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## Data sets to assess methane emissions from untreated cattle and pig slurry and solid manure storage systems in the German and Austrian emission inventories

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#### Abstract

Methane emissions have to be reported within the Framework Convention on Climate Change. They are assessed according to the guidelines provided by IPCC. However, the methane conversion factors provided in the guidance documents published in 1996, 2000 and 2006 differ considerably. The literature available was inspected in order to establish those parameters that allow for the most adequate description of the situation in Germany and Austria. Matching pairs for maximum methane producing capacities ( $B_{\circ}$ ) and methane conversion factors (MCF) were deduced for cattle and pig slurry and farmyard manure.

Keywords: methane, emission, model, manure management, cattle, pigs

#### Zusammenfassung

Datensätze zur Berechnung von Methan-Emissionen aus Lagern von unbehandeltem Flüssig- und Festmist für Rinder und Schweine im deutschen und österreichischen Emissionsinventar

Methan-Emissionen aus dem Wirtschaftsdünger müssen im Rahmen des Klimarahmenabkommens berichtet werden. Die Quantifizierung erfolgt nach Richtlinien, die IPCC vorgibt. Die in den Jahren 1996, 2000 und 2006 veröffentlichten Richtlinien enthalten jedoch stark voneinander abweichende Methan-Umwandlungsfaktoren. Die vorhandene Literatur wurde mit dem Ziel gesichtet, die für die Situation in Deutschland und Österreich am ehesten geeigneten Parameter zu ermitteln. Für Rinderund Schweinegülle und -festmist wurden Wertepaare für die maximale Methan-Bildungskapazitäten ( $B_{\rm o}$ ) und die Methan-Umwandlungsfaktoren (MCF) ermittelt.

Schlüsselwörter: Methan, Emission, Modell, Wirtschaftsdüngerlager, Rinder, Schweine

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#### 1 Introduction

Methane (CH<sub>4</sub>) emissions in animal husbandry originate from enteric fermentation (in particular from ruminants), from storage of animal slurries and manures and from subsequent application. The latter are very low (Chadwick et al., 2000) and are usually ignored in emission inventories. Emissions from enteric fermentation exceed those from storage of slurry and manure and are regarded a key source in greenhouse gas emission reporting. However, emissions from storage are also a key category in many states, including Germany and Austria. The assessment of emissions from stored manures is difficult due to lack of experimental data. So it is customary to model them. Mechanistic models are still being developed (e.g. Huang et al., 2010), and at present not utilizable for inventory purposes. It is customary to use the methodology provided by the Intergovernmental Panel on Climate Change (IPCC). The three IPCC Guidelines (IPCC 1996, 2000a, 2006) propose a general pathway and default values. However, these default values differ considerably.

The goal of this paper is the derivation of an instrument to describe methane emissions from manure management (cattle and pigs) in Germany and Austria that allows either for the establishment of national data sets or for a decision concerning the best IPCC default value to use.

## 2 Reporting of emission rates and emission explaining variables

In this section, we consider the origins and basis for the IPCC approach for calculating  $\mathrm{CH_4}$  emissions. We then consider the extent to which the constants used are indeed constants and to what extent default values are adequate.

#### 2.1 The IPCC methodology

IPCC uses the calculation procedure proposed by Safley et al. (1992) that relates  $\operatorname{CH_4}$  emission factors EF to the amount of total volatile solids excreted (VS), their maximum methane producing capacity ( $B_{\circ}$ ) and methane conversion factors (MCF). Emission rates have to be reported as mass flows in kg a-1  $\operatorname{CH_4}$  for single animal categories together with the  $B_{\circ}$  and MCF used for their assessment. Many categories (e.g. other cattle, pigs) consist of subcategories whose emissions have to be calculated separately. Here, the entity used for comparison is the implied emission factor IEF which is the weighted mean of the subcategory emission factors taking into account the various manure management systems:

$$IEF_{\text{CH4, MM, i}} = \frac{1}{\sum_{k} n_{k}}$$

$$\sum_{k} \left( n_{k} \cdot VS_{k} \cdot \alpha \cdot B_{o,k} \cdot \rho_{\text{CH4}} \cdot \sum_{j} MCF_{j} \cdot X_{k,j} \right)$$
(1)

with

$$\sum_{i} X_{k,j} = 1$$

for any k and

$$\sum_{k} n_{k} = n_{i}$$

where

 $IEF_{\mathrm{CH4,MM,i}}$ implied emission factor for methane from manure management for animal category i composed of k subcategories with j manure management systems each (in kg place-1 a-1 CH<sub>4</sub>) number of animal places in subcategory k (in place)

 $VS_k$  volatile solid excretion of animal subcategory k (in kg place<sup>-1</sup> d<sup>-1</sup>)

 $\begin{array}{ll} \alpha & \text{time units conversion factor (365 d a$^{-1}$)} \\ B_{_{\mathrm{o},\,\mathrm{k}}} & \text{maximum methane producing capacity of} \\ & \text{animal subcategory k (in m$^{3}$ kg$^{-1}$ CH}_{_{4}}$) \end{array}$ 

 $ho_{\rm CH4}$  density of methane ( $ho_{\rm CH4}$  = 0.67 kg m<sup>-3</sup>)  $MCF_{\rm j}$  methane conversion factor for manure management system j (in m<sup>3</sup> m<sup>-3</sup>)

 $X_{\mathbf{k},\mathbf{j}}$  fraction of VS excreted by animal subcategory  $\mathbf{k}$  in manure management system  $\mathbf{j}$  (in kg kg<sup>-1</sup>) number of animal places in animal category i

(in place)

For a single livestock category i and a single manure management system j the relevant entities can be combined to describe the emission factor:

$$EF_{\text{CH4,MM,i}} = VS_{i} \cdot \alpha \cdot B_{o,i} \cdot \rho_{\text{CH4}} \cdot MCF_{i}$$
 (2)

where

 $EF_{
m CH4,\,MM,\,i}$  emission factor for methane from manure management for animal category i (in kg place-1 a-1 CH $_4$ ) 1

<sup>1</sup> The term "animal place" (unit: place) is used here to describe the number of animals counted at a certain date. The term "animal place" does not describe the number of places in animal houses potentially used for animal production. The number of places thus defined is equal to the IPCC term "annual average population". Places are the elements of the population.

 $\begin{array}{ll} \textit{VS}_{\text{i}} & \text{daily volatile solid excretion of animal category i} \\ & (\text{in kg place}^{-1} \text{ d}^{-1}) \\ \alpha & \text{time units conversion factor (365 d a}^{-1}) \\ B_{\text{o, i}} & \text{maximum methane producing capacity for animal} \\ & \text{category i (in m}^3 \text{ kg}^{-1} \text{ CH}_4) \\ \rho_{\text{CH4}} & \text{density of methane } (\rho_{\text{CH4}} = 0.67 \text{ kg m}^{-3}) \end{array}$ 

MCF<sub>j</sub> methane conversion factor for manure management system j, temperature dependent (in m³ m-³)

The theoretical background of the IPCC methodology is to relate  $\mathrm{CH_4}$  emissions to the mass or mass flow of degradable organic matter from which they originate (volatile solids, VS). A general approach makes use of a maximum formation rate, a practice-oriented reduction factor and a term that considers losses in the storage system, e.g. by oxidation within the natural crust, resulting in a relation as in Equation (3):

$$EF_{\text{CH4, MM, i, j, T}} = VS_{i} \cdot \alpha \cdot X_{\text{BD, i}} \cdot X_{\text{MS, i, j, T}} \cdot \left(1 - X_{\text{ox, j}}\right)$$
 (3)

where

 $\mathit{EF}_{\mathrm{CH4,\,MM,\,i,\,j,\,T}}$  annual emission factor for  $\mathrm{CH_{4}}$  from manure management for animal category i, manure management system j, and a storage temperature T (in kg place<sup>-1</sup> a<sup>-1</sup> CH<sub>4</sub>) daily input rate of VS into the manure  $VS_{i}$ management system of animal category i (in kg place-1 d-1) time units conversion factor (365 d a-1)  $\alpha$  $X_{\rm BD,\,i}$ amount of CH, that can be obtained from biological degradation of VS under optimal conditions (in kg kg<sup>-1</sup>)  $X_{MS, i, j, T}$ fraction of CH<sub>4</sub> that can be obtained from biological degradation under practical conditions, in relation to degradation under optimal conditions, for animal category i, manure management system j, and storage temperature T (in kg kg<sup>-1</sup>) fraction of CH<sub>4</sub> formed that is oxidized in the  $X_{\text{ox, j}}$ storage system j

As the volumes of gas collected are measured rather than the masses, the amount of  $CH_4$  from biological degradation of VS entering the storage system may be rewritten as:

$$X_{\mathrm{BD,i}} = \frac{v_{\mathrm{CH4,opt,i}} \cdot \rho_{\mathrm{CH4}}}{VS_{\mathrm{i}}} \tag{4}$$

where

 $X_{\mathrm{BD,\,i}}$  amount of  $\mathrm{CH_4}$  that can be obtained from biological degradation of VS under optimal conditions (in kg kg $^{-1}$ )

 $v_{\text{CH4, opt, i}}$  volume<sup>2</sup> of CH<sub>4</sub> emitted daily under optimal conditions, as a function of animal category i (in m³ kg<sup>-1</sup> d<sup>-1</sup> CH<sub>4</sub>)

 $ho_{\rm CH4}$  density<sup>2</sup> of CH<sub>4</sub> (in kg m<sup>-3</sup>)

VS<sub>i</sub> daily input rate of degradable matter into the manure management system of animal category i (in kg place-1 d-1)

In the IPCC terminology, the maximum methane producing capacity describes a specific volume rather than a specific mass. Hence, the term  $X_{\rm BD,i}$  corresponds to the maximum methane producing capacity for an animal category i  $(B_{\rm o,i}$ , in m³ kg¹ CH₄) times the density of methane  $\rho_{\rm CH4}$  (in kg m³) c.f. Equation (2), whereas  $X_{\rm MS,i,j,T}$  and  $X_{\rm ox,i}$  are elements of the methane conversion factor MCF.

