

1           **Reduction of ammonia emissions from dairy cattle cubicle houses via improved**  
2           **management- or design-based strategies: A modeling approach**

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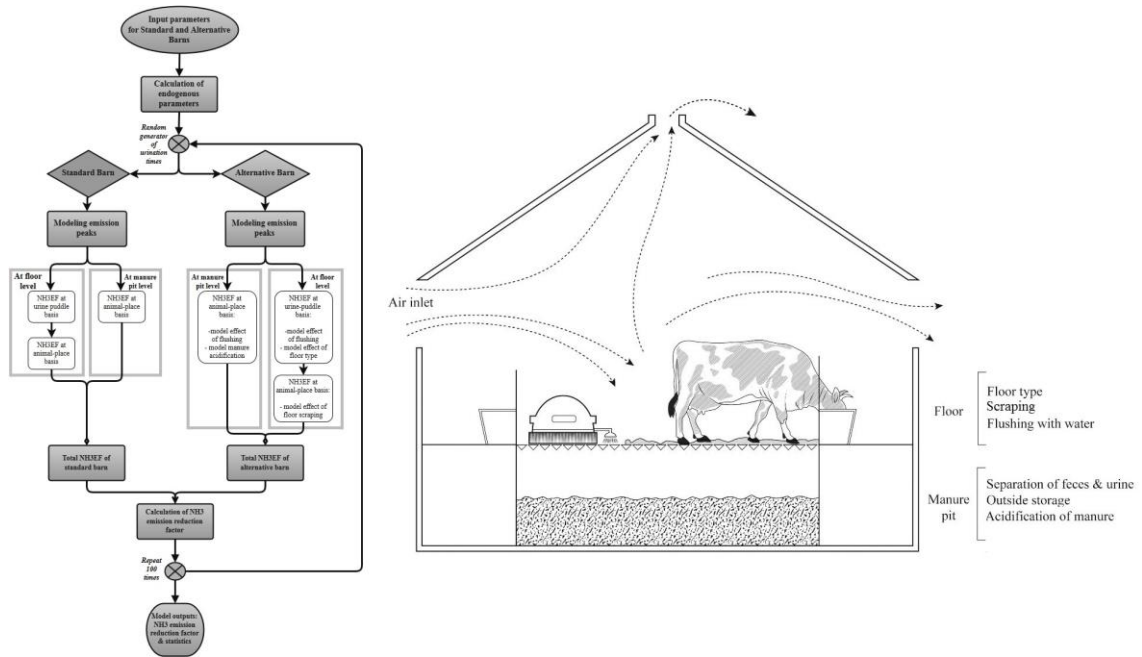
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21  
22           **Abstract**

23           Given the current scarcity of empirical data on ammonia (NH<sub>3</sub>) emissions from dairy cattle  
24           under different management-based mitigation techniques, a modeling approach to assess  
25           potential NH<sub>3</sub> emission reduction factors is needed. This paper introduces a process-based  
26           model that estimates NH<sub>3</sub> emission reduction factors for a dairy cattle barn featuring single or  
27           multiple management-based NH<sub>3</sub> emission mitigation techniques, as compared to another  
28           barn, to which no mitigation measure is applied. The model accounts for the following  
29           emission mitigation measures: (a) floor scraping, (b) floor type, (c) floor flushing with water  
30           and (d) indoor acidification of manure. Model sensitivity analysis indicated that manure  
31           acidification was the most efficient NH<sub>3</sub> emission reduction technique. A fair agreement was  
32           observed between reduction factors from the model and empirical estimates found in the  
33           literature. We propose a list of combinations of techniques that achieve the largest reductions.  
34           In order of efficiency, they are: (a) floor scraping combined with manure acidification  
35           (reduction efficiency 44 - 49 %); (b) solid floor combined with scraping and flushing (reduction  
36           efficiency 21 - 27 %); (c) floor scraping combined with flushing and (d) floor scraping alone  
37           (reduction efficiency 17 - 22 %). The model is currently being used to advise the Flemish  
38           Government (Belgium), on the performance of certain NH<sub>3</sub> emission reduction systems for  
39           dairy barns in Flanders.

40           **Keywords:** Process-based model; NH<sub>3</sub> emissions mitigation; Low NH<sub>3</sub> emission dairy barn;  
41           Policy making.

42 **Graphical abstract**



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45 **Research highlights**

- 46 • Modeled NH<sub>3</sub> emission reduction factors agreed with empirical data from literature
- 47 • Scraping and flushing of floor, floor type and manure acidification were modelled
- 48 • Floor scraping combined with manure acidification yielded highest emission reductions

49

## 50 1. Introduction

51 The amount of scientific evidence on the negative impacts of excessive gaseous ammonia (NH<sub>3</sub>)  
52 emissions from livestock systems on Earth biomes is significant (ApSimon et al., 1987; Sutton et  
53 al., 2013; Sutton et al., 2008). In different parts of the world, simultaneous efforts are underway  
54 in order to reduce NH<sub>3</sub> emissions. For instance, since 1992 a multinational effort has been  
55 underway in Europe to tackle the most urgent environmental issues including the deposition of  
56 excess of reactive nitrogen from all sectors of European society, including agriculture, into  
57 natural environments (Natura2000, 1992). In 2000, the European Parliament indicated that the  
58 Member States (EU28) should set their maximum allowed levels for NH<sub>3</sub> emissions. This resulted  
59 in NH<sub>3</sub> emission restrictions specifically for livestock farms (NEC-Directive, 2001). In the United  
60 States, the Emergency Planning and Community Right-To-Know Act (EPCRA) established since  
61 1986, requires that livestock systems' NH<sub>3</sub> releases exceeding 45 kg d<sup>-1</sup> (in a per barn basis or  
62 per operation basis where multiple barns may be used) must be reported (USEPA, 1986).

63 Agriculture in Europe is responsible for about 90% of NH<sub>3</sub> emissions (Sutton et al., 2013), a  
64 considerable part of which comes from cattle manure operations. These operations vary  
65 considerably in terms of design and management, depending on the country and region. The  
66 type of system discussed and modeled in this paper is typical in northern Europe, and is defined  
67 by Mosquera et al. (2014) as loose housing with cubicles, where the animals are kept loose in a  
68 barn divided into rows of individual cubicles, feeding and walking alleys. In these barns the floor  
69 is usually slatted, and the manure (mixture of feces and urine) is regularly removed from the  
70 floor and stored in a manure pit inside the barn. The barns are usually naturally ventilated, with  
71 air entering through openings at the walls' sides, being exhausted through the opposite opening  
72 and ridge, and the animals are confined year round. As for diets, cows are usually fed roughage  
73 (grass and maize silage) and concentrate.

74 The accurate determination of NH<sub>3</sub> emission factors from commercial naturally ventilated dairy  
75 cattle barns is currently a challenge (Calvet et al., 2013; Ogink et al., 2013; Takai et al., 2013).  
76 Multiple recent studies attempt to develop an emission measurement method for this type of  
77 barns (De Vogeleer et al., 2016; Joo et al., 2014; Van Overbeke et al., 2016, 2015, 2014a, 2014b),  
78 but experimentally determined management based NH<sub>3</sub> emission factors for real-scale dairy  
79 cattle barns in general are currently still non-existent. While a technique for accurate empirical  
80 assessment of NH<sub>3</sub> emission factors from this type of barns isn't established, the use of modeling  
81 approaches has proven to be beneficial.

82 Rotz and Oenema (2006) developed a mechanistic model to predict NH<sub>3</sub> emissions from dairy  
83 and beef cattle barns. Their model was validated with data from other studies that included  
84 emissions from cattle manure at multiple stages, i.e. in animal housing, storage, field application  
85 and during grazing. Elzing and Monteny (1997a, 1997b) assembled a process-based model that  
86 estimates NH<sub>3</sub> emissions from dairy cattle manure, which includes the most relevant physico-  
87 chemical properties related with NH<sub>3</sub> emissions. Their model was validated for laboratory  
88 conditions. Later, Monteny et al. (1998) scaled the model up to a full dairy cattle barn. A similar  
89 procedure was followed by Aarnink & Elzing, (1998), who developed a model scaled up to a pig  
90 barn. Although the NH<sub>3</sub> emission models of Rotz and Oenema (2006), Monteny et al., (1998) and  
91 Aarnink & Elzing, (1998) can predict emissions at a barn scale, they are not designed to

92 systematically assess the impact of barn management and design aspects that might mitigate  
93 emissions.

94 When it comes to animal housing, some specific changes in barn design have significantly  
95 reduced emissions in laboratory conditions. Such management techniques include scraping  
96 manure off the floor (Braam et al., 1997; Ogink and Kroodsma, 1996), flushing the floor with  
97 water (Bleijenberg et al., 1995; Braam et al., 1997; Ogink and Kroodsma, 1996) and indoor  
98 manure treatment, such as acidification (Bleijenberg et al., 1995; Kai et al., 2008). In addition,  
99 barn design aspects such as floor type have significantly changed the shape of NH<sub>3</sub> emission  
100 sources, i.e. area and depth of urine puddles (Snoek et al., 2014; Snoek et al., 2010). These types  
101 of emission reduction means have not yet been consistently tested in full-scale commercial dairy  
102 cattle barns because of the current technological limitations for determination of emission  
103 factors in these types of barns, as already mentioned.

104 The first known modeling attempt to estimate NH<sub>3</sub> emission factors from different barn  
105 management strategies is the work of Rotz et al. (2014). In their study, the developed model  
106 calculates emissions across different barns with or without floor scraping and flushing systems  
107 as well as different floor types. A model-based tool that is able to evaluate the intensity, duration  
108 and combination of multiple management techniques such as floor scraping and flushing, and  
109 the effects of different floor types and manure treatment on NH<sub>3</sub> emission reduction is still  
110 lacking in current scientific literature. Such model would be useful, not only to assess the current  
111 management practices and designs, but also to propose a suite of the best measures that can  
112 be used in combination to develop 'low NH<sub>3</sub> emission' housing barns for dairy cattle.

113 The aims of this research study were therefore to: (a) develop a process-based NH<sub>3</sub> emission  
114 model which is able to calculate the NH<sub>3</sub> emission reduction potential of new or adapted dairy  
115 cattle barns comprising individual or combined management- or design-based emission  
116 reduction techniques; (b) validate the model results by comparing them with empirical emission  
117 reduction factors from other studies using combinations of mitigation measures; (c) use the  
118 model to quantify the NH<sub>3</sub> emissions reduction potential of the following management-based  
119 techniques: floor scraping, flushing with water, indoor manure acidification and use of different  
120 types of floor; and (d) use the model to propose 'low NH<sub>3</sub> emission' housing barns for dairy  
121 cattle.

122

### 123 *1.1 Theory on NH<sub>3</sub> emission from cattle manure*

124 A common pathway of nitrogen (N) flow in livestock systems generally involves its uptake,  
125 metabolism, excretion, hydrolysis, mineralization, nitrification, denitrification and volatilization  
126 in various gaseous forms. In dairy cattle barns, the main form of N uptake by the animals is via  
127 the protein present in feed (forage + supplements), which is then partially metabolized into live  
128 weight gain and/or milk production. The remaining N consumed is excreted on the floor in the  
129 form of urine and feces. The parcel of urine on the floor will have its urea mineralized into  
130 ammonium (NH<sub>4</sub><sup>+</sup>) which might in turn be transformed into gaseous N (N<sub>2</sub>), nitrous oxide (N<sub>2</sub>O)  
131 and NH<sub>3</sub> (Sutton et al., 2013). The remainder of urine and feces falls through the floor slats into  
132 the pit, where urine and feces are mixed together originating manure. In the manure pit, a series  
133 of enzymatic reactions including bacteriological degradation will occur in addition to urea  
134 mineralization, ultimately leading to gaseous emissions of N<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub>. The mechanistic

135 model developed and used in this study only takes into account the enzymatic processes that  
136 lead to volatilization and emission of  $\text{NH}_3$  from cattle manure.

