefore ionized molecule (RH^+) and a neutral water molecule (H_2O). The proton transfer reaction is energetically possible for all VOCs with a proton affinity higher than that of water (166.5 kcal/mol).This non-destructive method can measure with a time span of minutes and give detailed diurnal information. However, a received signal heights may constitute of different VOCs and should be analysed carefully.

3.3. NMHC

NMHC (Non Methane Hydro Carbons) measurements are also used as proxies for NMVOCs. NMHC techniques are designed to measure the total, methane, and non-methane hydrocarbon content of gas samples. The analysers are based on different principles: photo acoustic analysers, flame ionization detector (FID) with an electronic control that delivers a small portion of the sample gas to the detector flame combined with MS or GC-MS. During the combustion process, organic or hydrocarbon-based gases in the sample are ionized and detected by an instrument and reported as a concentration. The amount of NMHC are sometimes reported as the amount of C or measured as the area under the individual peaks in

166 the MS. Sometimes the reference calibration is toluene. When using such measurements a conversion to
167 NMVOCs should be made in a defined way.

168 Based on the principal quantities of NMVOCs in the NAEM study (USEPA 2012) a multiplication factor from
169 total C to NMVOC could be ~1.5-2.0 because the majority of NMVOCs contains 2-4 carbon and 1-2 oxygen
170 atoms.

171 In the NAEM study different methodologies were used for VOC measurements: Canister sampling, photo
172 acoustic techniques and MS which may yield different amounts of VOCs. In one fattening barns where both
173 NMHC and VOC were measured the average difference on the specific days were 1:4 on an average for 16
174 different dates (Table 1). On one location in the NEAM study with broilers where both methodologies were
175 used the data with photo acoustic measurements were discharged due to unreliable results. The canister
176 measurements showed an NMVOC emission of 0.10 g VOC kg broiler-1 day-1. This can be compared with
177 another farm where NMHC were measured with 0.031 g NHMC broiler-1 day-1 (Table 2).

178 Table 1. Relation between VOC measurements and NMHC measurements on specific days in a pig finisher barn and in a dairy barn.

Category	Cite	Monitoring area	Day	VOC emission, kg·d-1	NMHC emission, kg·d-1	VOC/NMHC
Finishing	IN3B	R5	06/01/09	0.66	0.26	2.50
Finishing	IN3B	R5	06/08/09	0.81	0.11	7.11
Finishing	IN3B	R5	06/24/09	0.81	0.16	5.09
Finishing	IN3B	R5	07/13/09	0.29	0.17	1.75
Finishing	IN3B	R5	07/22/09	1.23	0.29	4.21
Finishing	IN3B	R6	06/08/09	4.06	0.43	9.40
Finishing	IN3B	R6	07/13/09	0.79	0.34	2.35
Finishing	IN3B	R6	07/22/09	1.49	0.48	3.11
Finishing	IN3B	R7	06/01/09	0.95	0.33	2.88
Finishing	IN3B	R7	06/24/09	0.44	0.36	1.23
Finishing	IN3B	R7	07/13/09	1.12	0.42	2.69
Finishing	IN3B	R8	06/01/09	1.01	0.24	4.14
Finishing	IN3B	R8	06/24/09	0.52	0.17	3.11
Finishing	IN3B	R8	07/13/09	1.48	0.34	4.34
Dairy (barn)	IN5B	B1	08/17/09	78	20.70	3.77
Dairy (barn)	IN5B	B2	08/17/09	84.2	14.80	5.69
					Average	3.96

179

180 Table 2. Preliminary and not verified EFs from different measurements in average daily emissions, g NMVOC animal^{-1} day^{-1}. The
181 data are not corrected for differences in climatic conditions and other relevant parameters.

	g VOC kg animal-1 day-1		
	Canister, GC-MS	NMHC, GC-MS	PRT-MS
Broilers	0.10 (±0.079) (1)	0.031 (±0.020) (2)	
Egg layers	0.114 (±0.309) (3)		
Fatteners	0.97 (±0.84) (3)	0.36 (±0.33) (4)	2.91 (9)
			8.67 (10)
Dairy cows	107 (±86.6) (7)	27.0(±8.4)(8)	23.9 (5)
			1.8 (6*)
Sheep			6.9 (11)

182 1: NAEMS (CB1B). Average weight, 1.23 kg/bird.

2: NAEMS (KY1B). Average daily emission independent of size (0.04 – 2.8 kg/bird).
3: NAEMS, different sites. Average emission per day for pigs of 65-130 kg.
4: NAEMS, different sites. Estimated for 70 kg pig.
5: Ngwabie et al. 2008.
6: Shaw et al. 2007. * Chamber measurements probably only hay feeding without silage.
7: NAEMS (WA5B and WI5B)
8: NAEMS (IN5B)
9: Feilberg et al. 2010.
10: Ngwabie et al. 2007. Upscaling based on the CH4 emission and 11.0 million fatteners.
11: Ngwabie et al. 2007 Upscaling based on the CH4 emission and 2.77 million housed sheep on slats. No information on feed type, hay or silage.

Traubue et al. (2010) who used both canisters and sorbent tubes combined with GC-MS in their analysis for emissions from a poultry building found that if they only used canisters alone for VOC specification, only 55 % of the compounds in their study would have been quantified and in areas where poultry were present less than 50 % would have been quantified. The same were also found if only sorbent tubes were used and only 45 % in the areas where poultry were present.

This could explain some of the observed differences for fatteners.

Precautions should therefore be taken when giving absolute estimates of the EFs depending on the used methodology and quantified uncertainty estimates.

4. The effect of climate

The overall emission can be divided into two components:

- Emissions that are independent on climate
- Emissions that depends on climate

Exhaled NMVOC emissions from the endothermic animals will be independent of the local climatic conditions and must assumed as being constant over the EMEP area for animals having the same productivity/feeding.