 $\dot{M}CF$  cannot be measured as such. It should be assessed by emission measurements and back-calculated using  $VS_i$  and  $B_{o,i'}$  i.e. by solving Equation (2) for  $MCF_i$ .

#### 2.2 Constants and variables in the IPCC methodology

The method given by IPCC (1996) and (2006) relates emissions to VS excreted,  $B_{\circ}$  and MCF (see Equation (2)). The assessment of VS excretion rates was described in detail in Dämmgen et al. (2011a, b).

 $B_{0}$  and  $B_{11}$ 

 $B_{\rm o}$  is the maximum cumulative methane yield that can be gained from the biological degradation of the organic material.  $B_{\rm o}$  falls below the theoretical methane yield  $B_{\rm u}$  that would result from the complete degradation of all the organic compounds. This is because not all the organic material is biologically degradable under the anaerobic conditions pertaining in manure storage. In particular, lignin-containing compounds are decomposed incompletely (lanotti et al., 1979; Møller et al., 2004a).

Volumes of gases ( $\nu$ ) have to be reported in combination with the relevant temperature and pressure. It is customary to "reduce" them to standard conditions. However, these vary between nations and regions. The US National Institute of Standards and Technology (NIST) recommended the use of a standard temperature  $T_{\rm n, NIST} = 293.15$  K and a standard pressure  $p_{\rm n, NIST} = 1013$  hPa, whereas German standard DIN1343 uses a standard temperature  $T_{\rm n, DIN} = 273.15$  K. Standard pressures are identical:  $p_{\rm n, NIST} = p_{\rm n, DIN}$ . Gas densities ( $\rho$ ) can then be adjusted using the relation  $T_{\rm n, 1}/T_{\rm n, 2} = \rho_2/\rho_1$ .

Within the IPCC methodology,  $B_0$  is provided as a single default value for each animal category (or subcategory). In principle and in practice,  $B_0$  for a given livestock category is not a constant entity, but a variable that depends on feed composition (e.g. Buswell and Mueller, 1952; Külling et al., 2001; Velthof et al., 2005; Amon et al., 2006; Massè et al., 2008; Klevenhusen et al., 2010). Hence, it should be related to national feeding data and reflect typical feeding practices.

 $B_{o}$  default values for pigs supplied by IPCC (1996) and IPCC (2006) have for some time been criticized as being too high (see IPCC, 2000b).

Buswell and Mueller (1952) and lanotti et al. (1979) provide methodologies that allow calculating methane yields from fermentation of "practically any sort or kind of organic matter ... used as a substrate". However, their calculation procedure only describes the fate of organic matter that is completely converted into CH<sub>4</sub> and CO<sub>2</sub>, and also presupposes knowledge of the chemical analysis of the substrate that is decomposed (expressed as C<sub>p</sub>H<sub>a</sub>O<sub>b</sub>). In practice, some of the organic matter (particularly lignin) is resistant to decomposition, so  $B_{\alpha}$  is only a fraction of  $B_{\alpha}$ . The ratio of the two is termed the biodegradability, and a range of values is given in Møller et al. (2004a). B can also be modelled using the chemical composition of the feed and the degradability (see Sommer et al., 2002a).

 $\rho_{\mathrm{CH4}}$ 

As  $B_0$  is to be reported as volume per unit of VS (m<sup>3</sup> kg<sup>-1</sup>), the density of CH<sub>4</sub> has to be taken into account. The IPCC guidelines use a density of 0.67 kg m<sup>-3</sup> without further information on temperature and pressure. However, at German and Austrian standard temperature and pressure (273.17 K and 1013 hPa), a density of 0.72 kg m<sup>-3</sup> should be used. Nevertheless, for sake of consistency with the IPCC guidelines, we will continue to use the value of  $0.67 \text{ kg m}^{-3}$ .

MCF

The IPCC methodology assumes that values of MCF are typical for each storage system (and independent of the type of manure stored). IPCC (1996, 2006) clearly state that MCF are temperature dependent.

For reasons of practicality, the IPCC methodology does not take storage times or the kinetics of the fermentation process into account (e.g. Chen et al., 1980; Linke, 1997) which results in an additional uncertainty of the values provided. Nor does it reflect the influence of the composition of excreta (e.g. their protein contents) and the viscosity of slurries. The latter may vary considerably (see e.g. Sommer et al., 2009; also data provided by Massè et al., 2003, in Table 16).

In principle, the incorporation of losses by oxidation (e.g. during penetration of a natural crust) into MCF contradicts the meaning of the term "methane conversion factor" describing the conversion of VS to CH<sub>4</sub>.

Without giving an explanation, the MCF default value for liquid storage provided in IPCC (1996), IPCC (2000a) and IPCC (2006) varies by a factor of almost 4 (see Table 13). A temperature dependency is likely, see Chapter 5.2.

#### 3 Empirical and modelled methane emission rates from manure management

Information about  $B_0$  and MCF is gained by measurements of specific CH<sub>4</sub> emissions. The IPCC methodology is based on measurements that are commonly related to VS available. In this work, these VS related emissions are called specific emissions,  $\varepsilon_{\text{CH4}}$  .

$$\varepsilon_{\text{CH4}} = \frac{E_{\text{CH4}}}{VS} = B_{\text{o}} \cdot MCF \tag{5}$$

where

specific emission of methane (in m<sup>3</sup> kg<sup>-1</sup> CH<sub>a</sub>)  $\varepsilon_{\text{CH4},}$ 

CH<sub>4</sub> emission rate (in m<sup>3</sup> d<sup>-1</sup> CH<sub>4</sub>)

 $E_{\rm CH4} \\ VS$ volatile solids input into the system (in kg d<sup>-1</sup> VS)

 $B_{\rm o}$ maximum methane producing capacity

(in  $m^3$  kg<sup>-1</sup> CH<sub>4</sub>)

MCFmethane conversion factor (in m<sup>3</sup> m<sup>-3</sup>)

Such specific emissions have been reported for cattle and to a lesser extent for pig slurry. For solid manures data are very rare (see also Webb et al., 2012).  $\varepsilon_{\rm CH4}$  calculated from measured data is collated in Tables 1 and 2 (cattle) and 6 and 7 (pigs), a comparison with emission rates backcalculated using IPCC default values is made with Tables 4 and 5 (cattle) and 8 and 9 (pigs). Table 3 contains modelled values for cattle for low temperatures.

All tables report volumes using a density  $\rho_{\text{\tiny CH4}}$  of 0.67 kg m<sup>-3</sup>.

Tables 1 and 2 as well as 5 and 6 show a considerable variability of experimentally-derived specific emissions of CH<sub>4</sub> from cattle and pig slurry and solid manure. They also indicate a temperature dependence (see Chapter 5.2). No conclusion can be drawn yet which of the default values provided by IPCC (1996, 2000a, 2006) are most adequate. Hence an investigation into the elements  $B_0$  and MCF that can be used to establish the specific emission is undertaken below.

Table 1: Experimentally derived specific emissions for slurry. **Cattle**. Partly recalculated from original data. All values in m³ kg¹¹ CH $_4$ . Temperatures mentioned are ambient air temperatures.

	$\varepsilon_{\mathrm{CH4}}$		Reference
cattle	0.019	crust at times	Husted (1994)
	0.003	slurry, 10 °C and 9.2 % DM; crust not mentioned	Massé et al. (2003)
	0.008	slurry, 10 °C and 4.2 % DM; crust not mentioned	Massé et al. (2003)
	0.0129	May to September, partly covered with crust, no temperature provided	Rodhe et al (2009)
	0.0096	annual average, mean temperature 8.4 °C	Rodhe et al (2009)
	0.0023	slurry, cold season, crusted <sup>a</sup>	Amon and Hörtenhuber (2010), summary of measurements in Amon et al. (2002)
	0.0893	slurry, warm season, crusted <sup>A</sup>	Amon and Hörtenhuber (2010), summary of measurements in Amon et al. (2002)
dairy cows	0.0012	slurry, cold season, crusted <sup>A</sup>	Amon et al. (2002), pg. 110
	0.0821	slurry, warm season, crusted <sup>a</sup>	Amon et al. (2002), pg. 109
	0.146	March to June, mean temperature 14.9 °C <sup>A</sup>	Amon et al. (2004)
	0.107	slurry without straw cover, summer, no temperature provided	Amon et al. (2002, 2006c)
	0.115	slurry with straw cover, summer , no temperature provided	Amon et al. (2006c)
	0.026	no temperature provided; crust not mentioned, but unlikely	Klevenhusen et al. (2010)

Table 2: Experimentally derived specific emissions for farmyard manure. **Cattle.** Value in m³ kg-¹ CH $_{\rm A}$ .