137 Three main physico-chemical mechanisms are responsible for the emission of  $\text{NH}_3$  from cattle  
138 urine or manure: (1) Enzymatic conversion of urea ( $\text{CO}(\text{NH}_2)_2$ ) into ammonium ( $\text{NH}_4^+$ ) and carbon  
139 dioxide ( $\text{CO}_2$ ) in the presence of water and the enzyme urease; (2) The dissociation of liquid  $\text{NH}_4^+$   
140 into  $\text{NH}_3$  as a function of media pH and air temperature (T), and (3) the convective mass transfer  
141 of volatilized  $\text{NH}_3$ , which in its turn is a function of wind speed (v)

142 Urea is abundantly present in cattle urine while urease is supplied by feces and naturally present  
143 in the environment. The enzymatic conversion of urea into  $\text{NH}_3$  in the presence of water is  
144 described in equation 1 (table 1). This table gives the complete list of equations for the main  
145 chemical and physical processes, including the process constants included in the model. The  
146 degradation of urea into  $\text{NH}_3$  can be mathematically represented by the Michaelis-Menten  
147 kinetics (Johnson and Goody, 2011), shown in equation 2. However, since urea degradation is  
148 not an instantaneous process, a linear increase of maximum urinal urea conversion rate ( $K_m$ ) was  
149 applied, as suggested by Elzing and Monteny, (1997a), in equation 2 was adopted.

150 In cattle urine and manure,  $\text{NH}_4^+$  will co-exist in equilibrium with liquid  $\text{NH}_3$ . As the media pH  
151 increases,  $\text{NH}_4^+$  is converted into  $\text{NH}_3$ , or vice versa in case the pH decreases, as described by the  
152 reversible chemical reaction in equation 3. This conversion is a function of the dissociation  
153 constant ( $k_D$ ). Equation 4 represents the volatilization of liquid  $\text{NH}_3$  from the emission source, a  
154 reaction characterized by the Henry constant (H). Under isothermal conditions, for  $\text{pH} > 9.4$ , the  
155 fraction of liquid  $\text{NH}_3$  in the emission source is higher than that of  $\text{NH}_4^+$ , and the equilibrium of  
156 equations 3 and 4 is shifted to the right and consequently, more gaseous  $\text{NH}_3$  will be formed.

157 The empirical models proposed by Hashimoto & Ludington, (1971) and applied by Elzing &  
158 Monteny, (1997b) were used to calculate  $k_D$  (equation 5) and H (equation 6) because their  
159 coefficients were determined from experiments made with cattle manure. The fraction of  $\text{NH}_3$   
160 in the emission source (F), as a function of pH and  $k_D$ , was calculated with equation 7.

161 The exchange between gaseous and liquid  $\text{NH}_3$  is influenced by the properties of airflow (Ni,  
162 1999) just above the liquid surface, which drives the convective transfer of gaseous  $\text{NH}_3$ ,  
163 disturbing the equilibrium and stimulating the formation of more gaseous  $\text{NH}_3$ . This process is  
164 related to the volume of the emission source (e.g. urine puddle on the floor or manure in the  
165 pit) and its nitrogen content (urea in urine and total ammoniac-nitrogen or TAN at manure pit).  
166 According to Ni (1999), two models have been used to explain the convective transfer of  
167 volatilized  $\text{NH}_3$ : the two-film theory and the concentration boundary layer theory. The latter was  
168 used in the developed model. Both theories are dependent on an  $\text{NH}_3$  mass transfer coefficient  
169 (k), and have been applied to describe  $\text{NH}_3$  transfer from agricultural sources, such as animal  
170 manure. In this study the equation proposed by Liang et al, (2002), and also used by Monteny  
171 et al., (1998) (equation 8), was applied to estimate k, mainly because the conditions of the study  
172 of Liang et al. (2002) are relatively similar to those that we want to emulate with our model.

173 The conditions of use of the ammonia emission model as applied in this study are valid for the  
174 first centimeters above emission surface and similar to those specified by Snoek et al., (2014).

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177

178 **2. Material and methods**

179 **2.1 Overall model architecture**

180 In general terms, the model described in this paper estimates the NH<sub>3</sub> emission factors for a  
181 dairy cattle barn that has at least one NH<sub>3</sub> emission mitigation technique (alternative barn), and  
182 compares it to a standard barn. We define as 'standard' a barn to which no relevant emission  
183 mitigation method has been applied. In terms of the model presented in this study, the  
184 characteristics of the standard barn are given in table 2. For the parametrization of the standard  
185 barn given in table 2, we took into account the descriptions of traditional dairy cattle barns in  
186 Northern Europe, as given by Monteny et al. (1998), Dai and Karring, (2014) and Ogink et al.,  
187 (2014). The comparison between standard and alternative barns yields an NH<sub>3</sub> emission reduction  
188 factor, expressed in percentage. The calculation algorithm was designed according to the  
189 following steps:

190 (1) All input parameters for both alternative and standard dairy cattle barns were listed. Then,  
191 the endogenously calculated parameters related to the processes of NH<sub>3</sub> formation and  
192 emission were calculated.

193 (2) A set of numbers fit to an Exponential-Weibull probability distribution function was randomly  
194 generated, in order to represent an animal's urination behavior during a 24 hour period.

195 (3) Via nitrogen mass balance, emissions of NH<sub>3</sub> from a single urine puddle were calculated at  
196 standard and alternative barn conditions. A description of how N mass balance at urine puddle  
197 level is given in section 2.2.

198 (4) NH<sub>3</sub> emissions from all possible urine puddles were integrated and an averaged emission rate  
199 value was obtained on an animal-place basis (the barn floor area occupied by one animal).

200 (5) Emissions at the manure pit level in both barns were calculated assuming that manure under  
201 given environmental conditions and TAN content emits NH<sub>3</sub> at a constant rate, because it is  
202 continuously being loaded with fresh feces and urine.

203 (6) Floor and manure pit level emissions were aggregated to yield NH<sub>3</sub> emission factor of the  
204 standard barn, in a per animal-place basis. The following two steps were then run concomitantly:

205 (6.a) For the alternative barn, the effect of floor scraping, flushing and floor type were modeled  
206 and accounted for in the total floor emissions, while the effects of flushing and manure  
207 acidification were accounted for in manure pit emissions. (6.b) Resulting floor and manure pit  
208 level emissions were aggregated to yield the total NH<sub>3</sub> emissions of the alternative barn.

209 (7) All the steps above were repeated 100 times, each time with a new set of randomly  
210 generated urination events. In each event, urination frequency and volume remained constant  
211 and equal to the values presented in table 2.

212 A flowchart of the calculation steps described above is presented as fig. 1. A more detailed  
213 description of the model is given in the following sections.

214

215 **2.2 Modeling NH<sub>3</sub> emissions at floor and manure pit levels**

216 At first, a single urine puddle is considered as a control volume. A mass balance for NH<sub>3</sub> involving  
217 the temporal change in its concentration ( $C_{NH_3}$ ), as released from the urine puddle was  
218 performed. The change in  $C_{NH_3}$  was written as a function of change in urea concentration ( $C_U$ )  
219 minus the emitted NH<sub>3</sub> (equation 10). With equation 10, the term  $dC_U/dt$  and the variable  $E$  were  
220 replaced by equations 2 and 8, respectively, yielding a first order ordinary differential equation.

221 This equation was solved using Euler's Method (Higham., 2001) with  $\Delta t = 30$  s, and by setting  
222  $C_U(t=0) = 4.75 \text{ kg}\cdot\text{m}^{-3}$  and  $C_{\text{NH}_3}(t=0) = 0 \text{ kg}\cdot\text{m}^{-3}$  (table 2). Instant  $\text{NH}_3$  emission rate values at floor  
223 levels were then obtained for floor conditions as a function of  $t$ . Plots of  $C_{\text{NH}_3}$  versus  $t$  yielded  
224  $\text{NH}_3$  emission peaks with the shape described in fig. 2.

225 The total number of times ( $n$ ) in which a single urine puddle is reloaded with fresh urine was  
226 calculated with equation 11. In order to be used in the model, the value  $n$  was rounded to a  
227 positive integer. In the case of this study,  $n$  was equal to  $2.286 \sim 2$ . The rounded value of  $n$  was  
228 interpreted here as the possible number of times in the course of a 24 h period that a single  
229 urine puddle location containing relatively "old" urine was replenished with "fresh" urine. In the  
230 case of this study ( $n = 2$ ) the first urination was set to happen at the start of the 24 h period ( $t =$   
231  $0$  s), while the remainder urination event was randomly picked with the aid of a random number  
232 generator, following an Exponential-Weibull distribution. The generic form of the Exponential-  
233 Weibull distribution function was adjusted so that the probability of occurrence of a certain  
234 urination event is relatively lower immediately after a urination just occurred, while this  
235 probability increases as time passes.

236 Next, floor level  $\text{NH}_3$  emissions were converted from a single urine puddle basis to an animal-  
237 place basis (fig. 1), with equation 12.

238 While calculations of emissions from the floor involved two steps, pit emissions were  
239 determined with a single step. Emissions of  $\text{NH}_3$  at the manure pit were calculated from TAN,  
240  $A_{\text{pit}}$ ,  $k_{\text{pit}}$ ,  $F_{\text{pit}}$  and  $H_{\text{pit}}$  with equation 13. It was assumed that the manure pit is an 'infinite' source  
241 of  $\text{NH}_3$ , and was constantly emitting it, hence negating the need to model emission peaks at  
242 manure pit level.

243 Lastly, total emission rate in a 'per cow' basis ( $E_{\text{cow}}$ ) was calculated by adding up the floor and  
244 pit emissions for the same barn with Eq. 14.

245

### 246 **2.3 Calculation of total barn $\text{NH}_3$ emissions and $\text{NH}_3$ emission reduction coefficient**

247 The procedures described in section 2.2 were performed simultaneously for both standard and  
248 alternative barns. The emission mitigation strategies applicable to the alternative barn were  
249 modeled, as described in section 2.4. With the  $\text{NH}_3$  emission factors obtained for both standard  
250 and alternative barns, an emission reduction factor was calculated with equation 15.

251 In order to account for the variability due to the random urine puddle generation feature of this  
252 model, as described in section 2.2,  $\text{NH}_3$  emission reduction factors calculated in each simulation  
253 were averaged after 100 automatic calculations, *ceteris paribus* and randomly determined  
254 urination times.

255

### 256 **2.4 Modeling specific management-based $\text{NH}_3$ emission mitigation strategies**

257 In fig. 3-A several management-based  $\text{NH}_3$  emission mitigation strategies are illustrated, related  
258 either to floor and manure pit levels.

259

#### 260 **2.4.1 Use of different floor types**

261 The effect of two different floor types, namely slatted and solid, was taken into account in the  
262 model by implementing different values of urine puddle area ( $A$ ) and depth ( $d$ ). The floor  
263 considered in the standard barn was a slatted floor ( $A = 0.77 \text{ m}^2$ ;  $d = 4.8 \times 10^{-3} \text{ m}$ , table 2). One

264 alternative floor type was taken into account in this study, i.e. a solid floor ( $A = 1.2 \text{ m}^2$ ,  $d =$   
 265  $4.8 \times 10^{-3} \text{ m}$ ). When a solid floor was considered, the contribution of  $\text{NH}_3$  emissions from the  
 266 manure pit to total emissions was set to zero.