Emissions from the silage store, the feeding table and the manure are going from a liquid phase into the air and have therefore to cross the liquid-gas film layer. For these sources a likely climate dependent gradient over the EMEP area will be seen.

4.1. Pigs and poultry

Pigs and poultry need high temperatures, 18-22 °C, to maintain optimum production conditions. Therefore they are kept in insulated houses with mechanical ventilation in cold and temperate climates and in more naturally ventilated houses in warmer climates, see Figure 2.

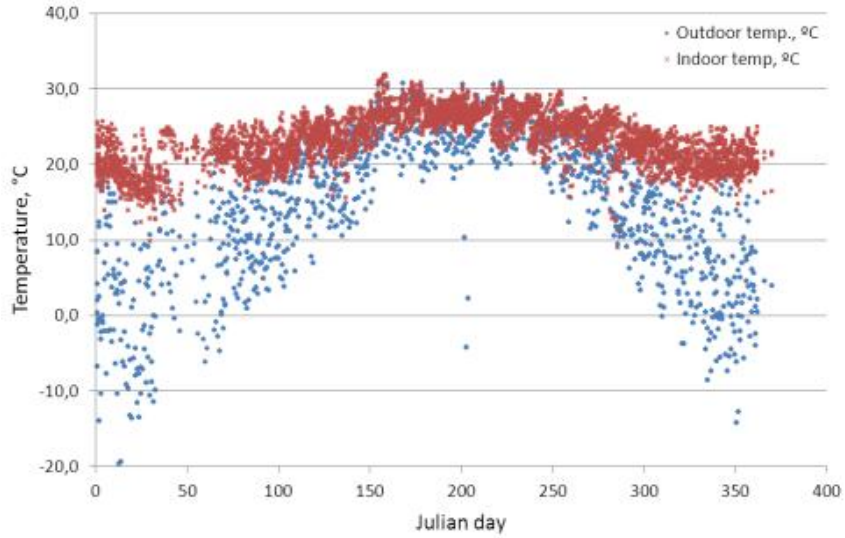


Figure 2.Measured outdoor and indoor temperature in fattening housing in the NAEM study (US EPA, 2012).

Despite the outdoor temperature varying from -20°C to +30°C, the indoor temperature is kept fairly constant over the year. During winter in the cold climates the ventilation rate is kept at a minimum to reduce the heat loss and in summer the ventilation rate is high to avoid over heating of the barns. The decreased ventilation rate in winter increases the NMVOC concentration in the building (Feilberg et al. 2010 and US EPA, 2012) but decrease the NMVOC emission from the surfaces as the air flow is reduced. This is similar to ammonia emission. How much the emission will decrease in winter compared to summer depends on the distribution between exhaled NMVOC and NMVOC from the manure because the exhaled NMVOC is independent of the ventilation rate.

If the difference between outdoor temperature and temperature in the barn is plotted against the outdoor temperature, it yields a nearly straight line, see Figure 3. For poultry and pigs a correction according to regional climatic conditions over the EMEP area is therefore possible based on the difference in the outdoor temperature and the indoor housing temperature (Δ T, °C).

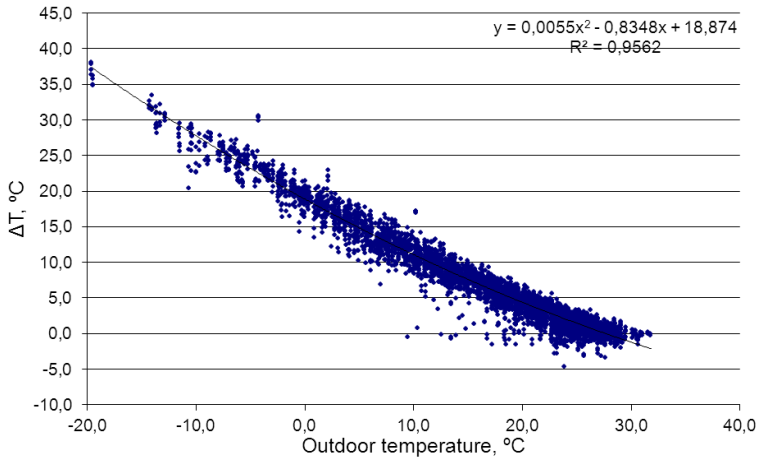


Figure 3. The difference between indoor and outdoor temperature (Δ T, C°) in fattening housing plotted against outdoor temperature.

In Figure 4 is shown the relationship between the NMVOC emission and Δ T for fattening pigs and in Figure 5 the relation between NMHC and Δ T. Although the relationship is not crystal clear, the tendency is that when it is cold outside (high Δ T), the ventilation rate is low and consequently the NMVOC emission is reduced.

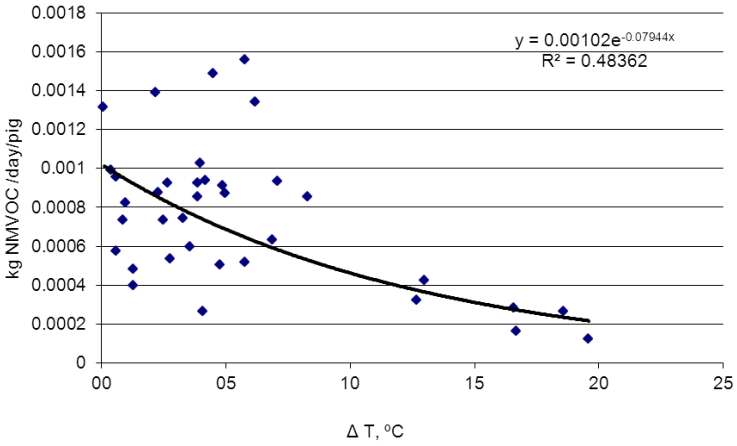


Figure 4. Relationship between the difference in indoor and outdoor temperature (Δ T, C°) and the NMVOC emission for fattening pigs. Weight interval 65-130 kg hd-1.Data from US EPA (2012).