	$arepsilon_{ ext{CH4}}$		Reference
cattle	0.005	farmyard manure	Husted (1994)

Table 3: Modelled specific emissions for slurry. **Cattle**. Values in m³ kg⁻¹ CH₄. Temperatures mentioned are ambient air temperatures.

	$\varepsilon_{_{\mathrm{CH4}}}$		Reference
cattle	0.020	slurry, 3.9 °C annual mean	Sommer et al. (2004)
	0.027	slurry, 7.3 °C annual mean	Sommer et al. (2004)

Table 4: IPCC specific emissions for slurry for comparison. **Cattle**. Recalculated from  $B_{\rm o}$  and MCF provided. Temperatures mentioned are ambient air temperatures.

	$B_{_{0}}$	MCF	$\varepsilon_{\mathrm{CH4}}$		Reference
	m³ kg-1	m³ m <sup>-3</sup>	m³ kg-1		
dairy cows	0.24	0.10	0.024	slurry, cool climate	IPCC (1996), Table B-3
dairy cows	0.24	0.39	0.094	slurry, cool climate	IPCC (2000a), Table 4.10
dairy cows	0.24	0.10	0.024	slurry with natural crust, annual tem- perature ≤ 10 °C	IPCC (2006), Tables 10A-4 and 10.17
	0.24	0.17	0.041	slurry without natural crust, an- nual temperature ≤ 10 °C	
	0.24	0.17	0.041	slurry below animal confinements, > 1 month, annual temperature ≤ 10 °C	
other cattle <sup>A</sup>	0.17	0.10	0.017	slurry, cool climate	IPCC (1996), Table B-4
other cattle	0.17	0.39	0.066	slurry, cool climate	IPCC (2000a), Table 4.10
other cattle	0.18	0.10	0.018	slurry with natural crust, annual tem- perature ≤ 10 °C	IPCC (2006), Tables 10A-5 and 10.17
	0.18	0.17	0.031	slurry without natural crust, annual temperature ≤ 10 °C	
	0.18	0.17	0.031	slurry below animal confinements, > 1 month, annual temperature ≤ 10 °C	

A The term "other cattle" is used in IPCC to describe all cattle apart from dairy cattle.

Table 5: IPCC specific emissions for farmyard manure for comparison. **Cattle**. Recalculated from  $B_{\rm o}$  and MCF provided. Temperatures mentioned are ambient air temperatures.

	$B_{\rm o}$	MCF	$\varepsilon_{\mathrm{CH4}}$		Reference
	m³ kg-1	m³ m-³	m³ kg-1		
dairy cows	0.24	0.01	0.0024	solid storage, cool climate	IPCC (1996), Table B-3
	0.24	0.01	0.0024	solid storage, cool climate	IPCC (2000a), Table 4.10
	0.24	0.02	0.0048	solid storage, cool climate	IPCC (2006), Tables 10A-4 and 10.17
other cattle	0.17	0.01	0.0017	solid storage, cool climate	IPCC (1996)
other cattle	0.17	0.01	0.0017	solid storage, cool climate	IPCC (2000a), Table 4-10
	0.17	0.39	0.066	deep litter, cool climate	
other cattle	0.18	0.02	0.0036	solid storage, cool climate	IPCC (2006), Tables 10A-5 and 10.17

Table 6: Experimentally derived specific emissions for slurry. **Pigs**. Partly recalculated from original data. Temperatures mentioned are ambient air temperatures.

	$arepsilon_{ ext{CH4}}$ m³ kg-1		Reference
pigs	0.148	slurry, cold climate <sup>A</sup>	Husted (1994)
	0.041	slurry, summer <sup>B</sup>	Amon et al. (2002), pg. 183
	0.01	slurry, winter <sup>8</sup>	Amon et al. (2002), pg. 182
	0.034	slurry, 10 °C and 11 % dry matter <sup>C</sup>	Massé et al. (2003)
	0.026	slurry, 10 °C and 4.9 % dry matter <sup>c</sup>	Massé et al. (2003)
	0.063	slurry, 15 °C and 11 % dry matter <sup>c</sup>	Massé et al. (2003)
	0.128	slurry, 15 °C and 4.9 % dry matter <sup>C</sup>	Massé et al. (2003)
	0.146	March to June <sup>B</sup>	Amon et al. (2004)
	0.092	slurry lagoon, American diet	DeSutter & Ham (2005)
	0.036	slurry, winter 10 °C, maize based diets <sup>c</sup>	Massé et al. (2008)
	0.077	slurry, summer 20 °C, maize based diets <sup>c</sup>	Massé et al. (2008)
	0.030	October to April <sup>D</sup>	Rodhe et al. (2010)
	0.076	May to September	Rodhe et al. (2010)
	0.0147	slurry, cold season <sup>B</sup>	Amon and Hörten- huber (2010)
	0.0174	slurry, warm season <sup>B</sup>	Amon and Hörten- huber (2010)
<sup>A</sup> Crus	t reported.		
		oned in the report. In Austria, the formation	of a crust is observed
almos	t without ex	ception.	

<sup>&</sup>lt;sup>c</sup> Obviously no crust.

Table 7: Experimentally derived specific emissions for farmyard manure. **Pigs**.

	$arepsilon_{ m CH4}$ m $^3$ kg $^{-1}$		Reference
pigs	0.064	farmyard manure "no emission", composted farmyard manure	Husted (1994) Sommer and Møller (2000)

Table 8: Modelled specific emissions for slurry. **Pigs**. Temperatures mentioned are ambient air temperatures.

	$arepsilon_{ m CH4}$ m $^3$ kg $^{ ext{-1}}$		Reference
pigs	0.036 0.058	slurry, 3.9 °C annual mean slurry, 7.3 °C annual mean	Sommer et al. (2004) Sommer et al. (2004)

Table 9: IPCC specific emissions for slurry for comparison. **Pigs.** Recalculated from  $B_{\rm o}$  and MCF provided. Temperatures mentioned are ambient air temperatures.

	$B_{\rm o}$ m $^{3}$ kg $^{-1}$	<i>MCF</i> m <sup>3</sup> m <sup>-3</sup>	$arepsilon_{ m CH4}$ m $^3$ kg $^{ extsf{-1}}$		Reference
pigs	0.45	0.10	0.045	slurry, cool climate	IPCC (1996), Table B-6
pigs	0.45	0.39	0.176	slurry, cool climate	IPCC (2000a), Table 4.10
pigs	0.45	0.10	0.045	slurry with natural crust, annual tempe- rature ≤ 10 °C	IPCC (2006), Table 10.17
	0.45	0.17	0.077	slurry without natural crust, annual temperature ≤ 10 °C	
	0.45	0.17	0.077	slurry below animal confinements, > 1 month, annual temperature ≤ 10 °C	

Table 10: IPCC specific emissions for farmyard manure for comparison. **Pigs**. Recalculated from  $B_{\circ}$  and MCF provided.

	$B_{\rm o}$ m $^3$ kg $^{-1}$	<i>MCF</i> m <sup>3</sup> m <sup>-3</sup>	$arepsilon_{ m CH4}$ m $^3$ kg $^{ extsf{-1}}$		Reference
pigs	0.45	0.01	0.0045	solid storage, cool climate	IPCC (1996), Table B-6
pigs	0.45	0.01	0.0045	solid storage, cool climate	IPCC (2000a), Table 4.10
pigs	0.45	0.02	0.0090	solid storage, cool climate	IPCC (2006), Table 10.17
	0.45	0.03	0.014	deep bedding, < 1 month, cool climate	
	0.45	0.17	0.077	deep bedding, < 1 month, cool climate	

D Crust not mentioned, but likely.

#### 4 Maximum methane-producing potentials

The maximum methane-producing potential  $B_{\alpha}$  is a function of the composition of slurry and solid manure. It may be derived from modelling or measurements.

#### 4.1 Measured maximum methane-producing potentials

The knowledge of "methane yields" is a prerequisite for planning and operation of biogas plants. Hence, such yields have been measured and can be used to derive  $B_{\alpha}$ values. German Guideline VDI 4630 was used to derive a German national guidance document for methane yields (KTBL, 2010).

The accuracy of these measurements is described in Heuwinkel et al. (2009). If inoculation is sufficient, a coefficient of variation of about 10 % can be assumed.

Tables 11 and 12 collate experimental  $B_0$  values and compare them to IPCC default values.

Table 11: Experimentally derived  $B_o$  values and IPCC default values. **Cattle**. All values in m³ kg⁻¹ CH₄. IPČC default values are given for comparison.