267

#### 268 2.4.2 Floor scraping

269 In this study, floor scraping refers to the use of manure scrapers (either robot or cable pulled).  
 270 The effect of a scraper was taken into account in the alternative barn by multiplying the  $\text{NH}_3$   
 271 emission factor at floor level on an animal-place basis ( $E_{\text{cow, floor}}$ , equation 12) by a 'scraping  
 272 inefficiency' factor ( $\eta$ ), the higher the  $\eta$  the less efficient floor scraping was. The  $\eta$  was dynamic,  
 273 and defined by the pulse function in equation 16, which depended on the time elapsed after a  
 274 scraping event ( $t_{\text{ac}}$ ). The function in equation 16 was adjusted to the experimental data of Dai &  
 275 Karring, (2014), who monitored the dynamics of urease activity of mixtures of fresh urine and  
 276 feces from dairy cows in the laboratory.

277 During a scraping event,  $\eta$  was set to a minimum value ( $\eta_{\text{min}}$ ), which reflects the 'clean' state of  
 278 the floor, immediately after a scraper passed. Although no information could be found in the  
 279 peer-reviewed literature concerning quantification of scraper cleaning efficiencies in dairy cattle  
 280 barns, it is known from observation in practice that  $\eta_{\text{min}}$  will rarely be zero, i.e., perfect scraping.  
 281 Instead, some manure and urine is usually left behind, which will depend on factors such as floor  
 282 type, scraper model and maintenance conditions. Because no information for  $\eta_{\text{min}}$  exists, a fixed  
 283 value of 0.4 was chosen based on expert judgement. This assumed value implies that  
 284 immediately after a scraping event happened, a residual  $\text{NH}_3$  emission of 40% was present. This  
 285 is a rather conservative value, and attempts to account factors such as floor type, (im)proper  
 286 maintenance and management of the scraping system.

287 The duration of a scraping event ( $t_{\text{dc}}$ ) was calculated with equation 17 and represents the total  
 288 time needed for the scraper to clean the floor area occupied by one cow. It is estimated as a  
 289 function of the length ( $L_{\text{alley}}$ ) and number of walking alleys ( $n_{\text{alleys}}$ ) in the barn and the traveling  
 290 speed ( $S$ ) of the scraper. A traveling speed value of  $0.07 \text{ m} \cdot \text{s}^{-1}$  was applied in this study based on  
 291 the results presented by Sagkob et al. (2011) and Buck et al., (2013).

292 The effect of floor scraping on mitigation of  $\text{NH}_3$  emissions was modeled as the number of times  
 293 per day that the floor was scraped (scraping frequency). In the calculation of the emission  
 294 reduction factor when floor scraping was applied to the alternative barn, no floor scraping was  
 295 considered in the standard barn.

296

#### 297 2.4.3 Flushing the floor with water

298 Floor flushing is defined in this study as homogeneously spraying water on the emitting surfaces,  
 299 with the purpose of rinsing off the urine puddles existing on the floor. The modeling approach  
 300 for flushing with water was based on the stoichiometry of a mixture of two solutions (urine and  
 301 fresh water) with two different pH values. The pH of a solution is the negative logarithm of the  
 302 total concentration of hydrogen ions ( $C_{\text{H}^+}$ ) in this solution. Hence, mixing solutions with different  
 303 pH values can be interpreted as mixing solutions with different  $C_{\text{H}^+}$ , the resulting  $C_{\text{H}^+}$  gives the  
 304 pH of the mixture.

305 The calculated pH of the mixture remained between those of the two solutions. Since the pH of  
 306 water is usually lower than that of cattle urine, a mixture of urine and water will normally lead



307 to a solution with resulting pH lower than that of pure urine. The pH decrease will shift the  
308 equilibrium between  $\text{NH}_3$  and  $\text{NH}_4^+$  (equation 3) to the left and consequently reduce emissions.  
309 In the calculation of resulting pH, we consider that enough water ( $> 5 \text{ L}\cdot\text{animal}\cdot\text{place}^{-1}\cdot\text{d}^{-1}$ ) is  
310 sprayed on the floor, so that the pH buffering capacity of urine is negligible.

311 The calculation of the pH of the mixture of urine and water was based on given values of flushing  
312 rate ( $\text{L}\cdot\text{animal}\cdot\text{place}^{-1}\cdot\text{d}^{-1}$ ) of water and pH (adopted water pH was 8.2, as typically found in  
313 Flanders, Belgium), as well as production rates and pH of urine and feces.

314 Both flushing rate and flushing efficiency (parcel of the sprayed water that remained on the  
315 floor) were included as input variables to the calculation tool. The pH of the total volume of  
316 urine, feces and water mixture that reaches the pit was calculated and the resulting pH at the  
317 manure pit (assuming homogeneous mixing) was recalculated as well.

318

#### 319 *2.4.4 Acidification of manure in the manure pit*

320 As described by Kai et al. (2008a), the effect of acidification is achieved in practice by mixing acid  
321 to the manure, and implementing an efficient (homogeneous) mixing system in the pit.  
322 Assuming that good mixing is achieved, the effect of acidification was applied to the alternative  
323 barn by lowering the pH of the manure. Values for pH between 5.0 and 6.5 have been achieved  
324 in practice (Kai et al., 2008), thus a manure pH value of 5.0 was adopted to represent manure  
325 acidification in this study. This procedure caused manure pit emissions (equation 13) to become  
326 zero.

327

#### 328 **2.5 Model sensitivity analysis and comparison with results from other studies**

329 A sensitivity analysis of the model for the tested management techniques was performed by  
330 changing input values according to the following: flushing rate, 5 to 30  $\text{L}\cdot\text{d}^{-1}\cdot\text{animal}\cdot\text{place}^{-1}$ (at  
331 increments of 5  $\text{L}\cdot\text{d}^{-1}\cdot\text{animal}\cdot\text{place}^{-1}$ ); acidification of manure, by changing manure pH from 4 to  
332 8 (at pH increments of 1); and scraping frequency, 2 to 24  $\text{d}^{-1}$  (at levels of 2, 4, 8, 12, 16, 20 and  
333 24  $\text{d}^{-1}$ ). During the sensitivity analysis simulations, only the above mentioned parameters were  
334 modified, while all other model parameters remained the same in both standard and alternative  
335 barns. The values that were not changed were equal to those presented in table 2.

336 Comparisons of model output with those from other studies were also performed. Namely, the  
337 model was used to simulate scenarios that were similar to those in the referred studies. Scenario  
338 1 consisted of solid floor combined with floor scraping. Scenario 2 consisted of solid floor  
339 combined with scraping and flushing, both scenarios were studied by Braam et al. (1997). In  
340 scenario 3, floor scraping and flushing were applied to a dairy cattle installation with slatted  
341 floor, to emulate the study conditions of Bleijenberg et al. (1995). In scenarios 4 to 7, the effects  
342 of manure acidification alone or combined with floor scraping and flushing were modeled in  
343 order to reproduce the conditions of the study of Bleijenberg et al. (1995).

344

### 345 **3. Results and discussion**

#### 346 **3.1 Modeling $\text{NH}_3$ emission peaks**

347 One essential part of the model is the proper calculation of the  $\text{NH}_3$  emission peaks. The  
348 dynamics seen in fig. 2 indicate that when fresh urine meets urease (assumed to be abundantly  
349 available at the floor),  $\text{NH}_3$  emissions reach a peak value and start to deplete. The shape and

350 maximum height of the emission curve presented in fig. 2 are similar to the results presented by  
351 Elzing & Monteny (1997b), who developed a laboratory-scale validation study for NH<sub>3</sub> emission  
352 peaks from dairy cattle manure, under conditions similar to those considered in this study. The  
353 model emulates the effect that, when undisturbed and if conditions are constant and favorable,  
354 the parcel of nitrogen from urea in the urine puddle will get nearly depleted by emitting NH<sub>3</sub>,  
355 and eventually get exhausted before it is replaced by a new puddle.

356 The effect of randomly assigning urination times to puddle generation and NH<sub>3</sub> emission can be  
357 seen in fig. 4-A, which shows samples of hourly and cumulative NH<sub>3</sub> emissions for 10 distinct  
358 runs.

359 Each run in fig. 4-A represents the occurrence of two NH<sub>3</sub> emission peaks, representative of two  
360 urinations. The first urination always occurred at  $t = 0$  s, while the second was randomly  
361 generated. In fig. 4-B, one can see how different urination times for different runs affected the  
362 cumulative emissions of NH<sub>3</sub>. For the runs in which the emission peaks occurred further away  
363 from one another, the daily cumulative NH<sub>3</sub> emission was higher (e.g. runs 3 to 10).

364 Conversely, for the runs in which the emission peaks were closer (e. g. runs 1 and 2), the daily  
365 cumulative emissions reached lower values. The lowest cumulative emission occurred for run 2,  
366 to which the urination times of both peaks occurred at the same time, meaning that only one  
367 emission peak took place over the course of 24 h.

368 The effect of different urination times on daily cumulative emissions was taken into account by  
369 automatically repeating the calculation 100 times, and averaging these for the final emission  
370 factor.

371 An important aspect to consider is that, for modeling purposes, floor level NH<sub>3</sub> emissions is first  
372 calculated at a single puddle basis, this is done with equation 9 (table 1). Then emissions are  
373 converted to an 'animal-place' basis with equation 12 (table 1), taking into account aspects such  
374 as stocking density and cow's urination behavior. Most of the NH<sub>3</sub> emission mitigation  
375 techniques are modeled at this broader 'animal-place' level. In the conditions of the standard  
376 barn, we consider a total of 10 urinations per day in the floor area occupied by one single cow  
377 of 3.9 m<sup>2</sup> (table 2), these urinations events will take place randomly as explained in section 2.2.  
378 This means that the floor area allocated per cow remains mostly covered with urine, and one  
379 can think of for floor area occupied by a one animal as a single urine puddle composed of  
380 multiple puddles, some older some newer.

381 In this context, instead of occupying floor area and replace urine, the fraction of feces that  
382 remain at the floor will be eventually covered by or mixed with urine (transforming into manure),  
383 and thus will continue to emit as well. Cow's activity on the walking alley likely enhances feces  
384 and urine mixing at floor level.

385 If floor is not cleaned, the gradual increase of dirt causes the layer thickness or depth of urine  
386 puddle to increase in time (see equation 10 in table 1), in fact floor dirt encloses urine, hence  
387 increasing volumes of puddles, preventing them from drying out or drain into the manure pit. In  
388 such cases, the emission peak described in fig. 2 will take much longer to start descending,  
389 leading to higher emissions.

390  
391  
392

393 **3.2 Modeling floor scraping**

394 Fig. 5 is an example of the dynamics of NH<sub>3</sub> emissions from the floor in a ‘per cow’ or ‘animal-  
 395 place’ basis, over a period of 24 h, both when no scraping is applied and when floor scraping  
 396 frequency is 6 d<sup>-1</sup>. The effect of scraping inefficiency ( $\eta_{\min}$ ) can be seen in this figure, i.e. when  
 397 the scraper is active, emissions from the alternative barn (orange line) are dropped down to  
 398 about 40% of emission from the reference barn (blue line). The sudden interruption of the  
 399 average emissions, by removing the emitting source is what characterizes the emission  
 400 reduction effect of floor scraping, since it means that regardless of  $\eta_{\min}$ , emissions will drastically  
 401 drop with a scraping event.