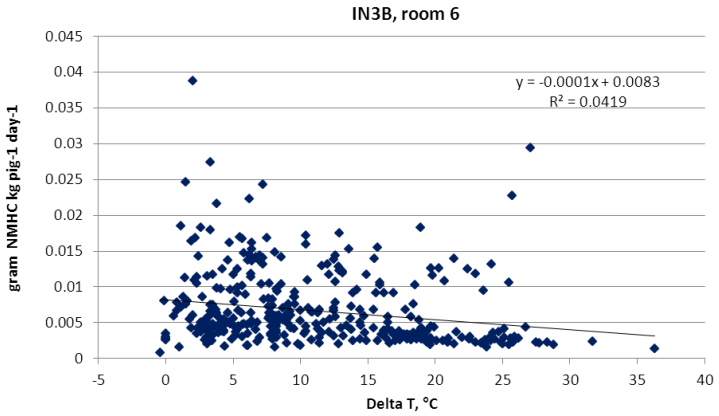


Figure 5. Relationship between the difference in indoor and outdoor temperature (Δ T, C°) and the NMHC emission for fattening pigs. Weight interval 7-130 kg hd-1. Data from USEPA (2012).

4.2. Cattle, sheep and goats

Cattle, sheep and goats has less temperature demands and are often in warm and temperate conditions housed in naturally ventilated barns where the temperature is following the outdoor temperature within a range of 4-5°C. In very cold climates their winter housing will probably be in half-insulated houses to avoid the very low temperatures. Here must, in general be assumed an emission which also depends on both temperature and wind speed. It is unclear, if the effect is larger or smaller compared to insulated barns.

The un-insulated barns with cattle will have a higher wind speed during winter, which may compensate for the decrease in the emission due to the lower temperature. A climatic effect over the EMEP area may therefore be seen here as well.

For dairy cows in the NAEM study is the temperature interval where NMVOC and NMHC has been measured very small and not big enough to give a clear recommendation of the effect of temperature (measurements are mainly carried out in June-August on one location with average barn temperatures in the whole period of 20.5 °C (+- 2.65). On the other hand Alanis et al. (2010) found a significant effect of temperature on the emission of acetic acids from feed sources (P<0.001) indicating that a regionalisation should take be taken into account as the acids and alcohols are the major NMVOC sources.

5. The effects of feeding and productivity

5.1. Diurnal emissions

When looking at the data from Ngwabie et al. (2007, 2008, 2011), Shaw et al. (2007) and Feilberg et al. (2010) measured by Proton-Transfer-Reaction Mass Spectrometry it can be seen that there is a large diurnal emission which can be related to the activities of the animals, Figure 6.

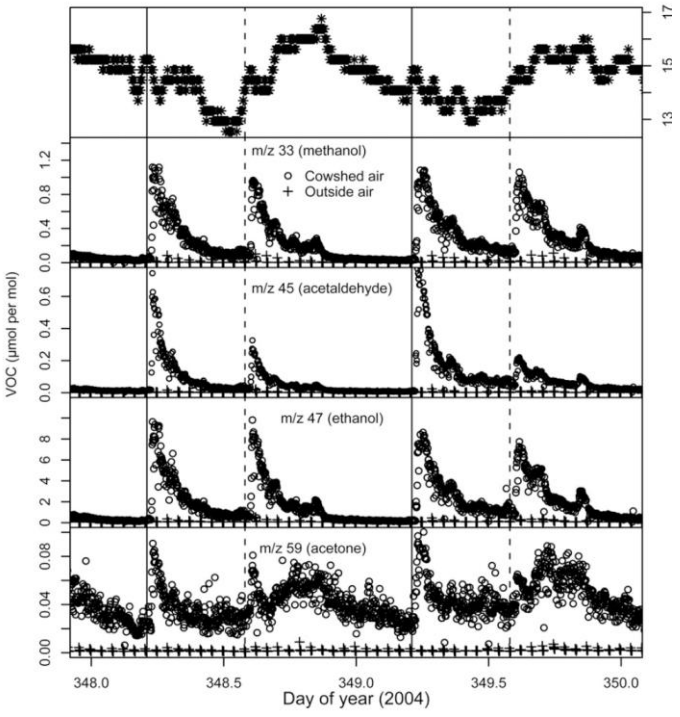


Figure 6. Diurnal emission of some NMVOCs from a dairy shed (Ngwabie et al. 2008)

For ruminants like cattle and sheep, which have distinct activities during the day, a split can be observed between the feeding/eating process and time when rumination takes place. During feeding/eating high emission of e.g. methanol, acetaldehyde and ethanol are seen immediately after activation of the animals and restricted to a few hours. These emissions can probably be related to emissions from the feeding activity, which is often silage (fermented grass/maize) and from exhalation during the feeding and dropping of faeces. Contrary to this, acetone can be measured for several hours and normally when the animals are at rest, indicating that this emission is from the ruminate process (Elliot-Martin 1997, Spinhirne et al. 2003, 2004). For non-ruminants like pigs, which have a more day/night activity the general pattern is low emissions during the night and high emissions throughout the day with low levels of acetone.

The use of grab sampling to estimate annual emission factors may therefore be biased depending on when the sampling has taken place and should be used with precaution.

5.2. Feed composition and amount of feed affects the NMVOC emission

5.2.1. Feed composition

By far the largest NMVOC sources are from fermentation and fat metabolisms, such as alcohols (methanol, ethanol, propanol, butanol), acids (acetic, propanoic, butyric), ketones (acetone), aldehydes (acetaldehyde) and acetates. Only a minor part (<4 %) is coming from the breakdown of amino acids like phenols and sulphur compounds like dimethyl sulphide and dimethyl disulphide (except for poultry, up to 10 %), See Appendix A (US EPA 2012).