	D	Reference	
	$B_{_{0}}$	Keterence	
dairy	0.24	Morris (1976)	
cows	0.17	Bryant et al. (1976) <sup>A</sup>	
	0.14	Hill (1984)	
	0.10	Chen et al. (1988)	
	0.154	Kryvoruchko et al. (2004)	
	0.148	Wood Venture (undated)	
cattle	0.380	Hashimoto (1983)	
	0.285	Hansen et al. (1998)	
	0.220	Sommer et al. (2001)	
	0.159	Møller et al. (2004a)	7 experiments, SD 0.044 <sup>B</sup>
	0.248	Vedrenne et al. (2005)	
	0.316	Rodhe et al. (2009)	
	0.226	KTBL (2010)	data recommended for biogas plants
bulls	0.33	Chen et al. (1980)	
(beef)	0.29	Hashimoto et al. (1981)	7 % corn silage, 87.6 corn
	0.33	Hashimoto et al. (1981)	corn-based high energy
	0.17	Hashimoto et al. (1981)	91.5 % corn silage, 0 % corn
	0.23	Hill (1984)	
	0.231	Wood Venture (undated)	
calves	0.239	Wood Venture (undated)	
other cattle	0.139	Kryvoruchko et al. (2004)	
dairy cows	0.24	IPCC (1996)	highest value out of 4 in Safley et al. (1992)
COVVS	0.24	IPCC (2006)	based on Safley et al. (1992)
other	0.17	IPCC (1996)	lowest value out of 4 in
cattle	5.17	11 66 (1990)	Safley et al. (1992)
	0.18	IPCC (2006)	based on Safley et al. (1992)
A as cited	l in Safley e	et al. (1992)	

It is assumed that these values are related to VS excreted rather than VS entering storage, as CH<sub>4</sub> emissions can also originate from temporary storage in slurry channels (Møller et al., 2004a).

#### All $B_a$ values are calculated using a density of 0.67 kg m<sup>-3</sup> as used by IPCC in order to maintain comparability.

The IPCC methodology provides VS inputs from faeces only (see Dämmgen et al., 2011a). However, solid manure systems have an additional VS input from bedding material that should be treated accordingly. However, it has to be taken into account that additional straw increases the oxygen availability and leads to a considerable reduction of net  $CH_A$  emission rates (see also Equation (3)). The fraction  $X_{\infty}$ of CH<sub>4</sub> that is oxidized is likely to increase with the amount of VS imported into the system with straw. For experimental data covering cattle and pig farmyard manures (FYM) see Yamulki (2006). The specific emissions  $arepsilon_{
m CH4,\,faeces}$  and  $arepsilon_{
m CH4,\,straw}$ are also depending on the share of VS added with straw.

Table 12: Experimentally derived  $B_0$  values and IPCC default values. **Pigs**. All values in m³ kg-1 CH<sub>4</sub>. IPCC default values are given for comparison.

	$B_{o}$	Reference	
pigs	0.47	Chen (1983)	"corn-based high energy"
	0.45	Fischer et al. (1975)	"corn-based high energy
	0.48	Stevens and Schulte (1979)	"corn-based high energy
	0.44	lanotti et al. (1979)	"corn-based high energy
	0.36	Summers and Bousfield (1980)	"barley-based ration"
	0.48	Hashimoto (1984)	"corn-based high energy
	0.32	Hill (1984)	
	0.52	Kroeker et al. (1984)	"corn-based high energy
	0.300	Hansen et al. (1998)	
	0.35	Møller et al. (2004b)	
	0.230 to 0.373	Vedrenne et al. (2005)	
	0.27	KTBL (2010)	data recommended for biogas plants
	0.286	Wood Venture (undated)	
fatteners	0.383	Møller et al. (2004a)	7 experiments, SD 0.030 <sup>8</sup>
sows	0.296	Møller et al. (2004a)	3 experiments, SD 0.039
pigs	0.45	IPCC (1996)	
	0.45	IPCC (2006)	

<sup>&</sup>quot;high energy" denotes an intake of 45 MJ animal-1 d-1, no energy content of the feed is provided.

<sup>8</sup> SD: standard deviation

<sup>&</sup>lt;sup>B</sup> SD standard deviation

$$E_{\text{CH4}} = \left(\varepsilon_{\text{CH4, faeces}} \cdot VS_{\text{faeces}} + \varepsilon_{\text{CH4, straw}} \cdot VS_{\text{straw}}\right) \cdot \left(1 - X_{\text{ox}}\right)$$
 (6)

where

 $\begin{array}{lll} E_{\rm CH4} & {\rm CH_4~emission~(in~m^3~CH_4)} \\ \varepsilon_{\rm CH4,~faeces} & {\rm specific~emission~of~methane~from~faeces} \\ & {\rm (in~m^3~kg^{-1}~CH_4)} \\ VS_{\rm faeces} & VS {\rm available~in~faeces~(in~kg~VS)} \\ \varepsilon_{\rm CH4,~straw} & {\rm specific~emission~of~methane~from~straw} \\ & {\rm (in~m^3~kg^{-1}~CH_4)} \\ VS_{\rm straw} & VS {\rm available~in~straw~(in~kg~VS)} \\ X_{\rm ox} & {\rm fraction~of~CH_4~formed~that~is~oxidized~in~the} \\ & {\rm storage~system} \end{array}$ 

Table 13: Experimentally derived  $B_{\rm o}$  values and IPCC default values. **Straw**. All values in m³ kg<sup>-1</sup> CH<sub>4</sub>

	$B_{_{\mathrm{o}}}$	Reference	
straw	0.260	Hashimoto (1983)	
	0.210	Møller et al. (2004a)	standard deviation 0.006
	0.226	KTBL (2010)	data recommended for biogas plants
		IPCC	

Hence it is assumed that the IPCC (1996) and (2006) emission factors relating  $CH_4$  emissions from solid manure systems to the amounts of VS excreted include typical amounts of straw and typical FYM storage conditions.

#### 4.2 Modelling maximum methane-producing potentials

Buswell and Mueller (1952) and lanotti et al. (1979), see Chapter 2.3, developed equations that allow the assessment of  $B_{\rm u}$  from the constituents of faeces and urine. Similarly,  $B_{\rm o}$  can be derived from faeces composition and the biological degradability of its constituents (Table 14).

Table 14: Modelled  $B_{\rm o}$  values and IPCC default values. Values in m³ kg-¹ CH $_{\rm 4}$ 

	$B_{_{\mathrm{o}}}$	Reference	
cattle	0.23	Sommer et al. (2002b)	recalculated using IPCC density of CH <sub>4</sub>
pigs	0.34	Sommer et al. (2002b)	
cattle	0.189	Boxer (undated)	
pigs	0.322	Boxer (undated)	
cattle	0.25	IPCC (2000b), pg. 343	
pigs	0.34	IPCC (2000b), pg. 343	

However, Dustan (2002) concludes that "the significant spread in the estimate of  $B_{\rm o}$  ... is likely to be a result of the dependence on diet and straw content, which vary from farm to farm and from country to country". Khan et al. (1997) explain the different  $B_{\rm o}$  contents of pig and cattle manures with their different shares in easily degradable constituents; straw has a high share of slowly degradable constituents.

#### 5 Methane conversion factors

#### 5.1 Measured and calculated methane conversion factors

Methane conversion factors MCF are determined from emission rate measurements, VS and  $B_{\rm o}$  using the following equation:

$$MCF = \frac{E_{\text{CH4}}}{VS \cdot B_{0}} \tag{7}$$

where

MCF methane conversion factor for a given storage system (in m³ m $^{-3}$ )  $E_{\text{CH4}}$  methane emitted from the storage system (in m $^{3}$  d $^{-1}$  CH $_{a}$ )

VS volatile solid input into the storage system (in kg d<sup>-1</sup> VS)

 $B_{\circ}$  maximum methane producing capacity (in m<sup>3</sup> kg<sup>-1</sup> CH<sub>A</sub>)

Data for cattle and pig slurry and farmyard manure are collated in Table 15. The results scatter considerably. For slurry, they are obviously temperature dependent and sensitive to crust formation. Both effects have to be studied in detail.

## 5.2 Temperature dependency of methane conversion factors

As indicated by some results shown in Table 15 and obvious from IPCC (2006), Tables 10A-4 to 10A-9, the temperature dependency of *MCF* definitely requires attention. Hence an attempt is made to identify potential explanations and descriptions.

#### 5.2.1 Theoretical background

The formation of methane is temperature dependent. In physical chemistry, temperature dependent equilibria are described with the van't Hoff Arrhenius equation:

Table 15: Experimentally derived MCF values and IPCC default values for cool climates.  $B_o$  values are provided whenever they are mentioned. Temperatures mentioned are ambient air temperatures.

	animal category	<i>MCF</i> m³ m⁻³	$B_{_{ m o}}$ m $^{ m 3}$ kg $^{ m -1}$	further details	Reference
slurry	any	0.002		10 °C, B <sub>o</sub> measured	Steed and Hashimoto (1994)
	any	0.553		20 °C, $B_{_{0}}$ measured	Steed and Hashimoto (1994)
	any	0.33		15 °C, from Figure 3, $B_{_{\rm o}}$ measured	Steed and Hashimoto (1994)
	cattle	0.091	0.213	crusted at times, $B_{_{\mathrm{o}}}$ from literature	Husted (1994)
	cattle	0.11			Sommer et al. (2002b)
	cattle	0.0097	0.24	cold season, crusted, $B_{\rm o}$ from IPCC (1996)	Amon and Hörtenhuber (2010)
	cattle	0.3722	0.24	warm season, crusted, $B_{_{0}}$ from IPCC (1996)	Amon and Hörtenhuber (2010)
	pigs	0.091	0.45	winter, crust not mentioned	Amon et al., (2002)
	pigs	0.0327	0.45	cold season, crusted, $B_{\rm o}$ from IPCC (1996)	Amon and Hörtenhuber (2010)
	pigs	0.0387	0.45	warm season, crusted, $B_o$ from IPCC (1996)	Amon and Hörtenhuber (2010)
	any	0.10	0.24 0.17 0.45	dairy cattle other cattle pigs	IPCC (1996), taken over from Safley et al. (1992) <sup>A</sup>
		0.39		$B_{_{o}}$ identical with IPCC (1996)	IPCC (2000b), see discussion below <sup>8</sup>
	any	0.17	0.24 0.18 0.45	dairy cattle other cattle pigs	IPCC (2006), without natural crust
	any	0.10	0.24 0.18 0.45	dairy cattle other cattle pigs	IPCC (2006), with natural crust
FYM	cattle	0.05			Dustan (2002), based on Amon et al. (1998)
	cattle	0.016		winter	Dustan (2002), based on Amon et al. (1998)
	cattle	0.04		summer	Dustan (2002), based on Amon et al. (1998)
	pigs	0.142			Husted (1994)
	any	0.002		10 °C, B <sub>o</sub> measured	Steed and Hashimoto (1994)
	any	0.457		20 °C, B <sub>o</sub> measured	Steed and Hashimoto (1994)
	any	0.25		15 °C, from figure 3, $B_o$ measured	Steed and Hashimoto (1994)
	any	0.01	0.24 0.17 0.45	cold climate dairy cattle other cattle pigs	IPCC (1996), Tables B-3, B-4 and B-6
	any	0.01		cold climate $B_{\circ}$ identical with IPCC (1996)	IPCC (2000b), Table 4.10
	any	0.02	0.24 0.17 0.45	cold climate dairy cattle other cattle pigs	IPCC (2006), Table 10.17
	any	0.03		deep bedding, cold climate, < 1 month	IPCC (2006), Table 10.17
	any	0.17		deep bedding, cold climate, > 1 month	IPCC (2006), Table 10.17