402 These results stress the importance of floor cleanliness (with  $\eta_{\min}$  as close to 0 as possible) to  
 403 ensure that the use of a scraper is an efficient NH<sub>3</sub> emission mitigation technique. This can be  
 404 achieved in practice by the appropriate choice of floor scraping system, and proper  
 405 maintenance.

406 *Ceteris paribus* and increasing scraping frequency from 2 to 12 times decreased floor NH<sub>3</sub>  
 407 emissions by 9% to 24% respectively (as compared to a floor under similar conditions without  
 408 scraping) (fig. 6). These results reveal the potential of hygienic practices and barn scrape  
 409 management to reduce emissions.

410

411 **3.3 Model sensitivity analysis and comparison of outputs with results from other studies**

412 The results of the sensitivity analysis performed on the model (fig. 7) indicate that reduction  
 413 efficiency increased in a non-linear fashion with increasing flushing rate, manure acidity and  
 414 scraping frequency. These results suggested that in practical terms, manure acidification is a  
 415 more efficient means for reducing emissions, because a relatively small change in pH leads to  
 416 the maximum reduction efficiency of 27%. Such reduction can only be achieved, for instance,  
 417 via floor scraping at relatively high scraping frequencies (> 16 d<sup>-1</sup>). However, we recommend that  
 418 the decision of which of the three management-based emission reduction means only be made  
 419 after an appraisal of the economic costs, which is outside the scope of this study.

420 We rather suggest that, instead of relying on a single management technique, several should be  
 421 applied simultaneously whenever feasible. Model simulations with combinations of multiple  
 422 techniques yielded reduction coefficients that are cumulative. Results from the model  
 423 combining multiple mitigation techniques are presented in section 3.4.

424 Concerning the results of the sensitivity analysis for manure acidification, we would like to  
 425 highlight the hazards of this practice and potential drawbacks of it. The developed model makes  
 426 no distinction of the type of acid used. However, in practice the addition of sulfuric acid, for  
 427 instance will lead to the introduction of additional environmental contaminants. If nitric acid is  
 428 used, then more N is added to the manure for land application. Furthermore, in fig. 7 it can be  
 429 seen that decreasing manure pH from 5 to lower doesn’t lead to any improvement of the  
 430 emission reduction factor. In fact, a manure pH of 5 is potentially a hazardous situation for  
 431 employee contact and under application conditions, and should be avoided.

432 The comparison (table 3) of the results of the model with those from the studies of Braam et  
 433 al., (1997) and Ogink and Kroodsma, (1996) shows generally good agreement, indicating that  
 434 the model can be used to simulate the effects of floor type, floor scraping and flushing and  
 435 manure acidification on NH<sub>3</sub> emission reduction factors from dairy cattle barns. As for the

436 comparison of the reduction factors obtained with the model when used to simulate the  
 437 conditions of the study of Bleijenberg et al., (1995), and presented in table 3 (scenarios 3 to 7),  
 438 consistently underestimated the reduction factors from that study. This systematic  
 439 underestimation might have stemmed from the rather conservative choice of scraping efficiency  
 440 applied to the alternative barn ( $\eta_{\min} = 0.4$ ). However, we consider an underestimation of the  
 441 emission reduction factor is less of a problem with regard to the use of this model for regulatory  
 442 purposes.

443

#### 444 **3.4 NH<sub>3</sub> emission reduction factors from alternative 'low emission' dairy cattle barns**

445 The model was used to estimate NH<sub>3</sub> emission reduction factors of a few alternative 'low  
 446 emission' barns. Namely, effect of floor scraping alone, floor scraping combined with manure  
 447 acidification, floor scraping combined with flushing with water, and the use of solid floors  
 448 instead of slatted floors (table 4).

449 Floor scraping frequencies of 6 and 10 d<sup>-1</sup> were simulated and yielded reduction factors of 17  
 450 and 22%, respectively (table 4). The adoption of lower frequencies (< 6 d<sup>-1</sup>) might require  
 451 increasing the assumed  $\eta$  values, since a larger amount of manure would have to be removed  
 452 every time. On the other hand, floor scraping frequencies > 10 d<sup>-1</sup> might be economically  
 453 challenging, since it would probably imply the use of more than one scraping robot.  
 454 Furthermore, higher frequencies might affect the welfare of the cows in the cubicles as  
 455 described by [Buck et al. \(2013\)](#).

456 Dairy cattle barns comprising floor scraping and manure acidification resulted in the largest NH<sub>3</sub>  
 457 reduction, varying between 44% - 49% (table 4). The NH<sub>3</sub> emission reduction effect of acidifying  
 458 the manure combined with floor scraping is cumulative. If stored manure pH reaches 5.0, its  
 459 contribution to reducing emissions is at least 27% (see Fig.7), since no emissions would come  
 460 from the manure pit. The reduction factors calculated from acidification of manure assume that  
 461 the properties of the manure pit (especially pH) are constant.

462 Finally, the effect of using solid floors instead of slatted floors combined with scraping and  
 463 flushing were also modeled (table 4). The obtained reduction factors were rather low, varying  
 464 between 13 and 27%. The benefit of using solid floors is that emissions from the manure pit level  
 465 are nearly zero, assuming that the manure pit is perfectly sealed. In the standard dairy cattle  
 466 barn, as considered in this study, the proportion of NH<sub>3</sub> emissions from floor and manure pit is  
 467 70 and 30%, respectively. Significantly lowering manure pit emissions with the use of indoors  
 468 emission reduction mitigation results in a manure that is richer in N, improving its quality when  
 469 used for composting and/or direct field application as fertilizer (De Vries et al., 2015a, 2015b).  
 470 When it comes to floor emissions, solid floors have the potential to emit much more than slatted  
 471 floors, simply because the urine puddles will be larger, or in the case when the urine-feces  
 472 transport to storage is not working properly, then even more feces and urine will be left on the  
 473 floor, potentially resulting in even more emissions. Hence, use of solid floors is recommended  
 474 only when combined with hygiene-assuring measures, such as scraping or scraping and flushing,  
 475 combined with transport of urine and feces to storage.

476

477

478

479 **3.5 Use of the model for regulatory purposes and model limitations**

480 The presented model is currently being used to advise the Flemish government (Belgium), on  
 481 the performance of certain NH<sub>3</sub> emission reduction systems for dairy barns in Flanders. In view  
 482 of EU regulations with regard to the NATURA2000 program (Natura 2000, 1992), Flanders'  
 483 government imposed a Programmatic Approach to Nitrogen (acronym in Dutch 'PAS'). Within  
 484 this specific regulation, for each dairy farm its contribution is calculated in the N deposition on  
 485 these sensitive nature protection areas. If such a contribution is overreaching the preset  
 486 threshold, then the respective dairy farm is obliged to provide measures to reduce its NH<sub>3</sub>  
 487 emissions significantly (e.g. with 30%). Therefore, the Flemish government asked a scientific  
 488 committee to certify a list with allowed NH<sub>3</sub> emission reduction techniques and their respective  
 489 emission reduction efficiencies. This list (VLM, 2015) was first established in 2015, based on a  
 490 (rather scarce) literature search and expert judgement. The scientific committee used the model  
 491 presented in this study as a tool to quantify the reduction efficiency of well-defined and general  
 492 floor-based reduction techniques (e.g. cleaning frequency of manure scrapers and robots  
 493 installed on both slatted and closed floor systems, frequency and volume of water spraying  
 494 devices installed at floor level) (see table 4). A safety factor was imposed to deduce a  
 495 conservative emission reduction efficiency since the model results could not be supported with  
 496 real measurement data. For more specific low emission floor types (e.g. profiled floors), model  
 497 results are still being used to support expert judgement if applicable. As previously  
 498 demonstrated in section 3.3, good comparison with empirical data was found and it is the aim  
 499 to obtain better uniformity between both assessment methodologies.

500 The model in principle can also be used to calculate NH<sub>3</sub> emission reduction factors from  
 501 management-based techniques such as feed manipulation, optimized ventilation, separation of  
 502 urine and feces and cooling of manure surface in the manure pit. Seasonality effects on the  
 503 modeled system, such as temperature changes at floor and manure pit, can also be accounted  
 504 for. However, a description of these techniques and their emission reduction factors was  
 505 omitted in this study, because of a lack of empirical data for validation.

506 In this context, the current version of the model neglects the fact that manure and urine pH are  
 507 rather dynamic (we assume pH to remain constant), while there is increasing amount of  
 508 evidence suggesting that pH actually decreases in time as observed by Dai and Karring (2014),  
 509 which can significantly impact emissions. However, we didn't find any study in the literature  
 510 providing empirical equations of urine and manure pH as a function of time and their resulting  
 511 impacts of NH<sub>3</sub> emissions.

512 Furthermore, we would like to highlight that floor cleanliness conditions after scraping events  
 513 are particularly important, in terms of residual NH<sub>3</sub> emissions. In fig. 8 three cases of floor  
 514 cleanliness conditions are specified. The case of fig.8-A can be considered as a reference, when  
 515 the floor hasn't been scraped for a while. The floor looks very wet, which indicates the presence  
 516 of urine and manure. The case represented in fig.8-B, the floor was cleaned by a pulled scraper,  
 517 and one notices that a thin layer of manure (mixture of urine and feces) is left behind. In this  
 518 case, scraping equipment likely needs maintenance. In the case of fig.8-C, the floor has just been  
 519 scraped by a robot, and looks fairly clean. We recommend that if the proposed model is used to  
 520 advice the use of floor scraping frequency as an NH<sub>3</sub> emission mitigation means, it be subjected  
 521 to the proper the choice of a scraping system that is well maintained.

522 Finally, we stress that the model cannot be applied to barns where litter, such as straw, is used  
523 to cover the floors. In these types of floors, an accurate determination of the emission surface  
524 and volume is more challenging due to the fact that manure is mixed with the bedding material.  
525 Additionally, the complexity of quantifying emissions from littered floors is increased because  
526 of the fact that bacteriological decomposition of manure also plays an important role in addition  
527 to the enzymatic breakdown of urea.

528

#### 529 **4. Conclusions**

530 A process-based model is proposed, which is able to calculate NH<sub>3</sub> emission reduction factors  
531 for dairy cattle barns that feature a single or multiple management-based NH<sub>3</sub> emission  
532 mitigation technique(s). The considered alternative 'low emission' management techniques  
533 include: (a) scraping the floor; (b) flushing the floor with water; (c) different types of floor and  
534 (d) indoor acidification of manure. The NH<sub>3</sub> emission reduction factor is calculated considering  
535 an alternative barn, in which at least one of the emission mitigation methods mentioned above  
536 is applied, and a standard barn, which has none.

537 The modeled NH<sub>3</sub> emission of the standard barn and the reduction factors agreed with estimates  
538 from empirical studies found in the literature.

539 A list of NH<sub>3</sub> emission reduction techniques was proposed. In order of efficiency, NH<sub>3</sub> emission  
540 reduction technologies were determined: manure acidification, floor scraping and flushing. For  
541 combinations of techniques, the order of efficiency was: (a) floor scraping combined with  
542 manure acidification (44 - 49%); (b) solid floor combined with scraping and flushing (21 - 27%);  
543 (c) floor scraping combined with flushing and (d) floor scraping alone (17 - 22%).