Alanis et al. (2010) measured the emission of volatile fatty acids from six different dairy facilities in Central California, USA. The climate here is warm to very warm the whole year around. The relation in the emission between acetic acid, propanoic acid, butanoic acid and hexanoic acid emission in summer is shown in Table 3a. The acetic acid was the far most important emitter of the four volatile fatty acids (VFA). This can also be found in the data in Appendix A.

Table 3a. Volatile Fatty Acid (VFA) emission from feeding tab le (Total Mixed Ratios) and silage stores, g hr^{-1} m^{-2} (Alanis et al. 2010).

	Acetic	Propanoic	Butanoic	Hexanoic
Feeding table	0.424	0.013	0.014	0.003
Silage store	1.206	0.080	0.004	0.006
Feeding table	100 %	3 %	3 %	1 %
Silage store	100 %	7 %	0 %	0 %

Furthermore Alanis et al. (2010) found that the emission of acetic acid in winter was only 50 % of what was measured during summer (Table 3b) compared to the winter period. Alanis et al. (2010) measured the acetic acid content in the feed of 1.9 %.

Table 3b. Acetic acid emission from TMR (Total Mixed Ratios) on the feeding table and from the silage store on six different dairies in Central California, g h^{-1} m^{-2} (Alanis et al. 2010).

	Feeding table	Silage store
Fall	0.09	0.31
Winter	0.08	0.15

Summer	0.18	0.47

Alanis et al. (2010) developed a temperature dependent acetic acid emission model where the flux is:

$$Flux = c_1 * [Acetic\ acid] * e(c_2 * T)$$

Where c_1 and c_2 are constants and [Acetic acid] is the mass fraction of acetic acid in the feed. T is the absolute temperature in °K.

Based on this model and approximate values for the area of the feeding table the temperature effect on the emission of acetic acid is shown in Table 4.

Table 4. The temperature effect on the emission of acetic acid from dairy cows fed with silage, TMR acetic acid emission, g acetic acid dairy cow^{-1} day^{-1} (calculated after Alanis et al. 2010)

Temperature, °C	**Measuring technique**		
	IR-PAD	SPME/GC-MS	Average
0	0.71	4.55	2.63
5	1.06	5.66	3.36
10	1.58	7.06	4.32
15	2.35	8.80	5.57
20	3.51	10.96	7.23
25	5.23	13.66	9.45
30	7.81	17.02	12.41

As can be seen from Table 4 a model which estimates the NMVOC emission for the EMEP area should include both feeding practice and temperature and especially where feeding with silage is taking place. On the other hand as shown in Figure 1 acetic acid has one of the lowest H_{CC} indicating that this compound is the most susceptible towards differences in different temperature regimes.

The effect of the feed composition on the amount of VFA in the manure was investigated by Kerr et al. (2006). They found the feeding had an effect on the VFA composition in the manure, primarily acetic acid ($P<0.05$) but this was not found in another study by Conn et al. (2007). It seems therefore not possible to include differences in the feeding in a model for estimating emissions from the manure.

The temperature dependent emission acetic acid model can be used for a temperature dependent emission calculation, where silage is used for feeding. Care should be taken in areas where silage feeding is not occurring as acetic acid is a major component of silage.

5.3. Difference in the productivity

Within the EMEP area there are large differences in the productivity and especially for dairy cows between countries. In Table 5 are given some basic data on productivity for dairy cattle reported to UNFCCC (www.unfccc.org). For example, are the milk yield per dairy cow approximately 4500 litres yr-1 in Poland and 8600 litres yr-1 in Denmark or measured as feed intake: 247 MJ day-1 in Poland and 343 MJ day-1 in Denmark, Table 5.

Table 5. Selected production parameters for dairy cattle

Temperature, °C	Poland*	Greece*	Russia*	Denmark*
Avg. weigth	500	600	-	575
Milk yield, kg day^{-1}	12.58	14.49	10.24	23.53
Feed intake, MJ day^{-1}	246.6	296.2	259.2	343.2
Digestibility, %	62.76	60	69.12	71
Excretion, kg VS day^{-1}	4.58	6.42	4.52	6.20
Grazing days	43	29	76	15

*Data submitted to UNFCCC for the inventory year 2009 (2011 submission), www.unfccc.org

The excretion rate of organic substances (Volatile Substance or VS) depends very much on the digestibility (DE) of the feed. High producing dairy cows are generally getting high quality feed and having a high DE of 70-72 % whereas low producing cows are having a DE of 60 %. The 2006 IPCC guidelines generally recommends a DE of 60 % in countries with low feeding efficacies, although it must be assumed for the EMEP area that the DE will be in a range of 66-72 %. The implication of differences in DE is that low yielding dairy cows are having a "relatively" high energy intake and a high VS excretion compared to the production level and high yielding cows which need high amounts of energy are having a high DE. The result is that if feed intake is used as a proxy for the NMVOC emission, Greece will have an emission which is similar to Poland and Russia and below a Danish emission (Table 5) and if excreted VS is used as a proxy for productivity, Poland and Russia will estimate low emission and Greece the same level as Denmark despite the differences in feed consumption.

The US EPA data (2012) cover only dairy cows and has not been analysed for productivity yet except for NMHC emissions from broilers. Shaw et al. (2007) showed that from whole dairy cow chamber measurements, there is a relation between NMVOC emission and feed intake. However, as shown in Table 2 their measured emission data are much lower than other measurements and it is unclear if these data include silage, which can be seen as a major component for dairy cows.

No data for non-dairy cattle have been found so far where feed consumption and weight has been measured.

The available data on NMVOC emission from fattening pigs from US EPA (2012) include only fatteners 65-130 kg hd^{-1}. In this weight interval the feed consumption, daily weight gain and the excretion is relatively constant (based on normative feeding tables) yielding similar emissions. Based on these data a relation to feeding cannot be made. The US EPA data based on NMHC measurements may show a relation but has not been analysed yet.