A The MCF for slurry, deep pit and litter in IPCC (1996) are taken from Safley et al. (1992) where they are labelled "author's estimate; no data available in the literature."

<sup>&</sup>lt;sup>8</sup> MCF for slurry and pigs of 39 % was presented in IPCC (2000b) with a reference to Zeeman (1994). In there, this value is listed as valid for 15 °C (which is the upper boundary condition of "cool climate"). For a temperature of 10 °C, a value of 0.27 is given by the same authors. Zeeman (1994) lists this MCF under "manure". It seems clear from the context that slurry is meant.

$$\frac{\mathrm{d}\ln k_{\mathrm{p}}}{\mathrm{d}T} = \frac{\Delta E_{\mathrm{A}}}{RT^2} \tag{8}$$

where

 $k_{\rm p}$  reaction velocity constant for a reaction under constant pressure (unit depending on order of reaction)

T absolute temperature (in K)

 $\Delta E_{\Lambda}$  energy of activation (in J mol<sup>-1</sup>)

R gas constant ( $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$ )

For any two temperatures  $T_1$  and  $T_2$  with  $T_2 > T_1$  the integration yields:

$$\ln \frac{k_{\rm p,2}}{k_{\rm p,1}} = \frac{\Delta E_{\rm A}}{R} \cdot \frac{T_2 - T_1}{T_1 \cdot T_2} \tag{9}$$

If one replaces the ratio of reaction velocity constants by the ratio of emission (production) rates  $P_1$  and  $P_2$  or methane conversion factors  $MCF_1$  and  $MCF_2$  at temperatures  $T_1$  and  $T_2$  (this is allowed for identical substrates only, as the fraction of reaction velocity constants then equals the fraction of products E formed and hence MCF), and if one considers the changes of the product  $T_1 \cdot T_2$  within the range of temperature differences insignificant the equation reads:

$$\frac{\ln \frac{P_2}{P_1}}{T_2 - T_1} = \frac{\ln \frac{MCF_2}{MCF_1}}{T_2 - T_1} = a \tag{10}$$

where a (in  $K^{-1}$ ) is an increment specific for the system under consideration and describes the increase rate of  $CH_4$  release per temperature unit.

Equation (9) also shows that the increment a can be derived from a known energy of activation<sup>3</sup>:

$$a = \frac{\Delta E_{\rm A}}{R \cdot T_1 \cdot T_2} \tag{11}$$

It is obvious that this increment is a function of the temperatures  $T_1$  and  $T_2$ .  $E_{\rm A}$  is also temperature dependent.

However, there are limitations: The original Equation (8) describes equilibria of chemical reactions where the reaction enthalpy does not change significantly with temperature. The processes governing  $\mathrm{CH_4}$  emissions from storage cannot be regarded in equlibria. The temperature considered is that of the (very dilute) solution where nevertheless the reaction velocity is not hampered by diffusion processes.

In practice, slurry is not a dilute solution. Experiments with different dry matter contents reveal that the reaction velocity is higher in diluted slurries with a lower viscosity (Massé et al., 2003).

In the manure storage systems described in this paper the composition of the microbial community is likely to be different at different temperatures. Hence the activation energy may change.

As the processes inside the storage system are exothermic the temperature of ambient air cannot be used to describe the temperature in the storage system in principle.<sup>4</sup>

Even with these restrictions, it might still be possible to find practice-oriented values of the increase rate a (similar to the evident increase rate in IPCC, 2006, Table 10.17). An attempt is made in the following section.

#### 5.2.2 Establishing the increase rate a

A small number of measurements were performed under different temperature regimes and may allow for a determination of a. The results are listed in Table 16.

The increase rates *a* listed above scatter to an extent that prohibits their use in principle. This may be due to the fact that emission rates at low temperatures are difficult to quantify. Khan et al. (1997) state that the specific emission rates are highly correlated with slurry temperature. They could not identify a relation between air temperature and specific emission rates. Against that, Husted (1993) points out that in his experiments "slurry and air temperature were highly correlated for pig slurry and cattle slurry".

For the purpose of inventories, only air temperature can be taken into account because slurry temperatures are not routinely available. IPCC (2006) relates MCF to air temperatures.

The van't Hoff Arrhenius equation (or its integrated form) may be a useful instrument that can be applied inpractice to estimate or evaluate the temperature dependence of CH<sub>4</sub> emission rates.

<sup>&</sup>lt;sup>3</sup> Care should be taken, as normally the experimental assessment of the energy of activation makes use of the inverted Equation (9) to derive  $E_{\rm A}$  from measurements of reaction velocities at two different temperatures.

Slurry temperatures inside the storage vary with depth (e.g. Patni and Jui, 1987; Rodhe et al., 2009). Citing just one slurry temperature may be misleading. Reactions in slurry and solid manure are exothermic. With a reaction velocity positively correlated to temperature, temperatures inside the storage facility are likely to exceed those of ambient air. Husted (1994) showed that major differences between the temperatures of ambient air and the contents of a slurry tank occur during winter. The variability of temperatures inside the tank exceeds the difference between outside and inside temperatures.

Table 16: Increments a derived from emission measurements at different temperatures t (in °C)

Source	$t_1$	$t_2$	а	comment
Husted (1993)	9.2	19.3	0.082	cattle slurry, LE <sup>A</sup> , ST <sup>B</sup>
Husted (1994)			0.27	cattle slurry, annual mean of monthly data; ST
Steed and Hashimoto (1994)	10	20	0.562	slurry type, not specified
Linke (1997)	24	35	0.120	pig slurry (laboratory scale)
Linke (1997)	24	35	0.094	cattle slurry (laboratory scale)
Massé et al. (2003)	10	15	0.033	cattle slurry, 9.2 % DM; AT <sup>c</sup>
Massé et al. (2003)	10	15	0.074	cattle slurry, 4.2 % DM; AT
Massé et al. (2003)	10	15	0.121	pig slurry, 11.3 % DM; AT
Massé et al. (2003)	10	15	0.317	pig slurry, 4.9 % DM; AT
Sommer et al. (2004)	10	20	0.068	calculation based on assumed activation energy <sup>1</sup>
Mangino (undated)	5	30	0.092	calculation based on assumed activation energy <sup>2</sup>
IPCC (2006)	10	20	0.092	slurry without natural crust, Table 10.17, results taken over from Mangino et al. (undated)
Massé et al. (2008)			0.076	pig slurry, maize based diet; ST
Klevenhusen et al. (2010)	14	27	0.152	cattle, hay based diet; LE, AT
Klevenhusen et al. (2010)	14	27	0.223	cattle, barley based diet; LE, AT

<sup>&</sup>lt;sup>A</sup> LE: laboratory experiment;

Table 17:

#### 5.3 Effects of crust and cover

The natural crust in slurry stores acts as a "biosphere" where methanotrophic microorganisms oxidize  $\mathrm{CH_4}$  to  $\mathrm{CO_2}$  (Petersen et al., 2005). About three quarters of the methane released from a tank can be converted (Ambus and Petersen, 2005). The crust should be 15 to 20 cm thick to act as an effective biofilter (Petersen and Ambus, 2006). Experimental results are compiled in Table 17.

Crust formation is a periodical process going along with changes in the populations of methanotrophic microorganisms and hence changing methane oxidation potentials (Petersen, 2011).

CH<sub>4</sub> emission and oxidation rates are moisture dependent. The natural crust must stay dry in order to allow for optimal aerobic conditions inside the crust. A crust that is subjected to rainfall gets wet and anaerobic. As a result, the rate of CH<sub>4</sub> oxidation will strongly be reduced.

Hence we assume that the data listed in Husted (1994) describe ideal conditions whereas the other authors give results for real (i.e. partly wet) conditions.

"Inorganic crusts" (such as formed by LECA<sup>5</sup> additions) are ineffective (Petersen and Ambus, 2006).