544

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550

#### 551 **6. References**

552 Aarnink, A.J.A., Elzing, A., 1998. Dynamic model for ammonia volatilization in housing with  
553 partially slatted floors, for fattening pigs. Livest. Prod. Sci. 53, 153-169.

554 doi:10.1016/S0301-6226(97)00153-X

555 ApSimon, H.M., Kruse, M., Bell, J.N.B., 1987. Ammonia emissions and their role in acid  
556 deposition. Atmos. Environ. 21, 1939-1946. doi:10.1016/0004-6981(87)90154-5

557 Bleijenberg, W., Kroodsma, W., Ogink, N.W.M., 1995. Techniequen om de ammoniakemissie  
558 uit ligboxenstallen met roostervloer te beperken [Techniques for the reduction of  
559 ammonia emission from a cubicle house with slatted floor]. Wageningen, The  
560 Netherlands.

561 Braam, C.R., Ketelaars, J.J.M.H., Smits, M.C.J., 1997. Effects of floor design and floor cleaning  
562 on ammonia emission from cubicle houses for dairy cows. Netherlands J. Agric. Sci. 45,  
563 49-64.

564 Braam, C.R., Smits, M.C.J., Gunnink, H., Swierstra, D., 1997. Ammonia Emission from a Double-

- 565 Sloped Solid Floor in a Cubicle House for Dairy Cows. J. Agric. Eng. Res. 68, 375–386.  
566 doi:10.1006/jaer.1997.0215
- 567 Buck, M., Friedli, K., Steiner, B., Gygax, L., Wechsler, B., Steiner, A., 2013. Influence of manure  
568 scrapers on dairy cows in cubicle housing systems. Livest. Sci. 158, 129–137.  
569 doi:10.1016/j.livsci.2013.10.011
- 570 Calvet, S., Gates, R.S., Zhang, G., Estellés, F., Ogink, N.W.M., Pedersen, S., Berckmans, D., 2013.  
571 Measuring gas emissions from livestock buildings: A review on uncertainty analysis and  
572 error sources. Biosyst. Eng. 116, 221–231. doi:10.1016/j.biosystemseng.2012.11.004
- 573 Dai, X., Karring, H., 2014. A Determination and Comparison of Urease Activity in Feces and  
574 Fresh Manure from Pig and Cattle in Relation to Ammonia Production and pH Changes.  
575 PLoS One 9, e110402. doi:10.1371/journal.pone.0110402
- 576 De Vogeleer, G., Van Overbeke, P., Brusselman, E., Mendes, L.B., Pieters, J.G., Demeyer, P.,  
577 2016. Assessing airflow rates of a naturally ventilated test facility using a fast and simple  
578 algorithm supported by local air velocity measurements. Build. Environ. 104, 198–207.  
579 doi:10.1016/j.buildenv.2016.05.006
- 580 De Vries, J.W., Groenestein, C.M., Schröder, J.J., Hoogmoed, W.B., Sukkel, W., Groot  
581 Koerkamp, P.W.G., De Boer, I.J.M., 2015a. Integrated manure management to reduce  
582 environmental impact: II. Environmental impact assessment of strategies. Agric. Syst.  
583 138, 88–99. doi:10.1016/j.agsy.2015.05.006
- 584 De Vries, J.W., Hoogmoed, W.B., Groenestein, C.M., Schröder, J.J., Sukkel, W., De Boer, I.J.M.,  
585 Groot Koerkamp, P.W.G., 2015b. Integrated manure management to reduce  
586 environmental impact: I. Structured design of strategies. Agric. Syst. 139, 29–37.  
587 doi:10.1016/j.agsy.2015.05.010
- 588 Elzing, A., Monteny, G.J., 1997a. Modeling and experimental determination of ammonia  
589 emissions rates from a scale model dairy-cow house. Trans. ASAE 40, 721–726.  
590 doi:10.13031/2013.21302
- 591 Elzing, A., Monteny, G.J., 1997b. Ammonia emission in a scale model of a dairy-cow house.  
592 Trans. ASAE 40, 713–720. doi:10.13031/2013.21301
- 593 Hashimoto, A.G., Ludington, D.C., 1971. Ammonia desorption from concentrated chicken  
594 manure slurries, in: Livestock Waste Management. Cornell, pp. 117–121.
- 595 Higham, D.J., 2001. An Algorithmic Introduction to Numerical Simulation of Stochastic  
596 Differential Equations. SIAM Rev. 43, 525–546. doi:10.1137/S0036144500378302
- 597 Johnson, K.A., Goody, R.S., 2011. The Original Michaelis Constant: Translation of the 1913  
598 Michaelis–Menten Paper. Biochemistry 50, 8264–8269. doi:10.1021/bi201284u
- 599 Joo, H.S., Ndegwa, P.M., Heber, A.J., Bogan, B.W., Ni, J.-Q., Cortus, E.L., Ramirez-Dorransoro,  
600 J.C., 2014. A direct method of measuring gaseous emissions from naturally ventilated  
601 dairy barns. Atmos. Environ. 86, 176–186. doi:10.1016/j.atmosenv.2013.12.030
- 602 Kai, P., Pedersen, P., Jensen, J.E., Hansen, M.N., Sommer, S.G., 2008. A whole-farm assessment  
603 of the efficacy of slurry acidification in reducing ammonia emissions. Eur. J. Agron. 28,  
604 148–154. doi:10.1016/j.eja.2007.06.004
- 605 Liang, Z.S., Westerman, P.W., Arogo, P., 2002. Modeling ammonia emission from swine  
606 anaerobic lagoons. Trans. ASAE 45, 787–798. doi:10.13031/2013.8859
- 607 Monteny, G.J., Schulte, D.D., Elzing, A., Lamaker, E.J.J., 1998. A conceptual mechanistic model

- 608 for the ammonia emissions from free stall cubicle dairy cow houses. Trans. ASAE 41, 193–  
609 201. doi:10.13031/2013.17151
- 610 Mosquera, J., Edouard, N., Guiziou, F., Melse, R.W., Riis, A.L., Somer, S., Brusselman, E., 2014.  
611 Decision document on the revision of the VERA protocol on air cleaning technologies:  
612 Measuring techniques for the determination of the removal efficiency of ammonia -  
613 Report 767. Wageningen, The Netherlands.
- 614 Natura 2000, 1992. Natura 2000 Network, European nature & biodiversity policy.
- 615 NEC-Directive, 2001. Directive 2001/81/EC of the European Parliament and of the Council.  
616 Belgium.
- 617 Ni, J., 1999. Mechanistic Models of Ammonia Release from Liquid Manure: a Review. J. Agric.  
618 Eng. Res. 72, 1–17. doi:10.1006/jaer.1998.0342
- 619 Ogink, N.W.M., Groenestein, C.M., Mosquera, J., 2014. Actualisering  
620 ammoniakemissiefactoren rundvee: advies voor aanpassing in de Regeling ammoniak en  
621 veehouderij [Update of ammonia emission factors for cattle categories: advisory report  
622 for amendments in regulations on ammonia and livestock]. Wageningen, The  
623 Netherlands.
- 624 Ogink, N.W.M., Kroodsma, W., 1996. Reduction of Ammonia Emission from a Cow Cubicle  
625 House by Flushing with Water or a Formalin Solution. J. Agric. Eng. Res. 63, 197–204.  
626 doi:10.1006/jaer.1996.0021
- 627 Ogink, N.W.M., Mosquera, J., Calvet, S., Zhang, G., 2013. Methods for measuring gas emissions  
628 from naturally ventilated livestock buildings: Developments over the last decade and  
629 perspectives for improvement. Biosyst. Eng. 116, 297–308.  
630 doi:http://dx.doi.org/10.1016/j.biosystemseng.2012.10.005
- 631 Rotz, C.A., Montes, F., Hafner, S.D., Heber, A.J., Grant, R.H., 2014. Ammonia Emission Model  
632 for Whole Farm Evaluation of Dairy Production Systems. J. Environ. Qual. 43, 1143.  
633 doi:10.2134/jeq2013.04.0121
- 634 Rotz, C.A., Oenema, J., 2006. Predicting management effects on ammonia emissions from dairy  
635 and beef farms. Trans. ASABE 49, 1139–1149. doi:10.13031/2013.21731
- 636 Sagkob, S., Niedermeier, J., Heinz, B., 2011. Comparison of a mobile scraping system with a  
637 fixed one for removal of liquid manure. Landtechnik - Livest. Mach. 66, 238–242.
- 638 Snoek, D., Koerkamp, P.G., Stigter, H., Ogink, N., 2014. IR-camera method to determine urine  
639 puddle area in dairy cow houses, in: International Conference of Agricultural Engineering.  
640 AgEng, Zurich.
- 641 Snoek, D.J.W., Stigter, J.D., Ogink, N.W.M., Groot Koerkamp, P.W.G., 2014. Sensitivity analysis  
642 of mechanistic models for estimating ammonia emission from dairy cow urine puddles.  
643 Biosyst. Eng. 121, 12–24. doi:10.1016/j.biosystemseng.2014.02.003
- 644 Snoek, J.W., Hansen, G.P.M.J., Koerkamp, P.W.G., Monteny, G.J., 2010. Effect of floor design in  
645 a dairy cow house on ammonia emission - Design, test and preliminary results with an  
646 experimental set-up for run-off experiments, in: International Conference on  
647 Agricultural Engineering. Cemagref, Clermont-Ferrand, p. 10.
- 648 Sutton, M.A., Bleeker, A., Howard, C.M., Bekunda, M., Grizzetti, B., Vries, W. de, Grinsven,  
649 H.J.M. van, Abrol, Y.P., Adhya, T.K., Billen, G., Davidson, E.A., Datta, A., Diaz, R., Erisman,  
650 J.W., Liu, X.J., Oenema, O., Palm, C., Raghuram, N., Reis, S., Scholz, R.W., Sims, T.,  
651 Westhoek, H., Zhang, F.S., 2013. Our Nutrient World: The challenge to produce more