As mentioned earlier the absolute NMVOC emission is the sum of the emission from surface areas and non-surface areas. It should therefore be discussed if a model should include productivity and how this eventually should be measured. As shown above neither the feed intake nor the excreted amount of VS is a single determining factor for the productivity level. Another implication is that the housing types for loose holding cattle across the EMEP area are similar in relation to the size of the feeding tables and the area with slats. So if the surface area is the dominating factor then the emission per animal will be less dependent of differences in the productivity level.

If the NMVOC EF for dairy cows and other animal types shall differ between different productivity levels a clear argumentation is needed for choosing either feed intake or excreted VS as driver for the Tier 2 EF. This complication is probably mostly an issue for dairy cattle due to large differences in productivity in the EMEP

area. There will probably not be any obvious solution on this before solid data on the magnitude of exhaled NMVOC compared to NMVOCs from excreted VS (and grazing) becomes available.

6. Emission from manure stores

The manure stores could both be deep-pit or outside storages. In general the surface area is reduced giving less emission per animal. If deep-pit is used or the surface of the manure stores are covered with straw or other material, which increases the roughness length (z_0) of the surface the emission of VOCs will be reduced (z_0 for free water surfaces ≈ 0.0001 m and for manure stores ≈ 0.01 m,(Parker et al. 2010)). This should probably also be taken into account when comparing VOC emissions from uncovered and covered manure stores/tanks. For large lagoons with no or limited surface cover the low z_0 will very likely lead to high emission rates of especially NMVOCs with low H_{CC} complicating an EF from manure stores. An optimum EF should therefore take into account the surface area of the manure store per animal. This is also partly supported by a long term storage experiment (195 days), where the VFAs levels decreased more in liquid manure with 0.5 % and 1.0 % total solid compared to 2 % and 4 % solids (Zhang and Zhu, 2006).

Alanis et al. (2008) compared the VFA emission from silage, feeding tables, slats and manure stores in California (Table 6). They found that for dairy cattle the silage store, the feeding and the lagoon were the largest emitters of VFA. These fractions are supported by Chung et al. (2010) who measured the total VOC emission from a dairy farm. However, these fractions should not directly be transferred to other animal species as the fraction coming from the silage will be absent here yielding a higher ratio between barns and outdoor manure stores for e.g. pigs, as well as the large lagoons are not common practise in the EMEP/EEA area.

Table 6. Emission of VFA and VOCs from different part of a dairy farm, g hr-1.

	VFA[1]		VOC[2]
	g hr-1	Fraction	Relative contribution to ozone
Silage	92	23%	40.0%
Feeding table	140	35%	54.0%
Open lot	51	13%	3.0%
Flushing lane	14	4%	0.1%
Lagoon	95	24%	3.0%
Bedding			0.4%
Total	395	99%	100%

[1]Alanis et al. (2008)
[2]Chung et al. (2010)

Covered outside storages such as concrete tanks are probably only minor sources compared to the barns. No final decision for an EMEP/EEA emission factor from outdoor manure stores has been taken yet.

7. Background concentration

In all measurements made by US EPA (2012) except one (an open dairy barn) no reference background concentration has been measured. Feilberg et al. (2010) extended the air inlet to 5 meter above the building to avoid higher contamination from neighbouring barn sections. Ngwabie et al. (2008) got reference air outside their sheep shed and their pig barn.

In the US EPA dairy barn where the NMVOC concentration were measured in both the inlet and the outlet, the inlet concentration were highest in two out of six measurements indicating the problems with measuring the absolute emission in open barns.

You et al. (2008) measured the concentration of 26 NMVOCs in rural areas in Canada and found most vegetation and oil industry related NMVOCs. In general, the concentrations of the NMVOCs were low (in ng m^{-3}). Many of the measurements were made close to grazing beef cattle but emission from these was not identified. Vegetation related NMVOCs has the highest concentration in summer at a level of <100 ng m^{-3}. This should be compared to the measured concentration in barns of 1000-10000 ng m^{-3} of the most important NMVOCs. The background emission can therefore be considered as negligible as also stated by Feilberg et al. (2010) for the pig measurements.

In Table 3 were shown some differences in measured NMVOCs. Taking into account the relative difference between animal species and the likely elevated emission from silage an approximate difference between pigs and dairy cattle could be 1:10 but not 1:30. It should therefore be investigated further if the high emission rates from especially the open dairy barns are caused by an elevated background concentration.

8. Available Emission data

8.1. Cattle

Most measured NMVOC data are from lactating dairy cows (US EPA 2012, Alanis et al. 2010, Shaw et al. 2007). Shaw et al. (2007) measured a few dry cows too. These data are whole barns and include therefore both exhaled emissions and from manure in the barns. The US EPA data covers a large range on climatic conditions. The whole barn measurements of NMVOCs are both from feed, feeding operations, exhalation from animal breaths and from the manure/fouled surfaces/manure stores inside the buildings and it is not possible difficult to split these measurements into different sources. The NMVOC data for dairy cattle cover only a few summer months.

No data have been found for non-dairy cattle.

Emission data from manure stores are very scarce and often from large lagoons and settling ponds (up to 10000-20000 m^2). These lagoon types are not common in Western Europe and probably also to a limited extend in Eastern Europe. Some odour measurement from manure stores may be available, although transformation into total NMVOC and fluxes is complicated.

Only a few air concentration data from feedlots where downwind measurements (primarily odour measurements) have been found (Trabue et al. 2010). These data do not include flux measurements and therefore it is not possible from these data to estimate annual emission factors.

8.2. Sheep and goats

Sheep and goats are normally grazing animals. The only data available is from a sheep shed in Germany (Ngwabie et al. 2008). Currently, there is no knowledge on NMVOC emission from grazing sheep.

8.3. Pigs and Poultry

The comprehensive data from US EPA (2012) include several sow farms, fatteners, egg layers and one broiler farm measured in up to two years including both with animals and down periods. No data from

turkeys, geese and ducks have been found. Feilberg et al. (2010) measured the emission from pigs (30-60 kg). The measurement by Ngwabie et al. (2008) is probably only measuring some of the NMVOCs and up scaled to German conditions based on a relation to CH_4. This type of up scaling is problematic if there are different climatic dependencies of the compounds.