Reduction of CH<sub>4</sub> emissions due to the **formation of a crust** 

Source	reduction		
Petersen et al. (2005)	20 %		
Petersen and Ambus (2006)	yes, but no data		
Clemens et al. (2006)	15 - 30 %		
Husted (1994)	97 %		
Husted (1994)	97 %		

Covering the tank with solid roofs or tent structures results in a decreased air exchange rate and longer retention time in the aerobic layer of the slurry (see also Petersen and Miller, 2006). Laboratory experiments with varied air flows above the slurry surface resulted in up to 90 % reduction of CH<sub>4</sub> emissions (Williams and Nigro, 1997). Rodhe et al. (2010) covered their tanks with plastic sheet and obtained reduced emissions, see Table 18. However, Husted (1993) reports that the emissions from covered pig slurry are independent of the air flow rate above the surface.

Covering the slurry tank prevents precipitation entering the crust and the drier conditions permit a good oxygen supply within the crust, which is a prerequisite for  ${\rm CH_4}$  oxidation.

<sup>&</sup>lt;sup>B</sup> ST: slurry temperature;

<sup>&</sup>lt;sup>c</sup> AT: air temperature

<sup>1</sup> using an energy of activation of 112.7 J mol-1

<sup>&</sup>lt;sup>2</sup> energy of activation of 63.5 J mol<sup>-1</sup> as in Safley and Westerman (1990). It is likely that the chemical compounds to which the activation energies are related, are different.

<sup>&</sup>lt;sup>5</sup> LECA: light expanded clay aggregates

Table 18: Reduction of specific CH<sub>4</sub>-C emissions (weight by weight) due to **covering** with plastic sheeting

Source	specific emissions without cover	specific emissions with cover	reduction	comment	
Rodhe et al. (2010)	2.7 g (kg VS) <sup>-1</sup> CH <sub>4</sub> -C	1.8 g (kg VS) <sup>-1</sup> CH <sub>4</sub> -C	33 %	cattle slurry, annual mean	
Rodhe et al. (2010)	2.6 g (kg VS) <sup>-1</sup> CH <sub>4</sub> -C	1.5 g (kg VS) <sup>-1</sup> CH <sub>4</sub> -C	43 %	pig slurry, annual mean	

# 6 Conclusions and derivation of German and Austrian national values to describe methane formation from animal manures

National data describing CH<sub>4</sub> emissions from storage have to fit Equation (5). Calculations should provide specific emissions  $\varepsilon_{\text{CH4}}$  from measured VS inputs and measured volumes of CH<sub>4</sub> released ( $E_{\text{CH4}}$ ). Another entity that can be measured is the maximum methane producing capacity  $B_{\circ}$ . Methane conversion factors MCF can then be derived from Equation (7).

Whereas the Austrian inventory is backed by national experimental data, the German approach has to rely on international measurements and data sets that might be "extrapolated" to describe the German situation. The derivation of German national data sets uses the experimental background provided in the Tables in Chapters 3 to 5 and compares them to default values provided by IPCC.

#### 6.1 Maximum methane-producing potentials B

#### 6.1.1 Applicability of B values provided by IPCC

In the 1996 IPCC Guidelines, "the  $B_{\rm o}$  values as adapted for the US are also used in the IPCC Guidelines for developed countries as it is assumed that the typical diets are similar." (IPCC, 2000b, pg. 341). However, this assumption is invalid for pigs, as pig feed composition in Central Europe differs significantly from the US feeds used to derive  $B_{\rm o}$ . Hence, the same source IPCC (2000b, pg. 343) states: "a re-estimation of the default  $B_{\rm o}$  values should be considered."

#### 6.1.2 German approach

Biogas plants convert VS using optimal conditions. Hence measured biogas yields, i.e. the biogas production rates as related to VS input rates can be used as adequate  $B_{\circ}$ . National data sets were generated for and collated by KTBL and reviewed by a team of German and Austrian experts. The results were published in KTBL (2010).

For dairy cows and other cattle, KTBL (2010) recommends<sup>6</sup> the use of 0.23 m<sup>3</sup> (kg VS)<sup>-1</sup> CH<sub>4</sub>. This value is supported by measurements in Central Europe (see Table 11: Hansen, Kryvoruchko, Møller, Rodhe, Sommer, Vedrenne). The experimental data available for Europe is insufficient for a differentiation to be made between dairy cows and other cattle.

Given the uncertainties in both the national recommendations (KTBL, 2010) and the IPCC default values, the agreement between national and IPCC data is sufficient for cattle

Table 12 indicates that the assumption on the use of US  $B_{\rm o}$  data (indicated by "corn-based high energy") is not met for **pigs** in Germany. Here, pig diets are based on grain (wheat and barley, see Dämmgen et al., 2011b) and not on maize as in the United States. KTBL (2010) recommends<sup>7</sup> the use of 0.27 m³ (kg VS)-¹. However, European data in Table 12 (Hansen, Møller, Sommer, Vedrenne) suggests a  $B_{\rm o}$  of about 0.30 m³ (kg VS)-¹. For pigs, Northwest European  $B_{\rm o}$  values deviate considerably from IPCC default values.

**We propose** the use of German national  $B_{\rm o}$  values in future inventories of 0.23 m³ kg<sup>-1</sup> CH<sub>4</sub> for cattle (dairy cows and other cattle), and 0.30 m³ kg<sup>-1</sup> CH<sub>4</sub> for pigs.

#### 6.1.3 Austrian solution

Austria has no country-specific  $B_{\rm o}$  values for cattle and pigs available.

The Austrian inventory uses IPCC (1996) default  $B_{\rm o}$  values for all animal categories: 0.24 m³ kg¹ CH<sub>4</sub> for dairy cattle, 0.17 m³ kg¹ CH<sub>4</sub> for other cattle, 0.45 m³ kg¹ CH<sub>4</sub> for breeding sows and fattening pigs.

 $<sup>^{6}</sup>$  calculated from 0.210 m $^{3}$  (kg VS) $^{-1}$ , a standard density of 0.72 kg m $^{-3}$  and an IPCC density of 0.67 kg m $^{-3}$ .

 $<sup>^7</sup>$  calculated from 0.250 m³ (kg VS)¹1, a standard density of 0.72 kg m³ and an IPCC density of 0.67 kg m³.

#### 6.2 Methane conversion factors MCF for slurry

#### 6.2.1 Applicability of MCF values provided by IPCC

From Equation (7) follows that MCF and  $B_{\rm o}$  form matching pairs. Hence, MCF have to be adjusted to the  $B_{\rm o}$  described above.

The IPCC assumption that *MCF* values are independent of the source of *VS* (i.e. cattle or pigs, see IPCC, 1996, Table 4-8; IPCC, 2006, Tables 10A4 to 10A-8) is not maintained, "because the amount of slowly degradable carbohydrates is much higher in cattle slurry than in pig slurry" (Sommer et al., 2002a) (see also IPCC, 2000b; Dustan, 2004). Furthermore, *MCF* values depend on temperature and dry matter content of the slurries, on the formation of aerobic zones (crusts) and the air exchange rate above the containment. This is reflected in the IPCC (2006) approach and ignored in the IPCC (1996) methodology.

The following discussion deals with those systems in the first instance that are likely to be described best in the literature or used most often, i.e. systems with crust for cattle and systems without crust for pigs.

#### 6.2.2 Experimental data – the problem of crust formation

The experimental data collated in Tables 1 and 6 can be used as guidance only, as reliable information about crust formation is sparse. Hence, the assumption that many of the slurry stores can be treated as always or temporarily crusted is considered adequate. However, the depth will vary, also the water content of the crust and the composition of its microcrobial populations.

### 6.2.3 Methane conversion factors for cattle slurries with crust

#### 6.2.3.1 German approach

In 2010, about three quarters of uncovered cattle slurry stores were reported to have a natural crust. As *MCF* are depending on storage temperatures, climate has to be taken into account. In accordance with the IPCC (1996) and (2006) methodologies, air temperatures can serve as auxiliary entities (see above).

There is a wide consensus that CH<sub>4</sub> emissions from stored slurry at air temperatures below 10 °C are small in comparison to those at higher temperatures (e.g. Steed and Hashimoto, 1994; Husted, 1994; Massé et al., 2003; Sommer et

al., 2007; Rodhe et al., 2009; Klevenhusen et al., 2010). In Germany this applies to the period from October to April, whereas monthly mean air temperatures are above 10  $^{\circ}$ C between May and September, as shown in Figure 1.

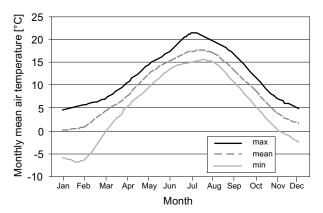


Figure 1: Monthly mean air temperatures in Germany (Data for 1970 to 2000, courtesy of German Weather Service)

However, the relation between *MCF* and temperature is not linear (see Chapter 5.2). Hence, mean temperatures below 10 °C do not necessarily result in negligible overall emission rates; the overall temperature profile has to be taken into account. As no use can be made of the increase rate *a* (see Chapter 5.2), annual means of *MCF* have to be established using winter and summer measurements.

Comparisons of *MCF* between different countries presuppose similar annual temperature profiles.

Emissions were measured during the summer months in Austria by Amon et al. (2004) and in Sweden by Rodhe et al. (2009) in regions with annual mean air temperatures of 9.8 and 9.7 °C, respectively. This compares with a mean German temperatures of 9.8 °C (see Rösemann et al., 2011).