- 652 food and energy with less pollution. Earthprint, Edinburgh.
- 653 [Sutton, M.A., Erisman, J.W., Dentener, F., Möller, D., 2008. Ammonia in the environment:](#)  
654 [From ancient times to the present. Environ. Pollut. 156, 583–604.](#)  
655 [doi:10.1016/j.envpol.2008.03.013](#)
- 656 [Takai, H., Nimmermark, S., Banhazi, T., Norton, T., Jacobson, L.D., Calvet, S., Hassouna, M.,](#)  
657 [Bjerg, B., Zhang, G.-Q., Pedersen, S., Kai, P., Wang, K., Berckmans, D., 2013. Airborne](#)  
658 [pollutant emissions from naturally ventilated buildings: Proposed research directions.](#)  
659 [Biosyst. Eng. 116, 214–220. doi:10.1016/j.biosystemseng.2012.12.015](#)
- 660 USEPA, 1986. The Emergency Planning and Community Right-to-Know Act (EPCRA) [WWW  
661 Document]. United States Environ. Prot. Agency. URL  
662 <http://www.epa.gov/superfund/contacts/infocenter/epcra.htm> (accessed 11.28.15).
- 663 [Van Overbeke, P., de Vogeleer, G., Brusselman, E., Pieters, J.G.J.G., Demeyer, P., 2015.](#)  
664 [Development of a reference method for airflow rate measurements through rectangular](#)  
665 [vents towards application in naturally ventilated animal houses: Part 3 : Application in a](#)  
666 [test facility in the open. Comput. Electron. Agric. 115, 97–107.](#)  
667 [doi:10.1016/j.compag.2015.05.009](#)
- 668 [Van Overbeke, P., De Vogeleer, G., Mendes, L.B., Brusselman, E., Demeyer, P., Pieters, J.G.,](#)  
669 [2016. Methodology for airflow rate measurements in a naturally ventilated mock-up](#)  
670 [animal building with side and ridge vents. Build. Environ. 105, 153–163.](#)  
671 [doi:10.1016/j.buildenv.2016.05.036](#)
- 672 [Van Overbeke, P., De Vogeleer, G., Pieters, J.G., Demeyer, P., 2014a. Development of a](#)  
673 [reference method for airflow rate measurements through rectangular vents towards](#)  
674 [application in naturally ventilated animal houses: Part 2: Automated 3D approach.](#)  
675 [Comput. Electron. Agric. 106, 20–30. doi:10.1016/j.compag.2014.05.004](#)
- 676 [Van Overbeke, P., Pieters, J.G., De Vogeleer, G., Demeyer, P., 2014b. Development of a](#)  
677 [reference method for airflow rate measurements through rectangular vents towards](#)  
678 [application in naturally ventilated animal houses: Part 1: Manual 2D approach. Comput.](#)  
679 [Electron. Agric. 106, 31–41. doi:10.1016/j.compag.2014.05.005](#)
- 680 VLM, 2015. Lijst van ammoniak-emissiereducerende maatregelen in het kader van PAS [List of  
681 ammonia emission reduction measures in the context of PAS] [WWW Document]. Vlaam.  
682 L. Maatsch. URL [https://www.vlm.be/nl/themas/Mestbank/mest/emissie/Lijst-van-](https://www.vlm.be/nl/themas/Mestbank/mest/emissie/Lijst-van-emissiereducerende-maatregelen-in-het-kader-van-PAS/Paginas/default.aspx)  
683 [emissiereducerende-maatregelen-in-het-kader-van-PAS/Paginas/default.aspx](#) (accessed  
684 2.4.16).
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- 686

687 Table 1. Equations used in the calculation tool to estimate NH<sub>3</sub> emissions reduction  
688 coefficients for adapted dairy cattle barns

Equation	Variable definitions and units	
$\text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O} \xrightarrow{\text{urease}} \text{CO}_2 + 2\text{NH}_3$	-	[1]
$\frac{dC_U}{dt} = \frac{-\mu_m \times C_U}{K_m + C_U}$	C <sub>U</sub> - urinal urea concentration (kg·m <sup>-3</sup> ); μ <sub>m</sub> - maximum urinal urea conversion rate (kg·m <sup>-3</sup> ·s <sup>-1</sup> ); K <sub>m</sub> - Michaelis-Menten constant (kg·m <sup>-3</sup> )	[2]
$\text{NH}_4^+ \xrightleftharpoons{K_D} \text{NH}_{3,L} + \text{H}^+$	k <sub>D</sub> - dissociation constant (dimensionless)	[3]
$\text{NH}_{3,L} \xrightleftharpoons{H} \text{NH}_{3,G}$	H - Henry's constant (dimensionless)	[4]
$k_D = 0.81 \times 10^{-10} \cdot 1.07^{(T_{\text{liq}} - 293.15)}$	T <sub>liq</sub> - urine temperature (K)	[5]
$H = 1384 \times 1.053^{(293 - T_{\text{air}})}$	T <sub>air</sub> - air dry-bulb temperature (K)	[6]
$F = \frac{1}{1 + \frac{10^{-\text{pH}}}{k_D}}$	F - fraction of ammonia in the urine (F <sub>floor</sub> ) or manure (F <sub>pit</sub> ) (dimensionless)	[7]
$k = 5.317 \times 10^{-5} + 2.012 \times 10^{-3} \times 1.5686 \times v$	k - ammonia mass transfer coefficient (m·s <sup>-1</sup> ); v - air speed (m·s <sup>-1</sup> )	[8]
$E_{\text{puddle, floor}} = \frac{C_{\text{NH}_3} \times k_{\text{floor}} \times A \times F_{\text{floor}}}{H_{\text{floor}}}$	E <sub>puddle, floor</sub> - ammonia emission rate at floor level for a single urine puddle (kg·s <sup>-1</sup> ·puddle <sup>-1</sup> ); C <sub>NH<sub>3</sub></sub> - ammonia concentration (kg·m <sup>-3</sup> )	[9]
$\frac{dC_{\text{NH}_3}}{dt} = 2 \times \frac{dC_U}{dt} - \frac{E_{\text{puddle, floor}}}{A \times d}$	A - urine puddle area (m <sup>2</sup> ); d - urine puddle depth (m)	[10]
$n = \frac{f \times A}{A_{\text{cow, floor}}}$	n - total number of times per day in which one urination puddle will be reloaded in a certain time period (d <sup>-1</sup> ); f - urination frequency (cow <sup>-1</sup> ·day <sup>-1</sup> ); A <sub>cow, floor</sub> - walking area per cow allocated at floor level (m <sup>2</sup> ·cow <sup>-1</sup> )	[11]
$E_{\text{cow, floor}} = \frac{E_{\text{puddle, floor}} \times A_{\text{cow, floor}}}{60 \times 10^6 \times A}$	E <sub>cow, floor</sub> - ammonia emission rate in a 'per-cow' basis at floor level (kg·s <sup>-1</sup> ·animal·place <sup>-1</sup> )	[12]
$E_{\text{cow, pit}} = \frac{17}{14} \times \frac{\text{TAN} \times k_{\text{pit}} \times A_{\text{cow, pit}} \times F_{\text{pit}}}{60 \times H_{\text{pit}}}$	E <sub>cow, pit</sub> - ammonia emission rate in a 'per-cow' basis at manure pit level (kg·s <sup>-1</sup> ·animal·place <sup>-1</sup> ); TAN - total ammoniac nitrogen (g·kg <sup>-1</sup> ). The ratio 17/14 converts N-NH <sub>3</sub> into NH <sub>3</sub> .	[13]
$E_{\text{cow}} = E_{\text{cow, floor}} + E_{\text{cow, pit}}$	E <sub>cow</sub> - ammonia emission rate in a 'per-cow' basis (kg·s <sup>-1</sup> ·animal·place <sup>-1</sup> )	[14]
$R = \left( \frac{E_{\text{cow, std}} - E_{\text{cow, alt}}}{E_{\text{cow, std}}} \right) \times 100$	R - ammonia emission reduction factor of the alternative barn in relation to the standard barn (%); E <sub>cow, std</sub> and E <sub>cow, alt</sub> - ammonia emission rate in a 'per-cow' basis for the standard and alternative barns, respectively (kg·s <sup>-1</sup> ·animal·place <sup>-1</sup> )	[15]
$\eta = \begin{cases} \eta_{\text{min}} & \text{during a scraping event} \\ \frac{t_{\text{ac}}}{t_{\text{ac}} - 0.5} & \text{between scraping events} \end{cases}$	η - floor scraping inefficiency (dimensionless); η <sub>min</sub> - minimum floor scraping inefficiency (dimensionless); t <sub>ac</sub> - elapsed time after a scraping event (s). The constant 0.5 s was determined via calibration with the data presented by Dai and Karring, (2014).	[16]
$t_{\text{dc}} = \frac{L_{\text{alley}} \times n_{\text{alley}}}{30 \times S \times n_{\text{cow}}}$	t <sub>dc</sub> - duration of a scraping event (s); L <sub>alley</sub> - length of the walking alley barn (m); n <sub>alley</sub> - number of walking alleys in the barn (dimensionless); S - traveling speed of the scraping robot across the barn (m·s <sup>-1</sup> ); n <sub>cow</sub> - total number of cows in the barn (dimensionless)	[17]

689

690 Table 2. List of input variables table for the standard dairy cattle barn

Variable	Value at floor	Value at manure pit	Reference
Number of cows in the barn ( $n_{cow}$ )	60	-	-
Walking area per cow ( $A_{cow}$ , m <sup>2</sup> )	3.9	8.0	-
Urine puddle area ( $A$ , m <sup>2</sup> )	0.77	-	Monteny et al., (1998)
Urine puddle depth ( $d$ , m)	$4.8 \times 10^{-3}$	-	Monteny et al., (1998)
Urination frequency ( $f$ , cow <sup>-1</sup> ·day <sup>-1</sup> )	10	-	-
Starting urea concentration ( $C_U(t=0)$ , kg·m <sup>-3</sup> )	4.75	-	Dai & Karring, (2014)
Manure TAN concentration (g·kg <sup>-1</sup> )	-	3.5	Dai & Karring, (2014)
Temperature of urine puddle ( $T_{liq}$ , °C)	10	10	Ogink et al., (2014)
Urine pH (dimensionless)	9.4	-	Ogink et al., (2014)
Air velocity near urine puddle ( $v$ , m·s <sup>-1</sup> )	0.15	0.05	Ogink et al., (2014)
Manure pH (dimensionless)	-	8.4	Ogink et al., (2014)
Starting NH <sub>3</sub> concentrations ( $C_{NH_3}(t=0)$ , kg·m <sup>-3</sup> )	0	-	-

697 \*The values that are not referenced were implemented into the model by the authors based on expert judgement.

698 Table 3. Comparison of NH<sub>3</sub> emission reduction factors for different cases, obtained via  
 699 modeling and empirically determined from studies found in the literature