As pigs and poultry normally are raised in buildings under standardized conditions the major differences in the EMEP area is most likely to be management and differences in slaughter weight.

8.4. Emission during grazing

No data from grazing cattle have been found so far.

9. The likely effect of the climatic conditions in the EMEP/EEA area

In Figure 7 is shown the more extreme temperature conditions in the EMEP area. Malaga in Spain is the warmest area with a coastal climate and comparatively low amplitude on the temperature curve. Dublin in Ireland has a lower temperature regime but also a low amplitude due to its coastal climate. The most extremes are found in Moscow in the Russian Federation with both low temperatures and large amplitude on the temperature curve.

If the temperature compartment of a NMVOC model is important these extremes should be taken into consideration. In the next section an attempt is made to include the measured data from the NAEM study in a EMEP/EEA approach.

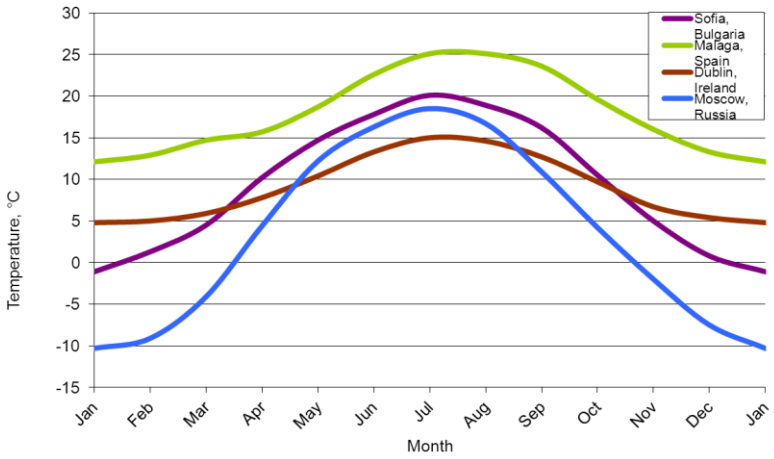


Figure 7. Temperature conditions in four different regions of the EMEP area. Data from: www.worldclimate.com

In Table 7 the likely effect of temperature on the emission of NMVOC (kg NMVOC pig place^{-1} yr^{-1}) is shown with an average pig of 65-130 kg without any downtime for different parts of the EMEP/EEA area. The estimates are based on the NMVOC model in Figure 4 and combined with the temperature function in Figure 3 and the temperature data in Figure 5. As shown the presumable effect of the extreme temperatures in the EMEP/EEA area is a difference of two (0.126 kg and 0.245 kg) for the same production.

This difference is partly supported for dairy cattle too by the data on acetic acid by Alanis et al. (2010) as shown in Table 4.

Table 7. Preliminary NMVOC emission from fatteners, 65-130 kg hd-1, without downtime in the housing for different part of the EMEP/EEA area, kg pig-1 yr-1.

Location	Average Outdoor Temp, °C	Average Indoor Temp, °C	Housing, kg NMVOC fattening pig-1 yr-1
Malaga	18.3	23.8	0.245
Bruxelles	10.1	21.3	0.161
Sofia	9.8	21.3	0.163
Dublin	9.3	21.0	0.151
Moscow	4.1	20.2	0.126
Copenhagen	8.2	20.8	0.146
Paris	11.0	21.5	0.170
Rome	15.0	22.8	0.211

If the temperature coefficients are suitable the most likely difference in the emission for the same production across the EMEP/EEA area is a factor of two.

It should be discussed if a regionalisation of the EMEP/EEA area should be made into different stratified regions with different climatic conditions or the uncertainty in the measurements are so large that such a climatic dependent regionalisation should not be made. If stratification is made, it is not recommended to include more than three regions.

10. Preliminary conclusions

An effect of temperature on the NMVOC emission is very likely. The current data shows an effect although there is a very high variability in the data.

The conclusion of the findings by Parker et al. (2010) on an EF is that there will be a higher emission of NMVOCs with especially low H_{CC} compared under dirty conditions than under well managed conditions and that the emission will be dependent on the fouled area and how wet the conditions are.

Quickly and frequently removals of the manure to manure stores and hereby reducing the surface area of the manure will reduce the emission of especially the NMVOCs with low H_{CC}.

10.1. The current Tier 1 default emission factors for NMVOC

In the current 2009 GB no default EF for NMVOC is given although EFs are given in the Appendix (Table B1 to B6). The emission factors in Table B1 to B6 are expressed in kg NMVOC per animal place. Only four countries, Germany, Italy, Portugal and Ukraine are reporting NMVOC emissions under 4B.The reported emissions vary greatly.

The estimated NMVOC emission ranges in the current GB are calculated from the NH_3 emission ratio primarily according to Hobbs et al. (1999, 2004). Such a relation has also been found by others. E.g. Feilberg et al. (2010) found a correlation of 0.4 – 0.6 between NH_3 and several of the individual NMVOCs.