Hence, The MCF of 0.10 m<sup>3</sup> m<sup>-3</sup> was obtained for similar annual mean temperatures and is regarded applicable for the German inventory.

It is also clear that the present IPCC (2000a) default value (0.39 m $^3$  m $^{-3}$   $^8$ ) is to be considered a "pure" summer value and is not adequate for the use as annual mean (see Austrian "summer" value for cattle and Steed and Hashimoto, 1994, in Table 15). Zeeman's model results that formed the basis for the *MCF* provided in IPCC (2000a) have been declared irrelevant (see review by Dustan, 2002, and DeSutter and Ham, 2005).

<sup>&</sup>lt;sup>8</sup> calculated for pig manure using a process (i.e. slurry) temperature of 15 °C and a storage time of 180 d. Zeeman's MCF for cattle manure with process temperatures of 15 and 20 °C are 0.27 and 0.41 m³ m³, respectively. All measurements relate to conditions in a continuously stirred reactor (CSTR) and are not hampered by diffusion processes.

However, it is accepted that the importance of crusts under practical conditions "remains uncertain" (Petersen, 2011).

Keeping in mind that the methane oxidizing properties of crusts vary with depth and water content, a "provisional" mean MCF can be deduced from the data provided in Table 1. The arithmetic mean of the specific emissions reported by Husted (1994), Rhode et al. (2009, annual mean) and Amon and Hörtenhuber (2010, weighted mean for 7 winter and 5 summer months) and a  $B_{\rm o}$  of 0.23 m³ kg¹ yields 0.10 m³ m⁻³ which is identical in practice with the IPCC (2006) default MCF of 0.10 m³ m⁻³ for cattle slurry with crust for cool climates.

**We propose** the use of an MCF for cattle slurry with natural crust of 0.10 m<sup>3</sup> m<sup>-3</sup> in association with a national  $B_o$  of 0.23 m<sup>3</sup> (kg VS)<sup>-1</sup> for dairy cows and other cattle in the German emission inventory. This MCF equals the value proposed in IPCC (2006).

No attempts should be made to further disaggregate with respect to regional climates, as information about the temporal variation of the amounts of slurry stored is not available.

#### 6 2 3 2 Austrian solution

In Austria, *MCF* assessed for cattle and pig slurries are considered to represent a situation with a natural crust. However, owing to a lack of activity data, it is unknown how many stores with natural crusts in Austria are really covered.

IPCC encourages measurements of emissions from manure management under field conditions in order to improve the basis of emission estimates. In Austria, a three-year measurement campaign on emissions from manure stores financed by the Federal Ministry of Agriculture, Forestry, Environment, and Water Management and the Federal Ministry for Education, Science, and Culture was carried out. Measurements were performed under field scale conditions. Campaigns covered emissions from stored cattle and pig slurry under cool (winter, spring, autumn) and under warm (summer) conditions. Emission rates were published in peer reviewed publications. They can therefore be used for calculating *MCF* values for liquid manure stores.

In Austria, a recent update of the national greenhouse gas inventory used national *MCF* values and distinguished between slurry storage in the warm and in the cold season (Amon and Hörtenhuber 2010). The updated inventories have successfully passed an external review process. The results were accepted within the UNFCCC expert review process.

Four seasons are distinguished for the application of MCF in Austria: spring, summer, autumn, winter. The extensive emission measurements under field conditions showed that a substantial increase in  $\mathrm{CH_4}$  emissions during slurry storage was only observed during the summer season. The low air temperatures in all other seasons in Austria hindered  $\mathrm{CH_4}$  formation during slurry storage. Emission measurements were carried out in one of the warmest Austrian regions and therefore may tend to overestimate MCF values.

From the data of all emission measurements during slurry storage the following country-specific *MCF* values for stored cattle slurry were deduced:

• cattle, cold seasons:  $MCF = 0.097 \text{ m}^3 \text{ m}^{-3}$ • cattle, warm season:  $MCF = 0.3722 \text{ m}^3 \text{ m}^{-3}$ 

A weighted annual mean MCF of 0.17 m m<sup>-3</sup> results for 9 winter and 3 summer months, which equals the respective default MCF for slurry *without* natural crust in IPCC (2006). However, the Austrian inventory does not distinguish MCF for stores with or without cover or crust.

6.2.4 Methane conversion factors for cattle slurries without crust for Central European climates

#### 6.2.4.1 German approach

Data describing slurry stores without crust are considered insufficient. MCF could be deduced from the data for storage with a crust, if the fraction  $X_{\rm ox}$  of  ${\rm CH_4}$  that is oxidized (see Equation (3)) was known.

IPCC (2006) assume a reduction of the *MCF* as result of crust formation of 40 %. This is within the range that might be deduced from Table 17. IPCC (1996), Table 4-8, does not differentiate between storage without and with

 $<sup>^9</sup>$  The detailed description of the experiments can be found in Amon et al. (2002). Pages 35 to 47 of that report describe the measurement technologies. The time table of the emission measurement is shown in Tables 11 and 12. Chapters 3 and 4 show the results of the emission measurement including air and slurry temperatures. Results have been published in the following peer reviewed publications (Amon et al., 2005, 2006, 2006a, 2006b and 2007). Chapter 3.2.6 in Amon et al. (2002) shows the results on MCF from stored cattle slurry.  $\mathrm{CH_4}$  emissions from untreated cattle slurry under summer conditions amounted to 0.342 m³ m³ of (IPCC standard)  $B_{_{\rm O}}$ . During the other seasons, only 0.005 m³ m³ of  $B_{_{\rm O}}$  were emitted as  $\mathrm{CH_4}$ . The cool conditions in winter, spring and autumn in Austria drastically reduced  $\mathrm{CH_4}$  emissions.

a natural crust. This is felt to be inadequate (see Chapter 6.2.3).

An increase of 40 % is equivalent to an MCF for storage without crust of 0.17 m<sup>3</sup> m<sup>-3</sup>.

The few measured data indicate that the IPCC (1996) default value of 0.10 m<sup>3</sup> m<sup>-3</sup> is too low for Central Europe (see Table 15: Husted, 1994; Amon and Hörtenhuber, 2010).

As neither IPCC (1996) nor IPCC (2000a) can provide satisfactory MCF, and experimental data do not allow for a well-founded MCF for uncrusted systems, the default data of IPCC (2006) is selected as the only alternative.

**We recommend** that an increased *MCF* for slurries without a natural crust by 40 % in agreement with IPCC (2006), i.e. 0.17 m<sup>3</sup> m<sup>-3</sup> be applied to cattle.

#### 6.2.4.2 Austrian solution

As described above, the Austrian *MCF* reflect the national situation and are considered to represent a situation with a natural crust.

6.2.5 Methane conversion factors for pig slurries without and with crust

#### 6.2.5.1 German approach

Table 6 contains several emission data for summer and winter conditions. For the derivation of a German data set, these MCF have to be re-calculated for summer and winter conditions using a  $B_{\circ}$  of 0.30 m<sup>3</sup> kg<sup>-1</sup>. Data clearly reflecting feeding not used in Germany were omitted. Of these, only data with no or almost no effective crust were used. Massé et al. (2003) provide two data sets for each temperature of which the set with the lower DM content is used. (KTBL, 2010, assumes a DM content of 6 % for German pig slurries.) These data are collated in Table 19.

If one calculates the weighted mean of the summer data (5 months) obtained from Amon et al. (2004) and Massé et al. (2003) of 0.49 and 0.43 m³ m⁻³, respectively, and the winter data (7 months) obtained from Rodhe et al. (2010) and Massé et al. (2003) of 0.10 and 0.09 m³ m⁻³, respectively, one obtains a mean MCF of about 0.25 m³ m⁻³ for pig slurry without crust.

This MCF is equivalent to the 17 % proposed in IPCC (2006) for any slurry without natural crust if one takes the ratio of German national  $B_{\rm o}$  to the IPCC  $B_{\rm o}$  (2/3) into account.

Table 19: CH<sub>4</sub> emissions rates and *MCF* for **pig slurry without natural crust** 

$\varepsilon_{\mathrm{CH4}}$	$B_{_{\mathrm{o}}}$	MCF	restriction	source
m³ kg-1	m³ kg-1	m³ m-³		
0.128	0.30	0.427	15 °C, 4,9 % DM	Massé et al. (2003)
			15 C, 4,9 /0 DIVI	` ′
0.146	0.30	0.487	summer	Amon et al. (2004)
0.030	0.30	0.100	winter	Rodhe et al. (2010)
0.026	0.30	0.087	10 C°, 4,9 % DM	Massé et al. (2003)

In a considerable share of German storage systems for pig slurry, a natural crust is not formed. With no data available, the IPCC (2006) approach is used that assumes a 40 % decrease of *MCF* for systems with crust. However, we maintain that this reasoning is unsatisfactory.

**We propose** to apply a national *MCF* for pig slurry without natural crust of 0.25 m<sup>3</sup> m<sup>-3</sup> and of 0.15 m<sup>3</sup> m<sup>-3</sup> for pig slurry with a natural crust in combination with a national  $B_0$  of 0.30 m<sup>3</sup> kg<sup>-1</sup> CH<sub>4</sub>.<sup>10</sup>

#### 6.2.5.2 Austrian solution

Amon et al. (2002) give data on MCF from pig slurry storage based on measurements. Here,  $CH_4$  emissions were considerably lower than those derived with the default IPCC MCF during the warm summer season and during the cooler seasons. Summer includes the months June, July and August.