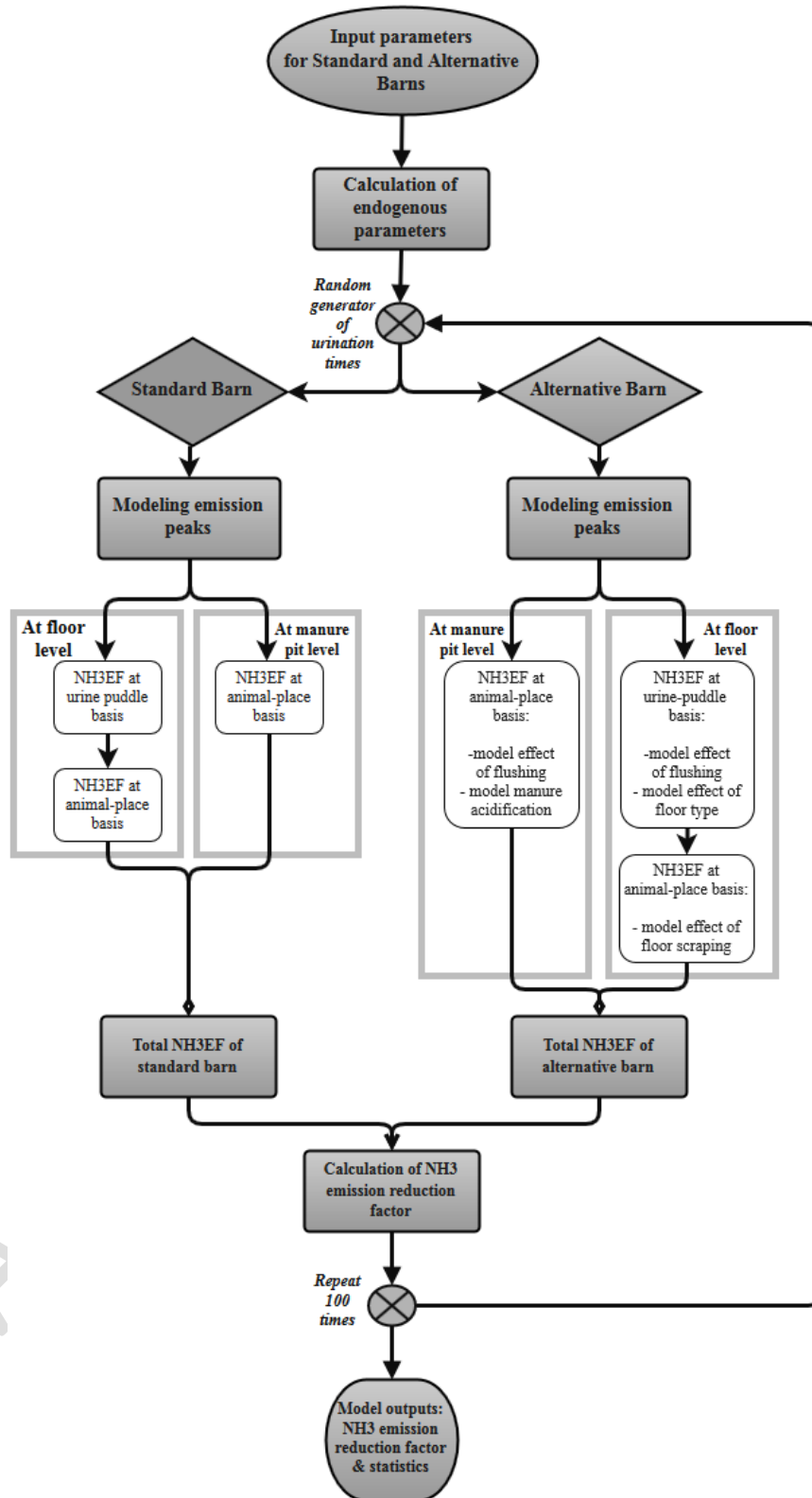
Scenario	Cited study	Description of reference barn	Description of alternative barn	NH <sub>3</sub> emission reduction factor (%)	
				Cited study	This study
1	Braam et al., (1997)	Slatted floor, no scraping mentioned	Solid (sloped) floor, and scraping frequency of 12 d <sup>-1</sup>	42 - 59	43 (42, 44)
2	Braam et al., (1997)	Slatted floor, no scraping mentioned	Solid (sloped) floor, scraping frequency of 12 d <sup>-1</sup> and spraying of water at a rate of 6 L d <sup>-1</sup> cow <sup>-1</sup>	53 - 67	54 (52, 55)
3	Ogink & Kroodsma, (1996)	Slatted floor, no scraping mentioned	Slatted floor scraped 12 d <sup>-1</sup> , flushing with water at a rate of 20 L d <sup>-1</sup> cow <sup>-1</sup>	9 - 19	21 (19, 21)
4	Bleijenberg et al., (1995)	Slatted floor scraped 12 d <sup>-1</sup>	Slatted floor scraped 12 d <sup>-1</sup> , flushing with water at a rate of 19 L d <sup>-1</sup> cow <sup>-1</sup>	10 - 23	10 (8, 10)
5	Bleijenberg et al., (1995)	Slatted floor scraped 12 d <sup>-1</sup>	Slatted floor scraped 12 d <sup>-1</sup> , flushing with water at a rate of 47 L d <sup>-1</sup> cow <sup>-1</sup>	23 - 33	17 (16, 18)
6	Bleijenberg et al., (1995)	Slatted floor scraped 12 d <sup>-1</sup>	Acidification of manure	33 - 42	27 (24, 27)
7	Bleijenberg et al., (1995)	Slatted floor scraped 12 d <sup>-1</sup>	Acidification of manure and flushing with water at a rate of 26 L d <sup>-1</sup> cow <sup>-1</sup>	44 - 55	39 (37, 40)

700

701 Table 4. List of alternative low ammonia emission dairy cattle barns and their reduction  
702 factors

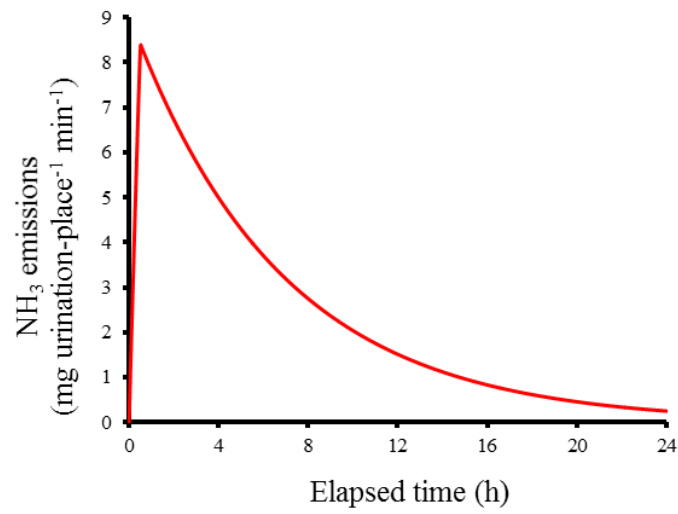
Scenario name	Description	Floor / Pit ratio (%)	Reduction factor (%)*
Scraping 1	Scraping frequency <sup>1</sup> : 6 d <sup>-1</sup>	67/33	17 (17, 19)
Scraping 2	Scraping frequency <sup>1</sup> : 10 d <sup>-1</sup>	66/34	22 (21, 22)
Scraping comb. w/ acidification of manure 1	Scraping frequency <sup>1</sup> : 6 d <sup>-1</sup> ; manure pH 5.0	100/0	44 (43, 45)
Scraping comb. w/ acidification of manure 2	Scraping frequency <sup>1</sup> : 10 d <sup>-1</sup> ; manure pH 5.0	100/0	49 (48, 50)
Scraping comb. w/ flushing 1	Scraping frequency: 6 d <sup>-1</sup> ; flushing w/ water at 10 L animal-place <sup>-1</sup> d <sup>-1</sup>	67/33	20 (17, 20)
Scraping comb. w/ flushing 2	Scraping frequency: 10 d <sup>-1</sup> ; flushing w/ water at 10 L animal-place <sup>-1</sup> d <sup>-1</sup>	64/36	25 (22, 25)
Solid floor comb. w/ scraping 1	Scraping frequency: 6 d <sup>-1</sup>	100/0	13 (12, 14)
Solid floor comb. w/ scraping 2	Scraping frequency: 10 d <sup>-1</sup>	100/0	20 (20, 21)
Solid floor comb. w/ scraping & flushing 1	Scraping frequency: 6 d <sup>-1</sup> ; flushing w/ water at 10 L animal-place <sup>-1</sup> d <sup>-1</sup>	100/0	21 (20, 23)
Solid floor comb. w/ scraping & flushing 2	Scraping frequency: 10 d <sup>-1</sup> ; flushing w/ water at 10 L animal-place <sup>-1</sup> d <sup>-1</sup>	100/0	27 (27, 30)

703 \*The number outside brackets represent the average of 100 simulations in which the urination  
704 events were randomly selected and the numbers between brackets represent minimum and  
705 maximum occurring values.



706

707 Figure 1. General setup of the flow of calculations in the model for the determination of total  
 708 NH<sub>3</sub> emission reduction factor of an alternative barn in relation to the standard barn. NH<sub>3</sub>EF  
 709 stands for NH<sub>3</sub> emission factor (g-animal-place<sup>-1</sup>·year<sup>-1</sup>).



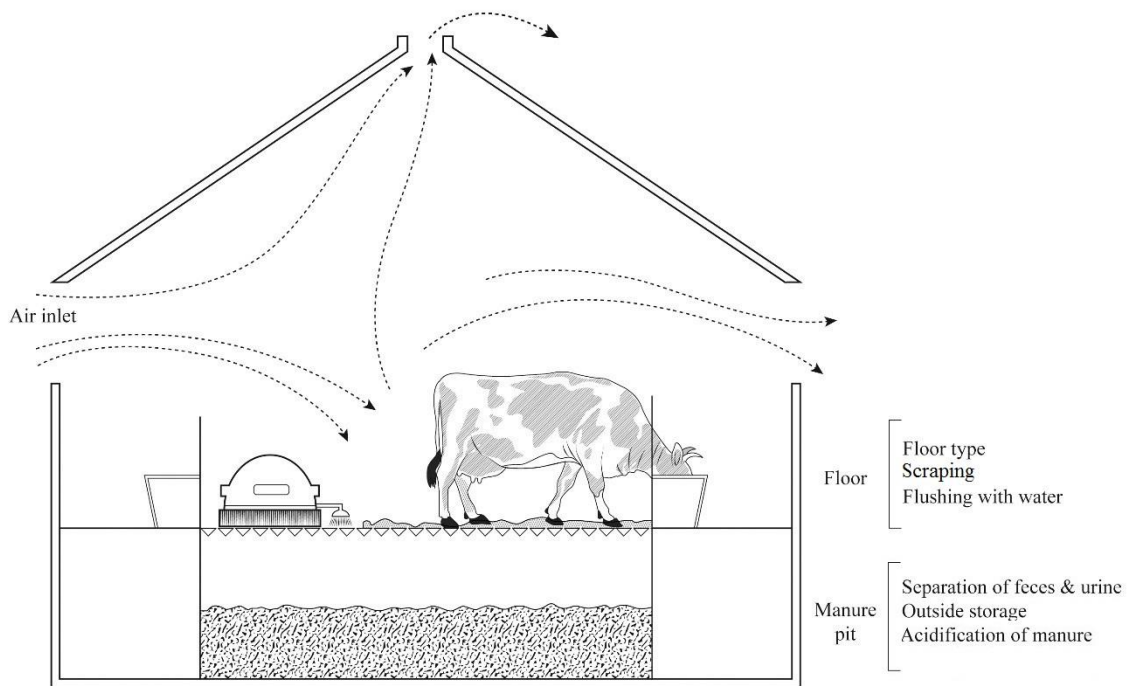
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711

712 Figure 2. Sample of the dynamics of NH<sub>3</sub> emissions from a single urine puddle after being  
713 loaded with fresh urine.