The emission factor for fattening pigs in the 2009 GB is a factor 20 higher than new measurements (US EPA 2012, Feilberg et al. 2010). Hobbs et al. (2004) used the relationship between measured NMVOCs and the NH_3 emission in a continuously stirred chamber with liquid slurry and found that the major measured NMVOCs were DMS, acetic acid and butanoic acid. Based on this an up scaling to a national level for Great

Britain was made. At least three different reasons can be found for the discrepancy between the current found NMVOC emission level for fattening pigs and Hobbs et al. (2004):

1. Hobbs et al. (2004) found a DMS emission which was 32 % of the ammonia emission measured in absolute amounts. This has not been verified in other measurements where the DMS emission is < 4 % of the total NMVOC emission (Feilberg et al. 2010, US EPA 2012). A mass balance calculation of the amount of sulphur in pig feed compared with proposed DMS emission factor furthermore shows that this high emission factor is not realistic.
2. The up scaling to national level is based on the ammonia emission in the UK inventory for year 2002. The current UK NH_3 inventory (2012 submission) for year 2002 has been recalculated so it is 20 % lower today. If the recalculated NH_3 emission is a correct estimate, the NMVOC emission per animal place (AP) in the 2009 GB is overestimated with approximately 20 %. Therefore, the use of a VOC:NH_3 relation by this methodology in the up scaling should be used with caution.
3. Acetic acid, butanoic acid and 4-methyl-phenol were the second, third and fourth largest source in the measurements made by Hobbs et al. (2004) having a share of 34 %, 13 %and 10 % respectively. In the dataset from US EPA (2012) the relationship between measured barn air concentrations of ammonia and the two acids are only approximately 1:10 to 1:20 and much lower than the relation obtained by Hobbs et al. (2004). Parker et al. (2010a) investigated the effect of chamber geometry on the emission. They showed that the emission of compounds with low Henry's Law constants (H_{CC}) are gas film controlled and that compounds with high H_{CC} are liquid film controlled (Figure 1). Acetic acid, butanoic acid and 4-methyl-phenol are all having low H_{CC}. The investigation made by Hobbs et al. (1999, 2004) was conducted to release odours and not for measuring the NMVOC emission. The measurement technique included a very vigorous propelled stirring at 15 °C slurry temperature and high ventilation rates at 20°C air temperature. The latter to decrease the condensation inside the equipment. Besides the unusual conditions Hobbs et al. may especially have increased the acid and phenol volatilisation rate compared to ammonia and making them unsuitable as valid data for the NMVOC emission.

The data from Hobbs et al. are therefore not taken into consideration.

10.2. Proposal for new NMVOC emission factors

Based on the above methodological discussion, the high variability in the existing measured data, the lack of data, difficulties in transferring data from one location to cover the whole EMEP/EEA area this section should be seen as a discussion and not for a comprehensive suggestion for a new methodology.

As there is a high uncertainty in what the individual measurement methodologies are actually measuring a discussion is needed on what is the most reliable methodology: Canister measurements, NMHC or PRT-MS. Generally underestimate the NMHC methodology by a factor of four compared to canister sampling combined with GC-MS and when corrected from amounts of C to apparent NMVOCs the underestimation is a factor of two. The few PRT-MS measurements are not comprehensive and very likely need further evaluation before they should be included.

10.2.1. Tier 1

A proposal for a new Tier 1 NMVOC default emission factor will be based on a Tier 2 approach and is therefore not established yet.

10.2.2. Tier 2

The determination of representative emission rates from individual sources with the goal of producing an NMVOC inventory for the EMEP/EEA area is complicated of several reasons:

- Few monitored data
- Many different compounds with different chemical and physical properties
- Different production conditions
- Different storage conditions
- Different climatic conditions

The high variability in measured NMVOC emissions in the NEAM study does not favour a very detailed inventory approach over the EMEP/EEA area. On the other hand it is very likely that the effects of productivity and climatic conditions should be taken into account.

The latter includes the type of animal housing and husbandry, type of manure storage (solid or slurry), and storage length. However, as there is limited data from solid manure handling, it is unlikely that there can be established separate NMVOC EFs for liquid and solid manure handling.

Based on the likely climate related differences within the in emission in EMEP/EEA area a regionalisation should be made, Table 4 and 7.

10.2.2.1. Cattle

10.2.2.2. Dairy cattle

The major available data are results from the US EPA study (2012) from lactating cows. US EPA has not finalised its analysis yet. The data include only emission from barns and not outdoor storages of manure similar to conditions in the EMEP/EEA area. The effect of feeding with silage is pronounced. This may cover the major conditions in EMEP/EEA area, but in some areas silage feeding is less important and in some cheese productions silage feeding is not allowed.

The emission from outdoor storage of manure has not been quantified yet, but should be included in a final EF.

The differences in temperature should be taken into account but relevant temperature coefficients is lacking unless a proxy developed for acetic acid can be used as a legal function for all compounds. This is partly questionable according to Figure 1 because of its low Henry's constant but probably the best current methodology.

10.2.2.3. Non-dairy cattle

As mentioned above the major data set is from housed lactating cows. A model for growing cattle and suckling cows could be their feed intake in relation to feed intake from lactating cows. This could either be based on feed intake measured in MJ day-1 taken directly from the individual countries submission to the Climate Convention (UNFCCC) or the amount of excreted volatile substance. The variation in DE for non-dairy cattle as discussed above will be less pronounced as non-dairy cattle are more uniform fed and having more grazing days.

An outstanding question is how to incorporate grazing days if the NMVOC emission during grazing is different from housing cattle fed with silage. No data on this have been found.

10.2.2.4. Sheep and goats

For sheep and goats the only available data are the investigation by Ngwabie et al. 2008. Although the up scaling is based on a relation to CH_4 the range seems reasonable for their size, Table 2 (taking into consideration the relation to the PRT-MS measurements made by Feilberg et al. (2010)). It will be investigated if a relation between cattle, which also are ruminants, and sheep and goats can be made in a proper way. This could be either based on feed consumption or the excretion of VS. Such relation should take into account that sheep and goats to a large extend are grazing. One major difficulty is that the major cattle data are from barns with slats or scrabers and that sheep and goats when housed are on solid manure/deep litter. Further investigation is needed.

10.2.2.5. Pigs and poultry

Pigs and poultry are normally raised in buildings under standardized industrialized conditions throughout the EMEP area. These are very likely comparable to the American conditions with only small differences in management and differences in slaughter weight.

As most countries in their current submissions to UNFCCC have chosen Tier 1 and hence do not give information on feed consumption there are limited data here for inclusion of the regional productivity level to be used in a Tier 2 model.