In the Austrian inventory, measured MCF are used: For pigs in the cold and warm seasons MCF values of 0.0327 m³ m³ and 0.0387 m³ m³ are used, respectively, in combination with the IPCC (1996, 2006) default  $B_{\rm o}$  of 0.45 m³ kg¹ CH<sub>a</sub>.

6.2.6 Methane conversion factors for cattle and pig slurries with cover

Solid covers or plastic sheets are used mainly in pig production to reduce odour. There is evidence that these covers result in oxidation of  ${\rm CH_4}$  at the surface of the slurries (see Table 18).

Within the MIDAIR project (Clemens et al. 2006) pilot scale measurements in Austria proved that a cover on cattle slurry that formed a natural crust was able to reduce methane emissions due to methane oxidation in the crust.

<sup>&</sup>lt;sup>10</sup> The national pair of  $B_o=0.30~{\rm m^3~kg^{-1}}$  and  $MCF=0.25~{\rm m^3~m^{-3}}$  is equivalent to the IPCC (2006) pair of  $B_o=0.45~{\rm m^3~kg^{-1}}$  and  $MCF=0.17~{\rm m^3~m^{-3}}$ . German data:  $\varepsilon_{\rm CH4}=0.075~{\rm m^3~(kg~VS)^{-1}}$ ; IPCC (2006) data:  $\varepsilon_{\rm CH4}=0.0765~{\rm m^3~(kg~VS)^{-1}}$ .

This was confirmed by a study of Petersen et al. (2005) who took samples of the crusts and could identify the presence of methane oxidising bacteria.

However, the data are at present considered insufficient to propose separate values for covered storages.

#### 6.2.6.1 German approach

In order to avoid underestimation of emissions, a worst case assumption is the use of the higher *MCF* for cattle and pig slurries.

**We propose** that an *MCF* of 0.17 m<sup>3</sup> m<sup>-3</sup> be used for covered cattle slurry storage and of 0.25 m<sup>3</sup> m<sup>-3</sup> for covered pig slurry storage systems.

#### 6.2.6.2 Austrian solution

The Austrian inventory does not differentiate between covered and uncovered storage systems.

6.3 Methane conversion factors for pit storage below animal confinements (underneath slatted floor)

In principle, the temperature inside slurry underneath slatted floor will exceed that of outside storage. This should be taken into account. However, only one reference is available for emissions from slurry stored underneath slatted floors without providing a temperature or temperature difference (Sommer et al., 2002a) (see Table 6). Sommer et al. (2009) contribute model assumptions for indoor and outdoor storage. At present, the knowledge is limited to an extent (Petersen, 2011) that the data provided do not justify any other conclusion than to treat emissions from pit storage below animal confinements in the same way as emissions from outdoor storage of slurry without crust.

#### 6.3.1 German approach

**We propose** that the German inventory use an *MCF* for cattle slurry underneath slatted floors of 0.17 m<sup>3</sup> m<sup>-3</sup> and for pig slurry the value of 0.25 m<sup>3</sup> m<sup>-3</sup> that was derived for slurry stores without a crust. This is likely to avoid underestimation of emissions.

#### 6.3.2 Austrian solution

In Austria, the GHG inventory only covers outside stores for cattle and pig slurry. No specific *MCF* is applied for pit storage below animal confinements.

6.4 Methane conversion factors MCF for farmyard manure stored in heaps

#### 6.4.1 Experimental and IPCC data

Few measurements report  $CH_4$  emissions from *cattle* farmyard manure. Table 15 collates the results as MCF related to IPCC default  $B_0$  values.

No measurements are available for *pig* manure that can be used as comparison to IPCC data.

In principle, the treatment of farmyard manure requires calculations according to Equation (6). For this purpose the amounts of bedding material added as well as the respective  $B_{\rm o}$ , MCF and  $X_{\rm ox}$  have to be known. With the exception of  $B_{\rm o}$  these values cannot be provided. However, it is common practice within the IPCC process not to quantify emissions from bedding.

IPCC (1996) and IPCC (2006) do not differentiate between cattle and pig farmyard manures with respect to *MCF*. However, cattle and pig solid manures differ with respect to their properties and storage conditions. Pig manures contain comparatively much bedding giving it a higher porosity that facilitates oxygen transport. Cattle manure exhibits a greasy consistency and is more compact. Under comparable conditions, pig manure heaps tend to generate more heat than cattle manure heaps and should hence be treated with different *MCF* ( Husted, 1994).

#### 6.4.2 German approach

The application of Equation (6) that relates emissions to the amounts of VS from faeces and bedding with their respective specific emissions and the availability of oxygen in the storage system is not feasible. No detailed information on input data can be found yet.

The experimental data base for specific emissions  $\varepsilon_{\text{CH4}}$  is very poor, see Tables 2 and 7. The reasoning leading to an MCF of 2 % provided in IPCC (2006), Table 10.17, indicates that an MCF of 2 % is likely to underestimate emissions 11: In contrast to the practice applied above that derived an annual mean from winter and summer MCF (see Chapters 6.2.3.1 and 6.2.4.1), the winter MCF of 2 % is chosen to represent the cool climate MCF of the entire year (in agreement with IPCC (2006). Hence, the MCF of 1 % as proposed in IPCC (1996) and IPCC (2000a) is definitively too low. This is underlined by the following comparison:

If European data (Dustan, 2002, based on Amon et al., 2001) are back calculated with the IPCC default  $B_o$  for dairy cows (0.24 m³ (kg VS)-1), specific emissions of 0.0038 m³

Expert judgement for MCF describing solid storage: ... "shows emissions of approximately 2 % in winter and 4 % in summer." (IPCC, 2006, Table 10.17)

(kg VS)<sup>-1</sup> are observed for winter months and 0.0096 m³ (kg VS)<sup>-1</sup> for summer months. The weighted mean of 5 summer months and 7 winter months is 0.0062 m³ (kg VS)<sup>-1</sup>. For *other cattle*, using the IPCC (2006) default  $B_o$  (0.18 m³ (kg VS)<sup>-1</sup>), the weighted mean of annual specific emissions is 0.0047 m³ (kg VS)<sup>-1</sup>.

Considering the ratio between dairy cow places and other cattle places which is about 1 to 2 in Germany (see Rösemann et al., 2011)) one obtains a weighted mean specific emission for cattle of 0,0052 m³ (kg VS)-1. Using the German  $B_o$  value for cattle (0.23 m³ (kg VS)-1), this leads to a national mean MCF of 0.023 m³ m-3 or about 2 % for cattle.

Due to lack of data, the approach applied to cattle is also used for pigs by analogy. However, the MCF of 2 % provided in IPCC (2006) relates to a  $B_{\circ}$  of 0.45 m³ kg¹ CH $_{4}$ . If the specific emissions resulting from IPCC (2006) MCF and  $B_{\circ}$  are considered correct then the national MCF is to be related to the national  $B_{\circ}$  of 0.30 m³ kg¹ CH $_{4}$ . A national MCF of 0.030 m³ m³ results.

**We propose** that the German inventory use an MCF of 0.02 m³ m⁻³ for cattle farmyard manure and of 0.03 m³ m⁻³ for pig farmyard manure stacked in heaps in combination with national  $B_{\circ}$  of 0.23 m³ kg⁻¹ CH₄ for cattle and 0.30 m³ kg⁻¹ CH₄ for pigs.

#### 6.4.3 Austrian solution

In Austria, the following MCF are applied to FYM:

- 'solid storage composted' (MCF from IPCC, 2006: 0.005 m³ m⁻³),
- 'solid storage untreated' (*MCF* from IPCC, 1996: 0.01 m³ m⁻³),
- 'deep litter composted' and 'deep litter untreated' with the *MCF* for deep litter applied in each case according to IPCC (2006) (*MCF* = 0.17 m<sup>3</sup> m<sup>-3</sup>).

The Austrian emission inventory does not distinguish summer and winter storage.

6.5 Methane conversion factors MCF for deep bedding systems

No experimental data can be provided for deep bedding systems. Both IPCC (2000a) and IPCC (2006) treat deep bedding stored for more than a month in the same way as slurry without crust.

Deep bedding systems are not mentioned in IPCC (1996). Hence, we recommend the use of the IPCC (2006) approach to equate these emissions with those of slurry without natural crust (see Chapters 6.2.4.1 and 6.2.5.1), as the storage times of the bedding material exceed 1 month.

#### 7 Conclusions

Whereas Austria is able to provide an almost comprehensive experimental data set describing CH<sub>4</sub> emissions from manure management, German data on CH<sub>4</sub> emissions from storage are scarce. Here, data from neighbouring countries with similar meteorological conditions and similar types of animal production were used to derive data sets for specific CH<sub>4</sub> emission rates. Experimental findings are very variable. However, where data sets could be established they tended to support the IPCC (2006) guidelines, rather than earlier versions (see sections on MCF for cattle and pig slurries). The IPCC (1996) and (2000a) approaches were here found to be inadequate for pigs in particular, because the application of North American pig feed composition data to Northwest European conditions is not justified. Hence, wherever missing national data had to be replaced by default values, the values proposed in IPCC (2006) were preferred and the reasoning provided.

The lack of experimental data relevant to the German animal husbandry is striking, and the almost complete absence of German data is considered a serious obstacle with respect to adequate reporting of  $\mathrm{CH_4}$  emissions from manure management.

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