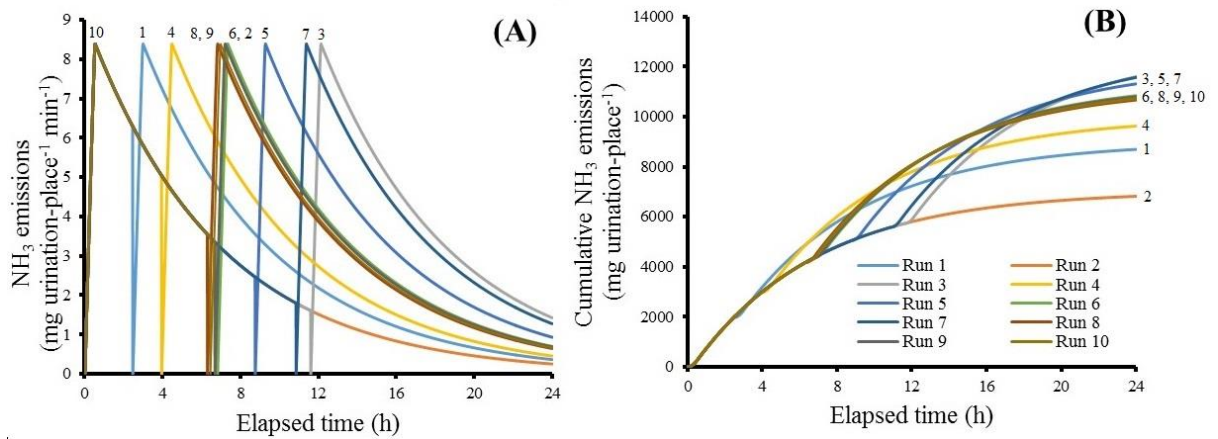
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715 Figure 3. (A) Disaggregation of  $\text{NH}_3$  emissions from a dairy cattle barn, and *loci* where mitigation  
716 strategies can be applied. Although all management-based  $\text{NH}_3$  emission mitigation techniques  
717 in this figure are taken into account in the model, focus was given to floor type, floor scraping  
718 and flushing with water, and acidification of manure; (B) Picture of a typical dairy cattle cubicle  
719 barn where the cubicles and walking alleys are shown.  
720





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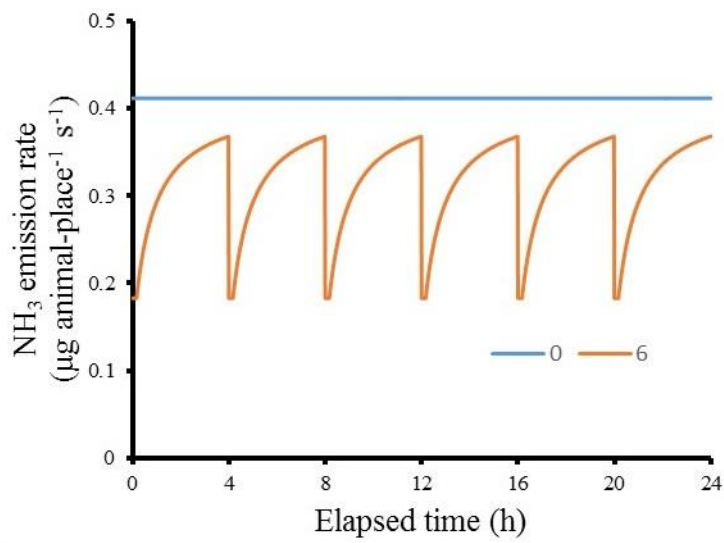
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Figure 4. Dynamics of NH<sub>3</sub> emissions rates (A) and cumulative NH<sub>3</sub> emissions (B) in 10 different runs. In each run, the urine puddle was loaded twice with fresh urine at random times.

724

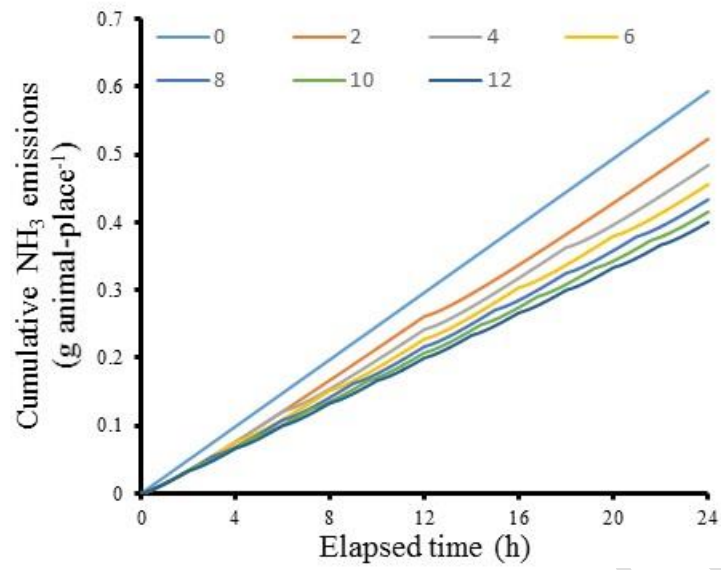
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726

727 Figure 5. Dynamics of the effect of scraping the floor with a scraper 6 times over a period of  
 728 24h (orange line), as opposed to no scraping (blue line). The valleys in the orange curve  
 729 represent the occurrence of a scraping event, after which the emission is restored following  
 730 the Michaelis-Menten Kinetics until a new scraping event takes place.

731



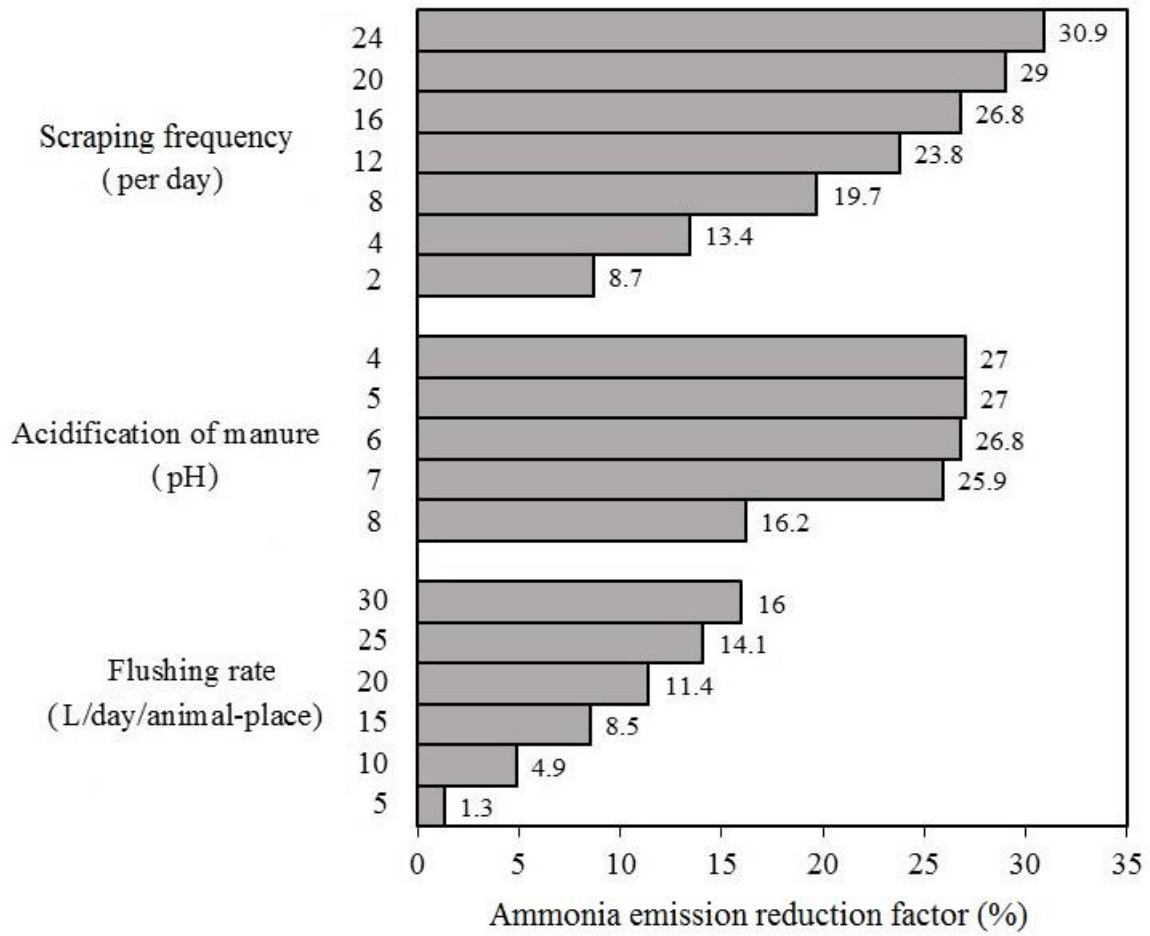
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Figure 6. Cumulative NH<sub>3</sub> emissions from floor at different scraping frequencies.



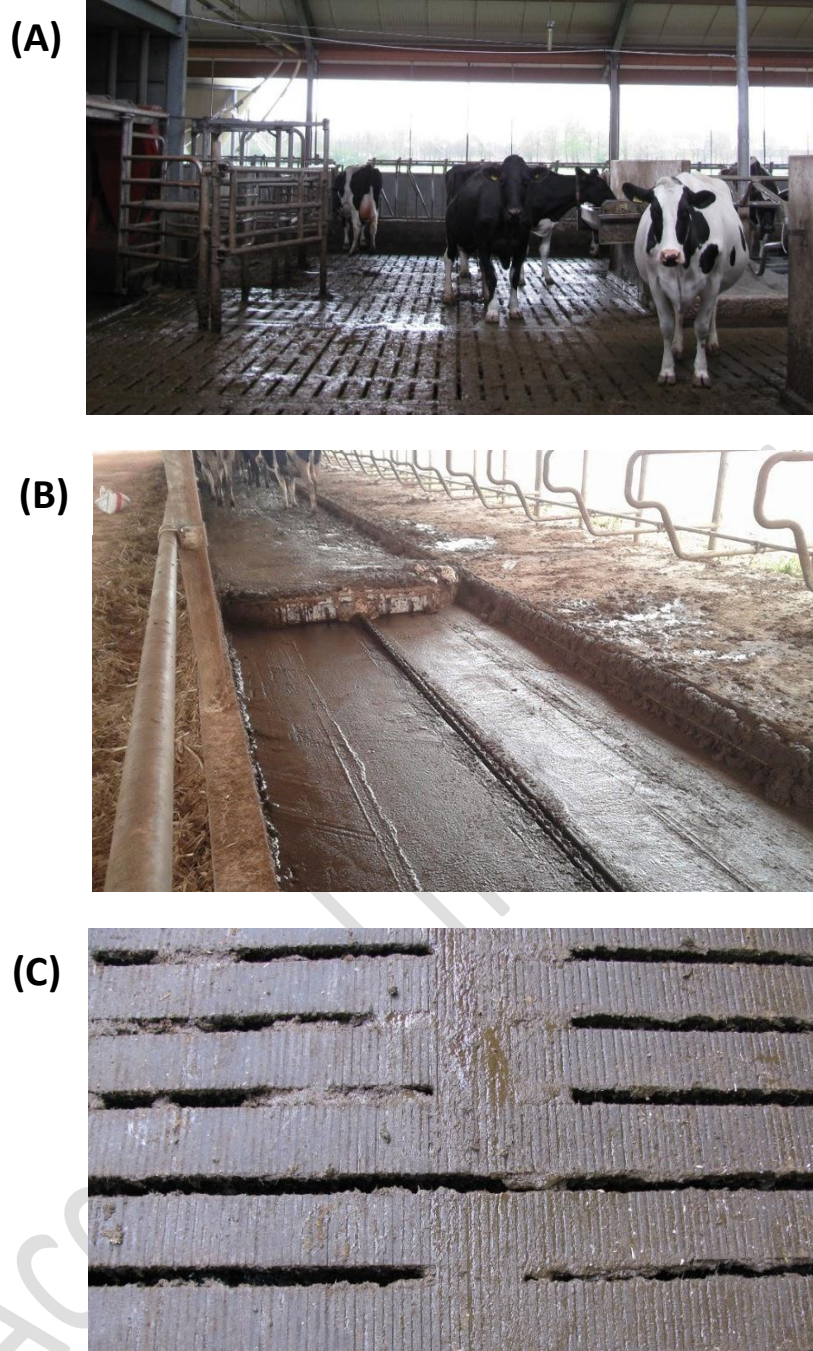
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737

Figure 7. Ammonia emissions reduction efficiencies obtained from the model after a sensitivity analysis for the management-based emission reduction techniques.

738

739



740 Figure 8. Pictures of dairy cattle barn floors at different cleanliness levels. (A) Hasn't been  
741 scraped in a while; (B) After being cleaned by a pulled scraper, a thin film of manure is left  
742 behind; (C) After being cleaned by a robot scraper, fairly clean.