The emission factors in current guidebook are based on animal places (AP) and not on the actual production level where the slaughtering weight may differ between countries as well as the number of days the animal building facilities are empty. It should therefore be discussed if an EF for pigs and poultry should be divided into sows and egg layers with EFs per AP and EFs for fatteners and broilers based on per produced unit. In the latter case a Tier 2 model could include average slaughtering weight as a parameter.

10.2.2.6. Grazing animals

There are a few measurements where some NMVOC has been measured from the breath from cattle (Elliott-Martin et al. 1997, Spinhirne et al. 2003, 2004). Furthermore, there could be a relation between conducted SF_6-measurements which have been used to monitor CH_4 emissions from e.g. grazing cattle measurements and NMVOC emission. These measurements can maybe be used as proxy data for emission from grazing cattle, but is found to be too complicated and outside the range of this project.

11. Conclusion

Preliminary conclusions are that further elaboration on the available data is needed before a final recommendation can be made.

The high variability in the measured compounds both between animal species and between farms having the same animal types indicate that simple models and assumptions should be used.

Further research is needed. Both in terms of measuring emissions from manure stores and grazing animals but also a comparison between the different measurements technologies in an attempt to quantify the observed difference and which compounds they actually are measuring.

The measured emissions with the different technologies are probably in line with each other within a factor of 2-3.

It looks like that that up 50 % of the NMVOCs from animal handling is iso-propanol and n-propanol followed by acetaldehyde and short chained acids (acetic acid, propionic acid, butanoic acid). Ethyl acetate was only found in major quantities in cattle barns. According to the classification made by UNECE (1991) the major part of the emissions from animal handling can be classified as “less important” as ozone precursor. It is therefore recommended that a combined judgement on the uncertainty in proposed emission factors and importance of the individual compounds are made.

612 # Appendix A.

Distribution, poultry	Pct.	Distribution, cattle	Pct.	Distribution, swine	Pct.
2,3-Butanedione	9.93	2,3-Butanedione	0.26	2,3-Butanedione	4.28
Dimethyl disulfide	5.12	Dimethyl disulfide	0.48	Dimethyl disulfide	0.97
Acetaldehyde	3.96	Acetaldehyde	6.68	Acetaldehyde	8.82
2-Butanone	5.79	2-Butanone	2.37	2-Butanone	10.23
iso-Propanol	23.00	iso-Propanol	6.96	iso-Propanol	19.27
Pentane	3.59	Pentane	3.38	Pentane	4.63
Dimethyl sulfide	2.79	Dimethyl sulfide	1.27	Dimethyl sulfide	3.68
Acetic acid	7.29	Acetic acid	2.89	Acetic acid	7.83
Hexanal	2.32	Hexanal	0.19	Hexanal	2.30
Ethyl acetate	0.40	Ethyl acetate	18.73	Ethyl acetate	2.08
Hexane	4.86	Hexane	0.25	Hexane	1.17
Propanoic acid	1.72	Propanoic acid	0.95	Propanoic acid	7.07
Pentanal	1.83	Pentanal	0.24	Pentanal	2.53
Phenol	1.78	Phenol	1.01	Phenol	3.57
1-Butanol	0.87	1-Butanol	0.63	1-Butanol	1.92
2-Pentatone	0.86	2-Pentatone	0.07	2-Pentatone	0.91
4-Methyl-phenol	1.22	4-Methyl-phenol	1.23	4-Methyl-phenol	6.04
Butanoic acid	0.00	Butanoic acid	0.00	Butanoic acid	1.60
Heptanal	0.99	Heptanal	0.16	Heptanal	1.74
Butanal	1.05	Butanal	0.08	Butanal	1.82
Octanal	0.82	Octanal	0.19	Octanal	1.47
Methyl cyclopentane	1.99	Methyl cyclopentane	0.06	Methyl cyclopentane	0.31
Nonatal	0.68	Nonatal	0.51	Nonatal	1.67
Toluene	1.97	Toluene	0.99	Toluene	0.38
n-Propanol	1.43	n-Propanol	41.35	n-Propanol	2.31
2-Butanol	0.51	2-Butanol	1.29	2-Butanol	0.49
4-Ethyl-phenol	0.11	4-Ethyl-phenol	0.00	4-Ethyl-phenol	0.28
1-Pentanol	0.10	1-Pentanol	0.00	1-Pentanol	0.00
Dimethyl trisulfide	0.22	Dimethyl trisulfide	0.00	Dimethyl trisulfide	0.23
2-Methyl-propenoic acid methyl ester	10.79	2-Methyl-propenoic acid methyl ester	0.00	2-Methyl-propenoic acid methyl ester	0.00
2-Methyl-propenoic acid	0.00	2-Methyl-propenoic acid	0.22	2-Methyl-propenoic acid	0.00
2-Methyl-hexanoic acid	0.00	2-Methyl-hexanoic acid	0.05	2-Methyl-hexanoic acid	0.00
Propyl propenoic ester	0.00	Propyl propenoic ester	0.21	Propyl propenoic ester	0.00
Indole	1.46	Indole	0.05	Indole	0.00
Benzaldehyde	0.28	Benzaldehyde	0.06	Benzaldehyde	0.00
o-Xylene	0.27	o-Xylene	0.00	o-Xylene	0.00
Decanal	0.00	Decanal	0.24	Decanal	0.00
n_propyl acetate	0.00	n_propyl acetate	4.84	n_propyl acetate	0.00
Benzene	0.00	Benzene	0.29	Benzene	0.18
Menthanol	0.00	Menthanol	1.69	Menthanol	0.00
Dimethyl sulfone	0.00	Dimethyl sulfone	0.00	Dimethyl sulfone	0.24
Ethanol	0.00	Ethanol	0.05	Ethanol	0.00
D-limonene	0.00	D-limonene	0.06	D-limonene	0.00
Sum	**100.00**	**Sum**	**100.00**	**Sum**	**100.00**

613

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